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CO_2 diffusivity in LiY and NaY faujasite systems: a combination of molecular dynamics simulations and quasi-elastic neutron scattering experiments

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Abstract Quasi-elastic Neutron Scattering combined with Molecular Dynamics simulations have been carried out to gain further insight into the CO_2 dynamics in LiY and NaY Faujasites. In both materials, it was pointed out that the transport diffusivity (D_T) increases with the loading whereas the self diffusivity (D_S) decreases. In addition, it was shown that LiY exhibits a significant slower CO_2 self diffusivity process due to a strong interaction between the Li^+ cation and the adsorbate molecules at the initial stage of diffusion. This result is consistent with higher simulated activation energy in this cation exchanged faujasite form. By contrast, the transport diffusivity is revealed to be slightly faster in LiY than in NaY.

Keywords CO_2 · LiY · NaY · Self and transport diffusivities · Quasi elastic neutron scattering · Molecular dynamics

1 Introduction

Alkali cation exchanged zeolites, are involved in many industrial applications involving selective adsorption and separation of various adsorbates (Corma 2003). It is well established that the diffusion of adsorbate molecules in these microporous materials plays a crucial role in such processes (Demontis and Suffriti 1997). For instance, it was revealed that the dynamics of the xylenes could explain the selectivity of the para and meta-isomers in the barium exchanged form of the Faujasite X (Jobic et al. 2001). The diffusion drives the chemical reactions by leading the reactants into the active sites and/or preferentially extracting the products of the reactions (Demontis and Suffriti 1997). Since the last few years, Quasi Elastic Neutron Scattering (QENS) (Jobic et al. 2006) and Pulsed-Field Gradient (PFG) NMR (Kärger and Ruthven 1992) have proved to be suitable experimental techniques to investigate the loading dependence of both self (D_S) and transport (D_T) diffusivities of a large family of adsorbates in zeolites materials. It was shown that D_S and D_T more generally decrease and increase (Jobic et al. 2004) respectively when the loading increases. Molecular modelling was then introduced to provide a microscopic interpretation of these experimental data. The main theoretical studies were based on Molecular Dynamics simulations and reliable interatomic potentials (Demontis and Suffriti 1997), some others dealing with Monte Carlo procedures coupled with transition state theory (Maginn et al. 1996). In a previous study, we have shown that combining QENS and Molecular Dynamics simulations is a powerful tool to investigate the diffusion of CO_2, a typical coherent scattered, in Faujasite systems as a function of the density of the cations (Plant et al. 2007a). Here, the diffusion of this adsorbate, is investigated in both LiY and NaY using the same approach, in

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order to emphasize the influence of the nature of the extra-framework cations on the dynamics of CO_2. Both the self diffusivity (D_S) for CO_2 in a wide range of temperature [300–600 K] and the activation energies corresponding to the adsorbate motions within the Faujasite supercages are simulated as a function of the loading. This modelling effort is based on reliable forcefields for reproducing the interactions within the whole system. For LiY, as the literature did not provide accurate and robust interatomic potentials for describing the interactions between Li^+ cation and both CO_2 and the zeolite framework, we derived our own self consistent set of potential parameters. For NaY, our previous forcefields (Maurin et al. 2005), validated by a direct comparison between Grand Canonical Monte Carlo simulations and Microcalorimetry, were selected. The QENS measurements allowed us to extract the transport (D_T) and thus the corrected (D_0) diffusivities via the Darken equation in the two Faujasite forms. The influence of the extra-framework cations on both the values and the loading dependences of each type of diffusivity is then discussed.

