Microporous and Mesoporous Materials 222 (2016) 218–225

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Adsorption of argon on pure silica MEL. Volumetric experiments and grand canonical Monte Carlo simulations

Vicente Sánchez-Gil [a], Eva G. Noya [a], [*], José María Guil [a], Enrique Lomba [a],
Susana Valencia [b]

[a] Instituto de Química Física Rocasolano, CSIC, Serrano 119, E-28006 Madrid, Spain
[b] Instituto de Tecnología Química (UPV – CSIC), Avda. de los Naranjos s/n, E-46022 Valencia, Spain

ARTICLE INFO

Article history:
Received 7 August 2015
Received in revised form
16 October 2015
Accepted 20 October 2015
Available online 27 October 2015

Keywords:
Adsorption
Zeolites
Ar
MEL
Molecular simulation

ABSTRACT

The adsorption isotherm of argon on the zeolite MFI at liquid nitrogen temperature exhibits a sub-step at high loading before saturation that, in spite of much theoretical and experimental effort, is still lacking a definitive microscopic interpretation. In this work, we try to get insight into this peculiar behaviour by investigating the adsorption of argon on MEL, a zeolite that is structurally very similar to the MFI. First, we performed volumetric experiments that confirm that the adsorption of argon on MEL presents the same qualitative behaviour as on the MFI, again a sub-step appearing at high loading before saturation. Subsequently, the microscopic origin of this behaviour was investigated by means of molecular simulation. The simulations indicate that, for loads lower than that of the experimental sub-step, argon atoms can accommodate at low energy positions within the zeolite pores, whereas, above this point, some reordering of the adsorbate is needed to host further argon atoms. Moreover, the flexibility of the zeolite can have a significant impact on the shape of the adsorption isotherm, although the magnitude of this change depends on the zeolite model potential.

1. Introduction

The adsorption of simple gases on the zeolite silicalite-1 (pure silica MFI) has attracted considerable attention over the last three decades. This is mainly motivated by the observation that some of them, such as argon, krypton and nitrogen, exhibit one or several sub-steps in the adsorption isotherm at liquid nitrogen temperature [1–3]. Interestingly, the appearance of the sub-step can coincide with an exothermic signature in the heat of adsorption, as in the case of argon, or an endothermic one, as for krypton [1,2]. This suggests that the microscopic origin of the sub-step might be different in these two cases.

For argon, the adsorption isotherm exhibits one step at loadings from about 20 to 25 atoms per unit cell [1,4]. Two main hypothesis have been put forward to explain the origin of this behaviour. According to the first one, the sub-step appears as a result of a liquid–solid-like transition of the adsorbate induced by the confinement [1]. This possibility is supported by the emergence of a number of high intensity peaks on the neutron diffraction patterns after the sub-step. Other authors argue that the sub-step is caused by a structural change of the zeolite [5]. The MFI zeolite is known to undergo reversible structural changes upon increasing the temperature or by adsorption of big aromatic molecules. Specifically, at low temperature the MFI adopts a monoclinic structure [6] which, above 380 K, transforms into an orthorhombic cell with group symmetry *Pnma* [7] or, upon the adsorption of p-xylene, into the so-called PARA configuration with group symmetry $P2_12_12_1$ [8]. The splitting of some diffraction peaks after the sub-step might be indicative of such zeolite structural change [9,10].

Simulations using different argon models (including even three-body contributions [11]) and keeping the zeolite framework rigid, were not able to quantitatively reproduce the experimental adsorption behaviour. In some cases, they yield smooth isotherms without any sub-step and, in other cases, they predict a jump in the adsorption, but at pressures several orders of magnitude higher than in experiments [5,10,12]. Furthermore, simulated diffraction patterns were not able to reproduce the appearance of all the experimental peaks after the step. This could mean that the adsorbate is less ordered in the simulations than in the experiments. However, it could also be indicating a zeolite structural

---

[*] Corresponding author.
E-mail addresses: eva.noya@iqfr.csic.es, eva.noya@gmail.com (E.G. Noya).

http://dx.doi.org/10.1016/j.micromeso.2015.10.023

change, a feature that, obviously, cannot be captured by simulations using a rigid framework. More recently, García-Pérez et al. [4] revisited these simulations, but explicitly incorporating the flexibility of the zeolite, an effect that had long been neglected in previous studies. This approach led to a more faithful description of the adsorption isotherm, from which the authors concluded that the sub-step was due to a combined effect of a structural change of the zeolite and of the adsorbate. However, a detailed description of those atomic structural changes is still lacking.

In this work, we will further investigate this phenomenon from a different perspective, which is by focussing on the related pure silica MEL zeolite, structurally very similar to the MFI but somewhat simpler (see Fig. 1). In particular, the MFI framework consists of parallel straight cylindrical pores that are intersected by sinusoidal channels, exhibiting four of that intersections per unit cell. The MEL zeolite exhibits a very similar structure, with the only difference being that in this zeolite all the channels are straight and, consequently, its unit cell has a higher symmetry (with space group I-4m2) [13]. In addition to that, there are experimental evidences that, similarly to MFI, MEL might also undergo a structural change upon increasing the temperature (at roughly 320 K) [14–16]. However, as far as we know, such structural transformation has not yet been fully characterized [13]. Given the structural similarity between both zeolites, it seems reasonable to think that both of them should exhibit a similar adsorption behaviour.

