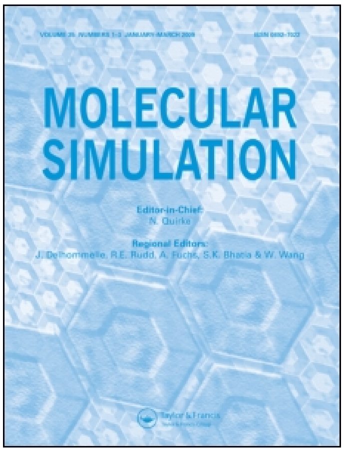

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Adsorption of Linear Alkanes in Zeolite Ferrierite from Molecular Simulations

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The adsorption of linear alkanes in zeolite ferrierite is investigated using a recently developed forcefield based on the anisotropic united atom potential scheme. The simulation model is able to reproduce the subtle changes in adsorption sites occupancies of *n*-alkanes ($n = 3-7$) in ferrierite with a good agreement with experimental data.

Keywords: Adsorption; Molecular simulations; Zeolite; Anisotropic united atom

INTRODUCTION

Zeolites are microporous materials that are widely used in catalysis and separation applications. An understanding of the physisorption behaviour of the guest molecules in the zeolite pores on the molecular level is essential in order to help in the design of a new process or in the improvement of an existing one. In addition to experiments, valuable information can be obtained from molecular simulation. The use of recently developed techniques allows the simulation of systems that a few years ago were considered impossible to study via computer experiments. Systems of relevance to applications such as normal and branched alkanes, benzene, alkyl benzene isomers and halo-carbon molecules in aluminosilicate hosts are now being studied by molecular simulation [1,2].

Among other interesting issues, molecular simulations have tried to reproduce the "kinks" observed in the adsorption isotherms of various guest–host systems at low temperature, instead of the usual smooth Langmuir (or "type I") isotherm. An inflection in the isotherm was predicted by Smit and co-workers [3,4] in the case of *n*-hexane and *n*-heptane in silicalite-1, while for shorter and longer alkanes the usual type I isotherm was computed. This was attributed to a so-called "commensurate freezing" effect [3,4].

Methane in neutral $AlPO_4$-5 (a zeolite-like open framework with cylindrical parallel pores) displays a step in the experimental low temperature adsorption isotherm [5]. This step was reproduced by Boutin *et al.* [6,7], using Grand Canonical Monte Carlo (GCMC) simulations and was attributed to a phase transition of the confined methane fluid. This is a rather subtle effect. Maris *et al.* [8] and Boutin *et al.* [9] have discussed in detail the degree of accuracy needed in the intermolecular potential in order to be able to reproduce this feature. It was found that only a 5% modification in the Lennard–Jones (LJ) methane–oxygen size parameter (σ_{CH_4-O}) could change a type I into a stepped isotherm displaying the known phase transition.

van Well *et al.* [10] have obtained a step in the computed isotherm of *n*-pentane in zeolite ferrierite in disagreement with the type I isotherms observed experimentally. These authors have tested another set of potential parameters proposed earlier by June *et al.* [11]. The simulation no longer showed any kink, but the loadings were greatly overestimated.

All of the above-mentioned computer experiments rely on a very simple united atom (UA) description of the guest hydrocarbon molecules together with the rigid framework hypothesis. Most of them also describe the guest–host interaction through a LJ repulsion–dispersion term that acts between each

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oxygen atom of the framework and each UA of the host molecules (the so-called Kiselev approximation). Given the difficulties in reproducing the observed kinks in the isotherms, whenever they exist, the validity of these simple forcefields is thus questionable. Whether or not some or all of the above-mentioned hypotheses should be abandoned, at the expense of more accurate models (and often much more expensive calculations) is still an open question. The *n*-alkane–ferrierite system, in which the adsorbate molecules fit tightly in the zeolite pore, is particularly interesting since it provides a very demanding test case for the simulation models.