2 Experimental

Quasi-elastic neutron scattering (QENS) experiments were performed on the time-of-flight spectrometer IN6, at the Institut Laue-Langevin, Grenoble, France. The QENS method is mainly used to study hydrogenated molecules, because of the large cross section of hydrogen (80 barns). We have found that it was possible to measure the scattering of molecules which do not contain hydrogen atoms, and which, like CO_2 are weak scatterers (the cross sections of carbon and oxygen are 5.55 and 4.2 barns, respectively). On IN6, the incident neutron energy was taken as 3.12 meV, corresponding to a wavelength of 5.1 Å. After scattered by the sample, the neutrons are analysed as a function of flight-time and angle. The wavevector transfer, Q, varies with the scattering angle, it ranged from 0.24 to 1.5 $Å^{-1}$. Spectra from different detectors were grouped in order to obtain reasonable counting statistics and to avoid the Bragg peaks of the zeolite. The line shape of the elastic energy resolution could be fitted by a Gaussian function, whose full width at half maximum (FWHM) varied from 81 μeV at small Q to 100 μeV at large Q.

The LiY and NaY samples were activated by heating under flowing oxygen, up to 720 K. The zeolites were cooled and pumped to 10^{-4} Pa, then heated up to the activation temperature while pumping (final pressure better than 10^{-3} Pa). The zeolites were transferred inside a glovebox into slab-shaped aluminium containers, which could be connected to a gas inlet system. After recording the scattering of the dehydrated zeolite, different concentrations of CO_2 were adsorbed in situ. The loadings were determined by volumetry during the QENS experiment for LiY, and from both the equilibrium pressures and the measured adsorption isotherms for NaY. The three investigated loadings labelled as $\theta 1$, $\theta 2$, and $\theta 3$ correspond to 13, 27, 68 and 25, 40, 71 CO_2 molecules/unit cell (u.c.) for LiY and NaY respectively.

Since the cross sections of carbon and oxygen are totally coherent, one can only extract the transport diffusivity of CO_2 from the QENS measurements.

3 Computational methodology

The chemical composition $Si_{136}Al_{56}M_{56}O_{384}$ (with M = Li^+ and Na^+) was considered in order to reproduce the experimental Si/Al ratio equal to 2.4 for the investigated LiY and NaY samples. The distribution of the extra-framework cations in NaY was modeled as follows, based on the structure refined from Neutron diffraction data (Fitch et al. 1986): 6 cations in SI sites located in the hexagonal prism connecting two sodalite cages, 18 in SI’ sites in the sodalite cage in front of the 6-ring window connected to the hexagonal prism, and 32 in SII sites in the 12-ring windows of the supercages. For LiY, the distribution of the extra-framework cations proposed by Forano et al. (Forano et al. 1989) has been considered with 24 Li^+ in SI’ sites and 32 Li^+ in SII sites. The Faujasite system is assumed to be semi-ionic with atoms carrying the following partial charges (in electron units): Si (+2.4), Al (+1.7), O_z (−1.2) consistent with those used for both Na and Li (+0.7) as previously reported (Maurin et al. 2005). These structures were then loaded with 23, 40, 63 and 25, 40, 71 CO_2 molecules/unit cell (u.c.) for LiY and NaY respectively, which allowed us to be close to the experimental conditions investigated in this work.

The interatomic potentials for describing the interactions between CO_2 and the zeolite framework and between the adsorbate molecules themselves are described in our previous paper (Maurin et al. 2005) where carbon dioxide was defined by an atomic point charge model with the following charges (in electron units) assigned to the carbon C (+0.72) and the oxygen O (−0.36) atoms. For both Na^+–CO_2 and Li^+–CO_2 interactions, our recent Buckingham potentials derived using *ab initio* cluster calculations were considered (Plant et al. 2007b and Maurin et al. accepted). They were validated by a good agreement between the simulated isotherms and the differential adsorption enthalpies in both Faujasite systems using Grand Canonical Monte Carlo simulations, and the experimental data obtained by Microcalorimetry. Additional interatomic potentials were then introduced to describe the flexibility of the framework : the short range interactions were described by Buckingham potentials, including explicit Si–O and Al–O terms, and the harmonic three-body terms were defined for the O_z–Si–O_z and O_z–Al–O_z intra-tetrahedral angles to describe the flexibility of the framework (Ramsahye and Bell 2005). The M^+–O_z interatomic potentials were extracted from previous work (Na^+–O_z) (Ramsahye and Bell 2005) or empirically derived (Li^+–O_z) which allowed to reproduce as fairly as possible both the experimental position and distribution of the cations in the respective Faujasites via energy minimization techniques implemented in GULP (Gale 1997). Table 1 reports the new set of parameters for the Li^+–O_z forcefield compared to those previously described for the Na^+–O_z.

