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
order to emphasize the influence of the nature of the extra-framework cations on the dynamics of \( \text{CO}_2 \). Both the self diffusivity \( (D_S) \) for \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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 \( \mu \text{eV} \) at small \( Q \) to 100 \( \mu \text{eV} \) 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 \( \text{CO}_2 \) 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 \( \varphi_1, \varphi_2, \) and \( \varphi_3 \) correspond to 13, 27, 68 and 25, 40, 71 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) from the QENS measurements.

3 Computational methodology

The chemical composition Si\(_{136}\)Al\(_{56}\)Mg\(_{56}\)O\(_{384}\) (with \( M = \text{Li}^+ \) 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 SII sites in the sodalite cage in front of the 6-ring window connected to the hexagonal prism, and 32 in SIII 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 SII’ 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 \( \text{CO}_2 \) 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 \( \text{CO}_2 \) 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\(^+\)–\( \text{CO}_2 \) and Li\(^+\)–\( \text{CO}_2 \) interactions, our recent Buckingham potentials derived using \textit{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 \( \text{O}_z\)–Si–\( \text{O}_z \) and \( \text{O}_z\)–Al–\( \text{O}_z \) intratetrahedral angles to describe the flexibility of the framework (Ramsahye and Bell 2005). The M\(^+\)–O\(_z\) interatomic