We reinvestigate here the adsorption of linear alkanes in zeolite ferrierite, using a recently developed forcefield based on the anisotropic united atom (AUA) potential scheme. As in the usual UA model, a CH_2 or CH_3 group is represented by a single centre of force. In the AUA scheme, this centre of force is no more located on the carbon atom but displaced towards the geometric centre of the group by a small distance δ of the order of a few tenth of an Angström. Ungerer and co-workers [12] have proposed an AUA model that reproduces quite well the liquid–vapour phase equilibria of linear, branched and cyclic alkanes [13,14] as well as alkenes [15]. An extension of this forcefield for simulating adsorption in zeolites has recently been proposed [16]. Within the rigid framework and the Kiselev approximation, LJ parameters for the framework oxygen atom of neutral silicalite-1 were obtained by adjusting simulation results to experimental data in the case of *n*-butane. Once these two parameters (σ_O and ϵ_O) were fixed, all cross potential parameters for the individual UA groups were obtained using the Lorentz–Berthelot combining rule. Adsorption quantities for linear and branched alkanes have been very accurately reproduced [16]. This procedure allows extending the computation to any other system without further adjustment of the parameters, as long as the forcefield parameters for the bulk fluid are available. The simulation of alkenes as well as alkane–alkene mixtures adsorption in silicalite-1 has provided a demonstration of this [17]. An interesting test case for the transferability of this forcefield is to carry out the simulations in a different zeolite, namely ferrierite.

MODELS AND SIMULATIONS

GCMC simulation is used to study adsorption of hydrocarbons in ferrierite zeolite. We used the ferrierite structure determined by Vaughan [18]. Ferrierite consists of straight 10-ring channels of pore diameter 5.4 × 4.2 Å (in the *z* direction; Fig. 1) that are interconnected perpendicularly (*y* direction) by cages with 8-ring windows of diameter 4.8 × 3.5 Å.

The zeolite framework is considered as rigid and the guest–host interactions are calculated on a grid of points prior to simulations. The grid mesh is about 0.2 Å in the three space directions.

The AUA model was used to describe the adsorbate molecules [19,20] (Table I). Intramolecular interactions include bond-bending and torsion potentials as well as non-bonded interactions described by a LJ 6–12 potential. More details on the intramolecular potential parameter values are given in previous works [12,16]. Guest–guest intermolecular interactions are calculated by a LJ potential with a cut-off distance fixed at half of the smallest box dimension. LJ parameters of alkanes (Table I) are taken from Ungerer and co-workers [12].

The guest–host potential is of the "Kiselev" type [1,21]. It contains a single effective LJ term that acts between the oxygen atoms of the framework and each of the AUAs of the guest molecules. The zeolite oxygen atom parameters obtained from a previous fit