These whole force fields were then implemented in the *DL_POLY* program (Smith and Forester 1996) in the NVT ensemble using the Evans isokinetic thermostat (Frenkel and Smit 1996). We selected for each loading, the structures obtained by Grand Canonical Monte Carlo (GCMC) simulations as starting configurations and the minimised cell dimensions were kept fixed during the Molecular Dynamics (MD) runs. All components of the system (adsorbate and adsorbent) were then treated as fully flexible during the MD simulation. The simulations spanned a range of temperatures between 300 K and 600 K, each for 10^6 steps (i.e. 1 ns) with a time step of 1 fs, following 50000 steps of equilibration. A short-range cut-off of 8.50 Å was used, whilst electrostatic interactions were evaluated using the Ewald method. The trajectory was recorded every 200 steps during the production stage, and radial distribution functions were recorded every 500 steps. The Mean Square Displacements (MSD) of the CO_2 molecule for each loading and at the different temperatures were then evaluated and the fit of these plots as a function of the time allowed the calculation of the self diffusivity (D_S) via the Einstein relation (Frenkel and Smit 1996).

Table 1 Buckingham potential parameters for describing the interactions between the Na^+ and Li^+ cations and the oxygen atom of the zeolites framework (O_z)

Buckingham potential
$A\exp(-r/\rho) - C/r^6$

Ion pair	A/eV	ρ/Å	C/eV Å^6
Li^+–O_z	4600.0	4.878	11.8
Na^+–O_z	8200.0	4.587	25.5

4 Results and discussion

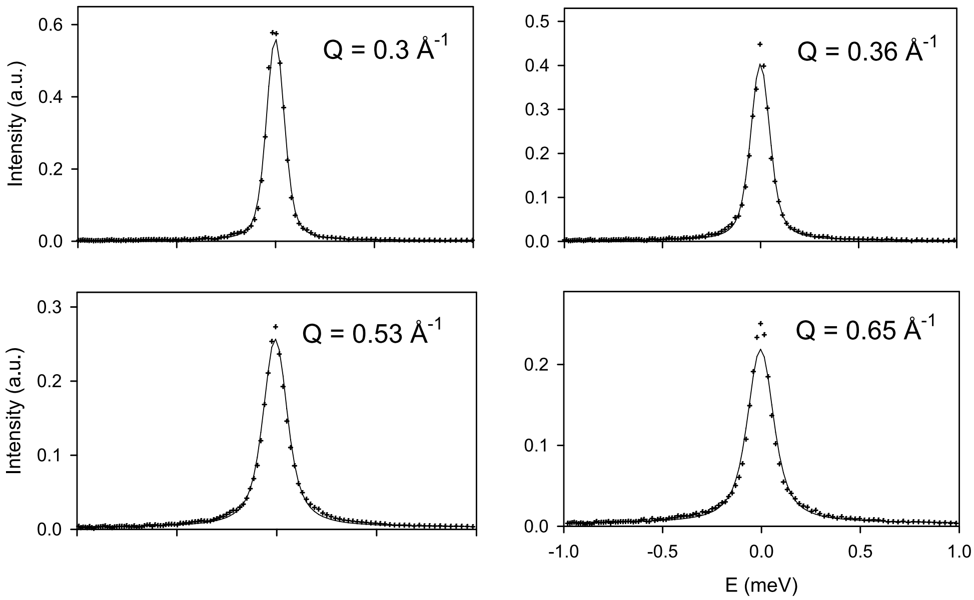
Some of the QENS spectra obtained for $\theta 1$ in LiY, at 300 K, are shown in Fig. 1. The spectra were first fitted individually with a Lorentzian function, corresponding to the diffusion motion, convoluted with the instrumental resolution. The spectra measured at small Q values were then fitted simultaneously using a jump diffusion model, in order to extract the transport diffusivity. The good agreement between experimental and calculated spectra is illustrated in Fig. 1.