2. Experimental procedure

Measurements were performed on an expressly synthesized pure silica ZSM-11 sample. Details of the synthesis of the ZSM-11(Si) sample are reported elsewhere [17]. In a previous work, using the “t”-method, we estimated that the micropore volume of the sample was 0.12 cm^3/g [17]. This value is agreement with the literature [18,19]. High purity Ar (99.999%, Air Liquide, Spain) was used as adsorbate.

2.1. Adsorption volumetry

In an adsorption experiment, small doses of Ar were successively added at increasing pressures, measuring the increment of amount adsorbed to obtain the volumetric isotherm, $n^\sigma - p$. The amount adsorbed, n^σ, was determined in a volumetric apparatus, equipped with two pressure transducers (Baratron 310, MKS, USA) of 0–1.33 kPa and 0–133 kPa ranges, respectively. Dead volumes were determined by mercury weighting and helium expansions. Reproducibility in the measurement of amount adsorbed, determined by successive helium expansions, was better than 0.2 μmol.

Before each experiment the samples were heated in oxygen flow, c.a. 30 cm^3/min, up to 723 K, and kept at this temperature for 4 h to eliminate any organic residue. After that, the sample was outgassed overnight at 723 K in a vacuum better than 1 mPa. All experiments were carried out at 77 K with the sample cell immersed in a boiling liquid nitrogen bath. Bath temperature was determined with a home made oxygen vapour pressure thermometer. Second virial coefficient correction was applied to take into account the non-ideal behaviour of Ar vapour. For the case of argon this correction is negligible, but we still included it because it is our usual protocol for any adsorbent/adsorbate experiment. An experimental range of relative pressure, p/p_0, from 10^{-6} to 1 was covered in the measurements.

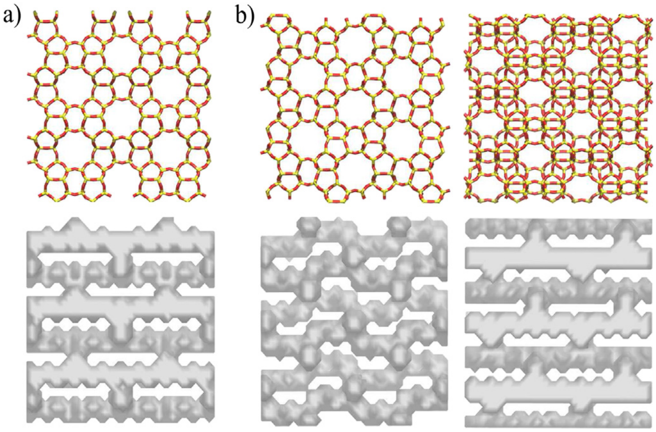

Fig. 1. Structure of the a) MEL and b) MFI zeolite frameworks. Two different views are shown for the MFI. The volume accessible to the argon atoms is shown in the bottom figures.

3. Modelling and simulation

3.1. Model potentials

In this work, interactions between argon atoms, and between argon and the zeolite, are described by the Lennard-Jones potential. The parameters for the argon–argon interaction are taken from Ref. [4], where they were fitted to the experimental liquid–vapour curve. The crossed argon–oxygen parameters were adjusted to reproduce the experimental adsorption isotherm, a usual approach in simulations of adsorption processes [4,20]. Given that silicon atoms are caged inside oxygen tetrahedra, only the oxygen atoms are considered when evaluating the van der Waals interactions between the adsorbate and the zeolite. Interactions with silicon atoms are thus implicitly incorporated in the crossed oxygen–adsorbate interactions. The Ar–Ar and Ar–O parameters used in this work are summarized in Table 1.

As regards the zeolite intramolecular interactions, numerous model potentials can be found in the literature [21–27]. In this work, we focused on the popular models proposed by Demontis et al. [21] and by Nicholas et al. [22]. Our choice is motivated by a recent study that showed that both were able to reproduce reasonably well the experimental infrared spectra of a large variety of zeolites, including that of MEL [28]. In particular, the best results were obtained for the Nicholas model, that incorporates bonding, bending and torsional, as well as van der Waals and Coulombic non-bonded terms, and whose parameters were fitted to *ab initio* and experimental data [22]. On the other hand, the Demontis model is rather simple, including only bonding terms between the O–O and Si–O atoms. Surprisingly, it was found to perform better than more sophisticated models, such as that proposed by Hill and Sauer [24]. The parameters for the Demontis model were fitted to experimental structural data and the infrared spectrum of zeolite LTA, but numerous studies have proven its transferability to study properties of other zeolites [28,29].

Besides using the original parameterization for these two models, we have also considered modified versions that, in what

Table 1
Parameters of the Lennard-Jones model used for the argon–argon and argon–zeolite interactions. For comparison, the parameters used in Ref. [4] to study the adsorption of argon on MFI are also provided.

	MEL (This work)		MFI (Ref. [4])	
	ε/k_B (K)	σ (Å)	ε/k_B (K)	σ (Å)
Ar–Ar	124.07	3.380	124.07	3.380
Ar–O	114.81	3.1265	107.69	3.150