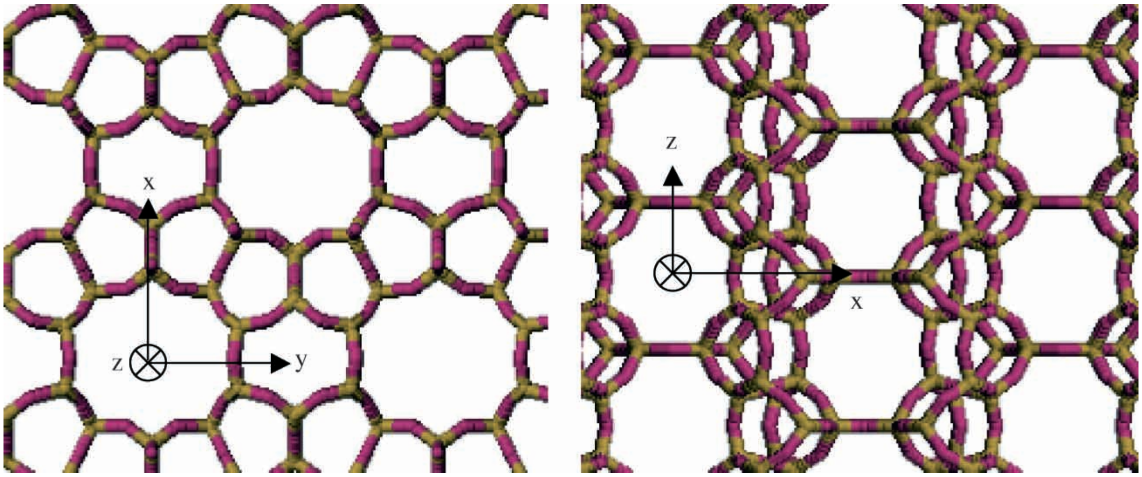

FIGURE 1 Schematic view of the ferrierite framework showing the 10-ring channels along the *z* direction. The 10-ring channels are connected in the *y* direction by cages having 8-ring windows. (Colour version available online.)

TABLE I LJ parameters of alkane force centres in the AUA model [12]

	σ (Å)	*ϵ (K)*	*δ (Å)*
CH_2 (*sp*3)	3.46	86.29	0.384
CH_3 (*sp*3)	3.61	120.15	0.216

of *n*-butane adsorption data in silicalite-1 [16] are equal to $\sigma_O = 3.00\,\text{Å}$ and $\epsilon_O = 93.53\,\text{K}$. The hydrocarbon–zeolite cross interaction parameters are determined from Lorentz–Berthelot combining rules. No further readjustment of the potential parameters was undertaken in this study.

Adsorption isotherms are computed using biased Grand Canonical Ensemble (μ, V, T) simulations as previously described in detail [16]. Typically, 5 million steps production runs were used. The chemical potential of each compound was calculated from the partial fugacity, y_iP_i of the vapour phase by using the ideal gas relation [Eq. (1)]

$$\frac{\mu_i}{k} = T \ln\left(\frac{y_iP_i}{P_0}\right) \tag{1}$$

where P_0 is the pressure of the reference state. We have checked that the approximation of ideal gas is satisfactory for alkanes under thermodynamic conditions used in this study by separately simulating the gas phase properties.

Talu and Myers [22] emphasised that simulation results yield total adsorption but experiments measure excess adsorption. We have checked in our case that the difference between total and excess quantities is always lower than 1% of the number of adsorbed molecules per unit cell.

The heat of adsorption at zero coverage Q^0_{st} is calculated from a fluctuations method [16,23]. The single (SSL) and dual site (DSL) Langmuir models [24] are used to fit simulated isotherms. A Bayesian approach is used to ascertain the identification of the set of fitting parameters [16].

RESULTS AND DISCUSSION

Figure 2 shows the computed adsorption isotherm of propane at 333 K, as compared to both experiments [25] and previous simulations [10]. A smooth type I isotherm was observed in all cases. At low pressure, propane molecules preferentially adsorb in the 8-ring cages (Table II). As pressure increases, the 10-ring channel occupancy increases smoothly. At saturation loading a 50% occupancy of each type of channel is observed, in agreement with earlier simulations [10]. In the case of *n*-butane (Fig. 3) the preferred site at low loading is the 10-ring channel (Table II). At high loading butane molecules occupy evenly the adsorption sites. This is consistent with the nuclear magnetic resonance (NMR) ^{13}C CPMAS results of van Well *et al.* [10] which shows that propane and butane are distributed over both the 10-ring channels and the 8-ring cages at all loadings but with a clear preference of 8-ring cages for propane and 10-ring channels for butane at low loading. Although two types of adsorption sites are found the difference in potential energy of these two sites is such that the adsorption isotherm can be described by a SSL fit (dashed line in Figs. 2 and 3).