Figure 2 reports the transport diffusivities D_T measured by QENS for both LiY and NaY as a function of loading. The corrected diffusivities D_0, also shown in Fig. 2 were derived by correcting the experimental transport diffusivities by the thermodynamic factor, extracted from the derivative of the experimental adsorption isotherms reported in Fig. 3 for both LiY and NaY, via the Darken equation (Jobic et al. 2004):

$$D_T(\theta) = D_0(\theta)\left(\frac{d\ln p}{d\ln\theta}\right) \qquad (1)$$

The self-diffusivities D_S computed from our MD simulations are also provided.

Fig. 1 Comparison between experimental (+) and calculated (*full lines*) QENS spectra obtained for CO_2 in LiY zeolite, at some selected values of the wavevector transfer Q (θ_1, $T = 300$ K)



We can observe that for both systems, D_S decreases as the loading increases due mainly to steric interactions, the characteristic d(C_{CO2}–C_{CO2}) distance between adsorbate molecules becoming significantly shorter. Furthermore, it can be observed that this self-diffusivity is faster in NaY for the whole range of loading. This behaviour is consistent with the lower activation energy calculated at the loading of 25 CO_2/u.c. for NaY (8.40 kJ·mol^{-1}) compared to those obtained for LiY (10.05 kJ·mol^{-1}) at the similar loading of 23 CO_2/u.c., as shown in Fig. 4.

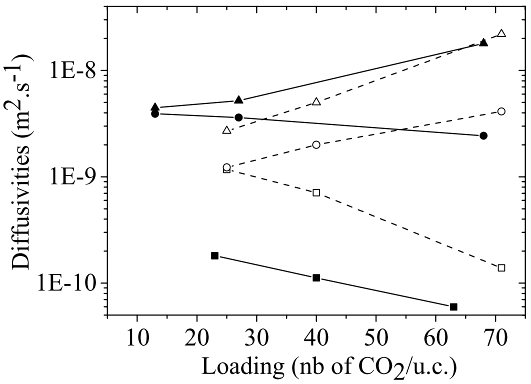


Fig. 2 Transport (△), corrected (○) (QENS) and self (□) (MD simulations) diffusivities for both LiY (*full symbols*) and NaY (*empty symbols*) as a function of the loading at 300 K

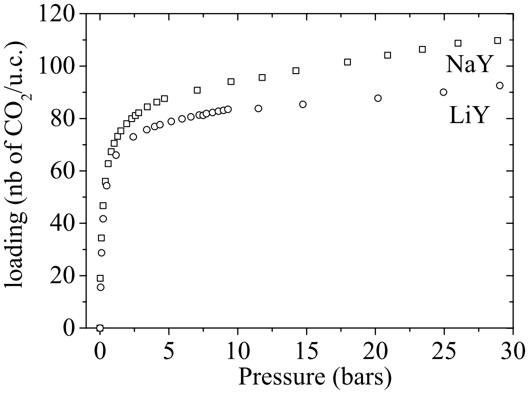


Fig. 3 CO_2 adsorption isotherms for both LiY (○) and NaY (□) obtained by microcalorimetry at 300 K