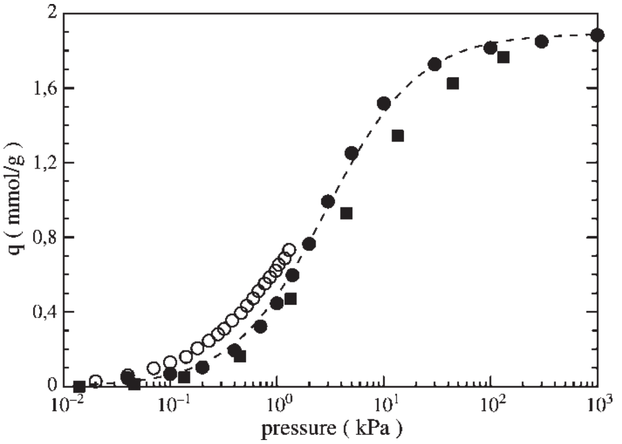

FIGURE 2 Simulated and experimental adsorption isotherms of propane in ferrierite carried out at 333 K. This work (filled circles) fitted by a SSL model (dashed line), van Well *et al.* simulations [10] (squares) and experiments [25] (open circles).

Figure 4a shows the computed isotherm at 333 K for *n*-pentane. At low pressure, pentane molecules occupy the 10-ring channels exclusively (Table II), in agreement with experiments [25] and previous simulations [10]. In our simulations, 8-ring cages are progressively occupied as pressure increases. The difference in potential energy between

TABLE II Probability (%) to find alkane molecule centre of mass in a 10-ring channels or in 8-ring cages of ferrierite at 333 K

	Low coverage			*Saturation*		
	N (mmol/g)	*10-ring (%)*	*8-ring (%)*	*N (mmol/g)*	*10-ring (%)*	*8-ring (%)*
Propane	0.10	23	77	1.73	48	52
Butane	0.08	66	34	1.81	49	51
Pentane	0.09	99	1	1.53	41	59
Hexane	0.12	100	0	1.48	42	58
Heptane	0.09	100	0	0.61	100	0

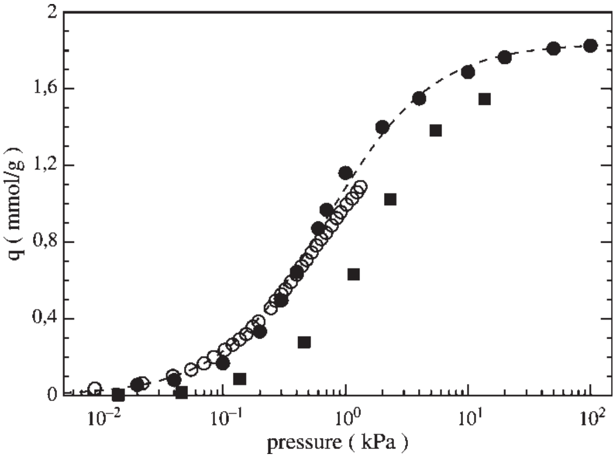

FIGURE 3 Simulated and experimental adsorption isotherms of *n*-butane in ferrierite carried out at 333 K. This work (filled circles) fitted by a SSL model (dashed line), van Well *et al.* simulations [10] (squares) and experiments [25] (open circles).