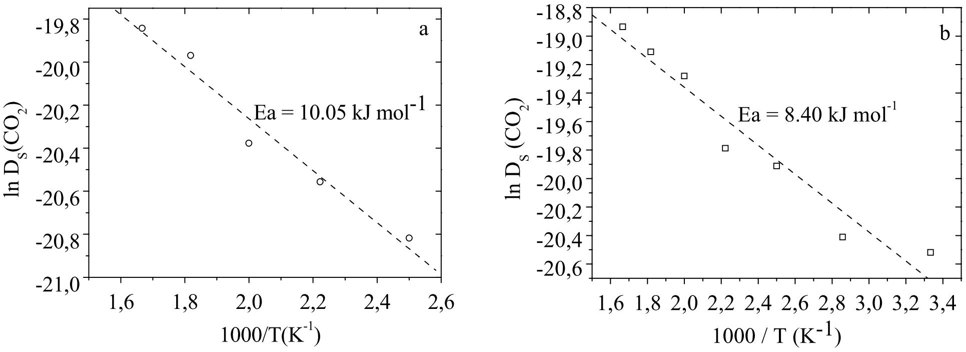
This observation can be explained by a stronger interaction between the adsorbates and the lithium cation which hence induces a higher activation barrier to initiate the diffusion process. This is supported by our recent GCMC simulations (Maurin et al. accepted) which revealed for LiY a higher enthalpy of CO_2 adsorption at low coverage due to an average Li^+ (SII)–O(CO_2) distance (2.10 Å) shorter than the Na^+ (SII) analogue (2.50 Å). However, our MD simulations show that beyond the initialisation of the diffusion, there is also a concerted (Li^+–CO_2) motion similar to those previously pointed for Na^+ (Plant et al. 2006) which induces a redistribution of the cations within the supercage. An illustration of the rearrangement of Li^+ upon CO_2 diffusion is provided in Fig. 5. It can be seen that some cations initially located in sites SII have been de-trapped by the CO_2 molecules and moved to SIII' sites.

To emphasize the influence of the cation mobility on the CO_2 self-diffusivity, we performed simulations for NaY where the cations were maintained fixed in their initial positions along the MD runs. As reported in Fig. 6, freezing the cations leads to a decrease of D_S by about 50% associated to a significant increase of the activation energy (11.2 kJ·mol^{-1} v.s. 8.4 kJ·mol^{-1}). This result confirms that the cation assists the CO_2 diffusion process as previously suggested their redistribution within the Faujasite supercage.

By contrast, the experimental transport diffusivity, D_T strongly increases in both cases (Fig. 2) with the loading in agreement with the trends already observed by both QENS and MD simulations for different gases in silicalite systems (Skoulidas and Sholl 2002; Papadopoulos et al. 2004). Furthermore, LiY exhibits a faster CO_2 diffusion process associated with the highest activation energy as shown in Fig. 7.

It is also pointed out in Fig. 2 that the corrected diffusivity slightly increases and decreases for NaY and LiY respectively. This result deviates from the approximate concentration independence of D_O reported in some zeolite systems (Skoulidas and Sholl 2002) and suggests that the Darken

Fig. 4 Arrhenius plots of the self diffusivities D_S from MD simulations for both LiY (**a**) and NaY (**b**) loaded by 23 and 25 CO_2 molecules per unit cell respectively



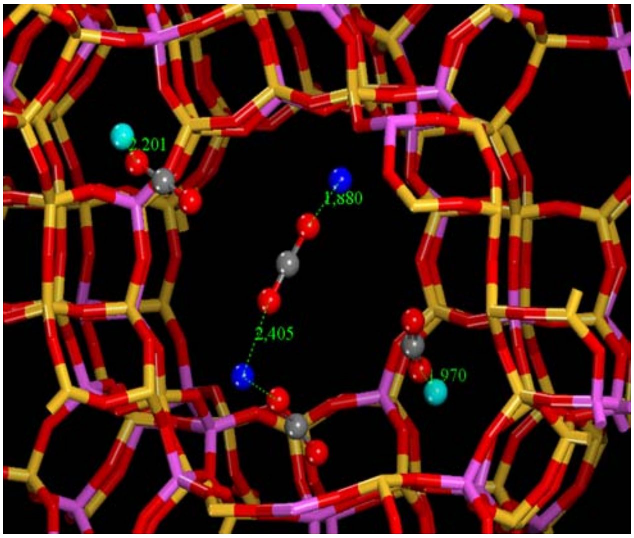


Fig. 5 (Color online) Typical illustrations of the Li^+ redistribution induced by the CO_2 molecules. All the Li^+ cations are initially located in sites SII (*light blue*). A part of them moves to the sites SIII' (*dark blue*)