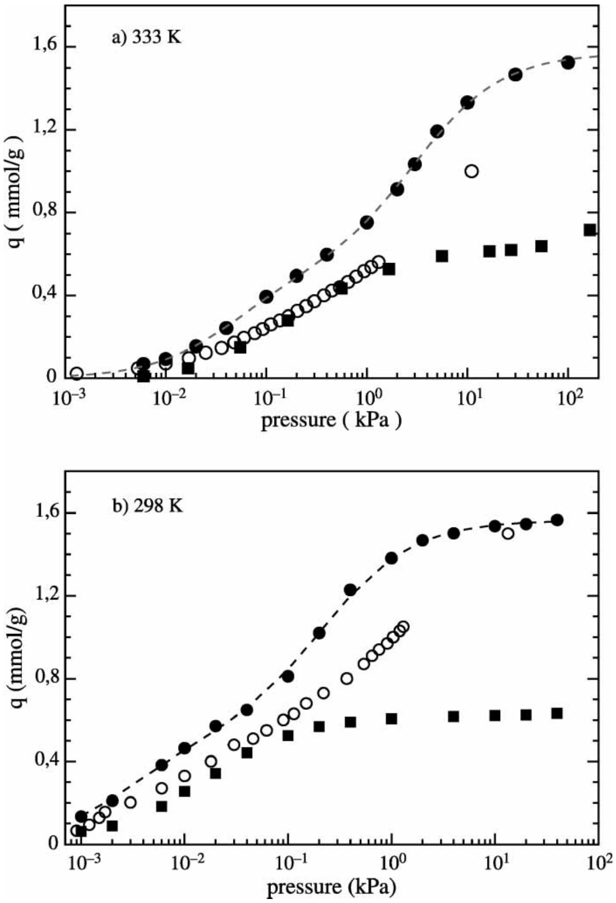

FIGURE 4 (a) Simulated and experimental adsorption isotherms of *n*-pentane in ferrierite carried out at 333 K. This work (filled circles) fitted by a DSL model (dashed line), van Well *et al.* simulations [10] (squares) and experiments [25] (open circles). (b) Simulated isotherm at 298 K where some other experiments are available [26]. The squares correspond to simulations carried out at 298 K using the model of van Well *et al.* [10].

the adsorption sites increases, with respect to the propane or butane cases shown above. In the temperature-programmed desorption (TPD) experiments reported by van Well *et al.* [26], a two-step desorption of pentane was observed with increasing temperature. However, this was not accompanied by a kink in the experimental adsorption isotherm. In our simulations, a SSL fit fails to reproduce the simulated isotherm. The result of the DSL fit is shown in Fig. 4a (dashed line). In the previous simulations of van Well *et al.* [10], a huge step was observed at a loading of about 0.6 mmol/g that has no experimental counterpart. This corresponds to a complete filling of the 10-ring channels. The model used in van Well *et al.*'s simulations yields a too high potential energy for the narrow 8-ring cage site. This site could only be occupied at pressures higher than the saturation pressure in these simulations [27].

In Fig. 4b, the simulated adsorption isotherm of *n*-pentane at 298 K is compared to available experiments [26] and also to simulations that we have performed, at this temperature, using van Well *et al.*'s model [10]. This provides a clear confirmation of the ability of the AUA model used here to reproduce the type I isotherm obtained experimentally. An analysis of the molecular conformations shows that *n*-pentane molecules occupying the 10-ring channels are in their all-*trans* conformation. Adsorption in the 8-ring cages is accompanied by an anti-gauche (more generally called *trans*-gauche) conformation transition. Again, this is consistent with the TPD and NMR data of van Well *et al.* [26] that describes the pentane molecules in the 8-ring cages as "highly constrained".

Figure 5 shows the adsorption isotherm for *n*-hexane at 333 K. At low pressure, *n*-hexane molecules adsorb preferentially in the 10-ring channels (Table II). The computed isotherm agrees

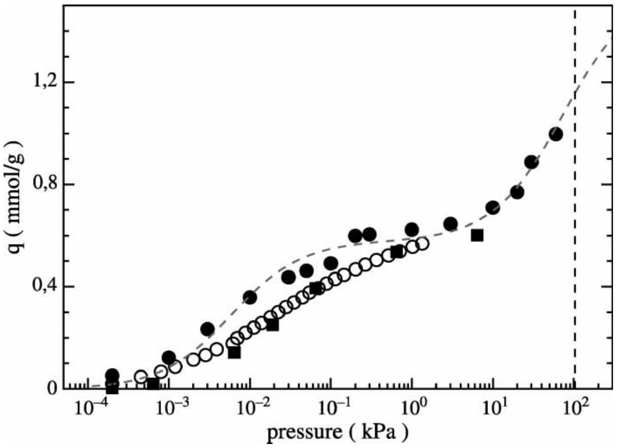

FIGURE 5 Simulated and experimental adsorption isotherms of *n*-hexane in ferrierite carried out at 333 K. This work (filled circles) fitted by a DSL model (dashed line), van Well *et al.* simulations [10] (squares) and experiments [25] (open circles). The vertical dotted line corresponds to the experimental vapour pressure.

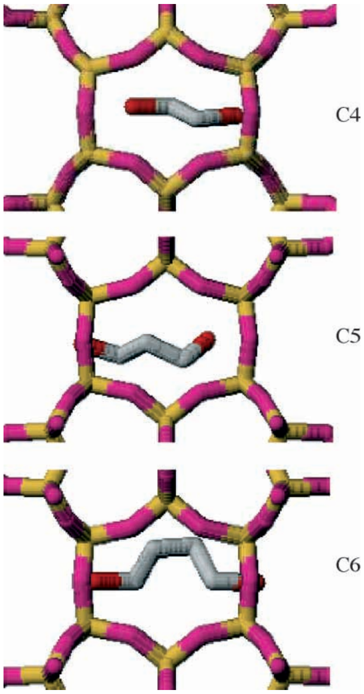

FIGURE 6 Snapshots of the *n*-butane, *n*-pentane and *n*-hexane molecules in the 8-ring cages of the ferrierite zeolite. (Colour version available online.)

with both experiments [25] and previous simulations [10] which were limited to a maximum pressure of 1 and 10 kPa, respectively. Above 10 kPa, we predict that hexane molecules can adsorb in the 8-ring cages. However, this is accompanied by an anti-eclipsed (more generally called *trans-cis*) conformation change of the molecules. This conformation change reduces the apparent size of the molecule, which now fits into the 8-ring cage without interfering with the molecules already adsorbed in the perpendicular 10-ring channels (Fig. 6). The constrained hexane molecule tightly fits into the 8-ring cage and this leads to an increase in potential energy with respect to the 10-ring channel site. Thus, the occupancy of the 8-ring cage is predicted at very high pressure. Actually, the simulations predict that only the beginning of the 8-ring cage filling would be observed (between 10 and 100 kPa) before the bulk saturation pressure be reached (Fig. 5). This interesting and unusual behaviour has not yet been confirmed by experiments.

In the case of *n*-heptane at 333 K (Fig. 7), only 10-ring channels are occupied at all loadings (Table II), in agreement with TPD and NMR experiments [26]. The heptane molecule is too large to fit in the 8-ring cage, whatever its conformation is. A small inflection point is observed in the predicted adsorption isotherm between 10^{-2} and 10^{-3} kPa. This is due to a double *trans-cis* conformation change of the heptane molecule (one at each end of the carbon chain). This is evidenced by the change in the intermolecular potential energy as a function of loading, shown on the same graph. This conformation change allows a more dense packing of the *n*-heptane molecules at high pressure. Accordingly, the adsorption isotherm could only be fitted by a DSL model (dotted line in Fig. 7).

Finally, the isosteric heat of adsorption at zero coverage Q_{st}^{0} as a function of the carbon number is shown in Fig. 8. The agreement with experiments is satisfactory, owing to the fact that the experiments