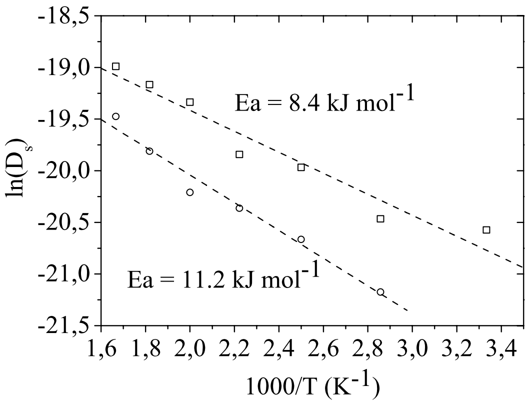


Fig. 6 Arrhenius plot of the self diffusivities D_S from MD simulations for NaY (25 CO_2 molecules per unit cell) considering fixed position for the cations (○). This plot and the resulting activation energy are compared to those obtained with the relaxation of the cation position (□)

approximation is not so accurate for such systems. Furthermore, the different trend observed for LiY and NaY can be explained by the strength of the interactions between the adsorbate molecules as previously suggested by Papadopoulos et al. (2004), which are significantly influenced by the nature of the extra-framework cations.

5 Conclusions

A combination of Molecular Dynamics simulations and Quasi-Elastic Neutron Scattering measurements allowed us to probe the effect of the nature of the extra-framework cations on the CO_2 diffusion behaviour of Y Faujasite systems. It was shown that:

(i) the trends observed for both self and transport diffusivities as a function of loading are identical in LiY and NaY.
(ii) D_S (NaY) > D_S (LiY). This behaviour has been explained by a stronger interaction between Li^+ and the adsorbates.
(iii) D_T (LiY) > D_T(NaY). Long MD simulation runs are still in progress to calculate first the corrected diffusivities and then to be able to explain this trend.

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References

Corma, A.: State of the art and future challenges of zeolites as catalysts. J. Catal. **216**(1–2), 298–312 (2003)
Demontis, P., Suffriti, G.B.: Structure and dynamics of zeolites investigated by molecular dynamics. Chem. Rev. **97**, 2845–2878 (1997)
Fitch, A.N., Jobic, H., Renouprez, A.: Localization of benzene in sodium-Y zeolites by powder neutron diffraction. J. Phys. Chem. B **90**, 1311–1318 (1986)

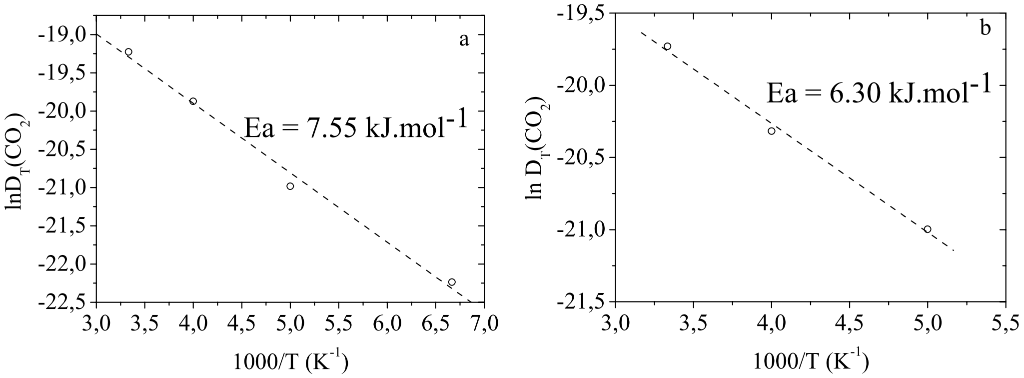

Fig. 7 Arrhenius plots of the transport diffusivities D_T from QENS measurements for both LiY (**a**) and NaY (**b**) loaded by 13 and 25 CO_2 molecules per unit cell respectively