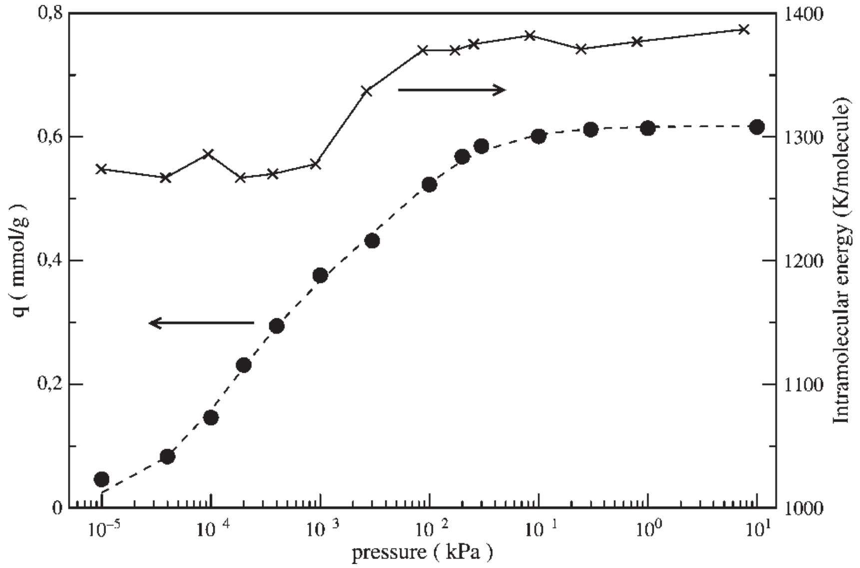

FIGURE 7 Simulated adsorption isotherms of *n*-heptane in ferrierite carried out at 333 K. The dashed line corresponds to a fit by a DSL model. On the same figure (scale on the right hand side) is shown the change in intramolecular potential energy (per molecule) as a function of loading.

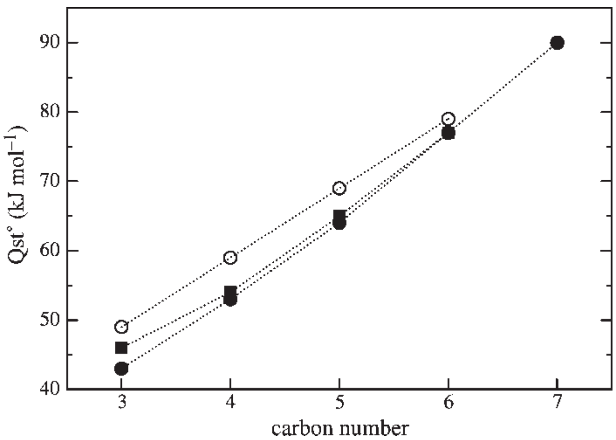

FIGURE 8 Heats of adsorption of linear alkanes in ferrierite as a function of the carbon number (filled circles), as compared to experiments (open circles) and previous simulations (squares).

have been performed in a slightly cationic ferrierite sample (Si–Al ratio of 30 [10]).

CONCLUSION

The simulation model used in this work was able to reproduce the subtle changes in adsorption sites occupancies of *n*-alkanes ($n = 3$–7) in ferrierite. The 8-ring cage site that connects two 10-ring channels is occupied at low pressure, as long as its size is smaller than the apparent length of the molecule. This holds for propane and *n*-butane. Pentane occupies, preferentially, the 10-ring channels at low pressure, but a progressive filling of the 8-ring cages is observed as pressure increases. The potential energy difference between the two sites is small, as this can be related to the fact that the apparent length of the pentane molecule in its gauche conformation is still close to the size of the 8-ring cage. Hexane is a very interesting case, in which the 8-ring cage occupancy is still possible provided that a *trans-cis* conformation molecular change is undertaken. We thus predict a two-step filling of the pores in the case of *n*-hexane. For $n > 6$, *n*-alkane molecules can only adsorb in the 10-ring channels for steric reasons. These results agree very well with the available experimental data, and this is particularly encouraging since, as mentioned earlier, no read-justment of the potential parameters was undertaken in going from the zeolite silicalite-1 to ferrierite.

This work provides some evidence that a carefully designed effective forcefield is able to capture the essential features of hydrocarbons adsorption in siliceous zeolites, even though the model used is based on rather crude assumptions such as rigid framework, UA description of the host molecules and the Kiselev approximation for the guest–host interaction.

Work to investigate the transferability of this model to cationic zeolites is in progress.

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