Forano, C., Slade, R.C.T., Krogh Andersen, E., Krogh Andersen, I.G., Prince, E.: Neutron diffraction determination of full structures of anhydrous LiX and LiY zeolites. J. Solid State Chem. **82**, 95–102 (1989)

Frenkel, D., Smit, B.: Understanding Molecular Simulation. Academic, London (1996)

Gale, J.D.: Gulp: a computer program for the symmetry-adapted simulations of solids. J. Chem. Soc. Faraday Trans. **93**, 629–637 (1997)

Jobic, H., Bée, M., Méthivier, A., Combet, J.: Influence of the cation composition on the dynamics of xylene in X-type zeolites. Microporous Mesoporous Mater. **42**, 135–155 (2001)

Jobic, H., Skoulidas, A.I., Sholl, D.S.: Determination of concentration dependent transport diffusivity of CF_4 in silicalite by neutron scattering experiments and molecular dynamics. J. Phys. Chem. B **108**, 10613–10616 (2004)

Jobic, H., Laloué, N., Laroche, C., van Baten, J.M., Krishna, R.: Influence of isotherm inflection on the loading dependence of the diffusivities of n-hexane and n-heptane in MFI zeolite. Quasi elastic neutron scattering experiments supplemented by molecular simulation. J. Phys. Chem. B **110**, 2195–2201 (2006)

Kärger, J., Ruthven, D.: Diffusion in Zeolites and Other Microporous Materials. Wiley, New York (1992)

Maginn, E.J., Bell, A.T., Theodorou, D.N.: Dynamics of long n-alkanes in silicalite: a hierarchical simulation approach. J. Phys. Chem. **100**, 7155–7173 (1996)

Maurin, G., Llewellyn, P.L., Poyet, T., Kuchta, B.: Influence of extra-framework cations on the adsorption properties of X-faujasite systems: microcalorimetry and molecular simulation. J. Phys. Chem. B **109**, 125–129 (2005)

Maurin, G., Belmabkhout, Y., Pirngruber, G., Gaberova, L., Llewellyn, P.: Influence of the extra-framework cations and the temperature on the CO_2 adsorption behaviour in Y-faujasite systems: molecular simulations compared to experiments. Adsorption (accepted)

Papadopoulos, G.K., Jobic, H., Theodorou, D.N.: Transport diffusivity of N_2 and CO_2 in silicalite: coherent quasi-elastic neutron scattering measurements and molecular dynamics simulations. J. Phys. Chem. B **108**, 12748–12756 (2004)

Plant, D.F., Maurin, G., Jobic, H., Llewellyn, P.L.: Molecular dynamics simulation of the cation motion upon adsorption of CO_2 in faujasite zeolite systems. J. Phys. Chem. B **110**, 14372–14378 (2006)

Plant, D.F., Jobic, H., Llewellyn, P.L., Maurin, G.: Diffusion of CO_2 in NaY and NaX faujasite systems: quasi-elastic neutron scattering experiments and molecular dynamics simulations. Eur. Phys. J. Special Top. **141**, 127–132 (2007a)

Plant, D.F., Maurin, G., Déroche, I., Llewellyn, P.L.: Investigation of CO_2 adsorption in faujasite systems: Grand Canonical Monte Carlo and molecular dynamics simulations based on new derived Na^+–CO_2. Microporous Mesoporous Mater. **2**, 440 (2007b)

Ramsahye, N.A., Bell, R.G.: Cation mobility and the sorption of chloroform in zeolite NaY: molecular dynamics study. J. Phys. Chem. B **109**, 4738–4747 (2005)

Skoulidas, A.I., Sholl, D.S.: Transport diffusivities of CH_4, CF_4, He, Ne, Ar, Xe and SF_6 in silicalite from atomistic simulations. J. Phys. Chem. B **106**, 5058–5067 (2002)

Smith, W., Forester, T.R.: DL_POLY 2.0: A general purpose parallel molecular dynamics simulation package. J. Mol. Graph. **14**, 136–141 (1996)