



# Bis-chlorinated aromatics adsorption in Faujasites investigated by molecular simulation-influence of Na<sup>+</sup> cation



J. Randrianandraina, I. Deroche<sup>\*</sup>, R. Stephan, M.-C. Hanf, Ph. Sonnet

Institut de Science des Matériaux de Mulhouse, UMR 7361- CNRS - UHA, 15 rue Jean Starcky, 68057 Mulhouse, France

## ARTICLE INFO

### Article history:

Received 16 March 2017

Received in revised form

12 May 2017

Accepted 23 May 2017

Available online 25 May 2017

### Keywords:

Adsorption

Chlorinated aromatics

FAU zeolite

DFT

Gibbs ensemble Monte Carlo

Adsorption isotherms

## ABSTRACT

Molecular simulations have been employed in order to explore at the microscopic scale the adsorption of bis-chlorinated aromatics (1,2- and 1,3-dichlorobenzene) in Faujasite, a large pore openings zeolite. Both, the purely siliceous and the sodium cation exchanged forms of zeolite structures have been respectively considered, aiming to clearly determine the role of the charge compensating cation in the adsorption phenomenon of the investigated aromatics. A suited combination of classical and electronic structure simulation tools provided a clear overall picture of the adsorption process, from both local and global points of view, well matching with the accessible experimental data. The adsorbate preferential locations, adsorbate/zeolite interaction nature and geometry as well as the adsorption energy were extracted from Density Functional Theory calculations. Furthermore, on the basis of classical force fields, the Gibbs ensemble Monte Carlo simulations allowed predicting the room temperature (298 K) adsorption isotherms for the investigated molecules in Faujasite, within the purely siliceous and Na<sup>+</sup> exchanged form, with mobile extra-framework cations upon the adsorption process. Finally, we accomplished a detailed analysis of the microscopic mechanism in play along the whole adsorption process, with a special highlight to the understanding of the interaction geometry of the molecule with the sodium cation, in function of its crystallographic site. Location of the charge compensating cation has been found to influence the nature of interaction with the adsorbate molecule.

© 2017 Elsevier Inc. All rights reserved.

## 1. Introduction

Nowadays, chlorinated benzenes (ClBs) are widespread substances in the overall environment, mainly in reason of their long period extended industrial processing for use such as solvents, pesticides, chemical raw materials etc [1]. It is actually clearly established that the toxicity of ClBs represents, for multiple reasons, an important environmental issue. First, because of their volatility and undegradability [2], those compounds embody major persistent pollutants for seawater and aquatic organisms [1]. Further, through their liposolubility, the ClBs easily accumulate in soils whence they enter the food chains and thus contaminate human's adipose tissue and/or blood, potentially causing a large scale of health troubles [3]. Finally, those compounds constitute precursors of dioxins, extremely toxic molecules [4]. Consequently, harmful for both the environment and the human health, the ClBs have been ranked as priority pollutants by the US Environmental

Protection Agency [5,6]. The major challenge of finding an environment-friendly solution of ClBs removal thus represents an urgent task. An appealing solution seems to be the selective adsorption of ClBs in porous materials, through both lower cost and higher efficiency compared to other techniques such as absorption in liquid solvents or condensation [7]. Various porous materials [8] like activated carbons [9,10] carbon nanotubes [11], hydrophobic hypercrosslinked polymers [12] or zeolites [13] have been tested for the gaseous chlorinated aromatic pollutants removal. Zeolites have been identified as particularly promising candidates for the ClBs adsorbents, since they gather relevant structural and textural properties: well controlled pore size distribution, high crystallinity, great thermal, chemical and mechanical stability, important surface area and porous volume as well as environmental safety [14]. Besides, zeolites can be synthesized in both the purely siliceous and the aluminosilicate, cations containing, forms. Thus, varying the chemical composition of the zeolite allows fine tuning of their hydrophobic/hydrophilic character, as well as their affinity for the adsorbate molecules [15,16].

<sup>\*</sup> Corresponding author.

E-mail address: [irena.deroche@uha.fr](mailto:irena.deroche@uha.fr) (I. Deroche).

Some mainly experimental investigations of gas phase ClBs adsorption in ordered microporous materials can be found in the literature. Hernandez et al. reported adsorption isotherms and isosteric heats of adsorption of chlorobenzene in several microporous purely siliceous adsorbents, investigated through inverse gas chromatography [17]. Rioland et al. measured the kinetics of adsorption of the 1,2-dichlorobenzene within the FAU zeolite, in the powder form and organic linkers containing beads, in order to determine the respective adsorption performances of such complex materials [4]. Room temperature liquid phase adsorption of selected chloroaromatics has been investigated experimentally by chromatography over various Metal Organic Frameworks (MOFs) [18].

In the present paper, we report the adsorption properties of chlorine bis-substituted benzene molecules in the zeolite with FAU topology, investigated through an appropriate combination of classical and Density Functional Theory (DFT) molecular simulation tools. On the one hand, based on the DFT calculations, we provide a detailed analysis of the zero coverage adsorbate/zeolite geometries, interaction types and energies. On the other hand, from the Monte Carlo simulations, we extract the whole adsorption isotherms as well as the intermediate/high loading molecules locations and structuring. The adsorbate molecules selected for this study are the ortho- and meta-dichlorobenzenes. The ortho-dichlorobenzene is known to imitate the properties of 2,3,7,8-tetrachlorodibenzo-p-dioxin [4] presenting extremely high toxicity [19]. The meta-dichlorobenzene is also considered in order to depict the influence of the chlorine substituents relative position on the adsorption properties. Particularly aiming to determine the role of the alkali cation in the adsorption process, we consider the FAU zeolite in both purely siliceous (hypothetic) as well as aluminosiliceous composition containing charge compensating sodium cations. The Faujasite zeolite can be synthesized with various Si:Al ratios, here we focused on the NaX polymorph with the Si:Al ratio of 1.1. Moreover, from several points of view the FAU-type topology is expected to favor adsorption of compounds such as dioxins and/or the DCIBs. First, the FAU-type topology displays a three-dimensional large pore structure (pore opening size of 7.4 Å), promoting fast mass transfer rates inside and outside the zeolite framework [20]. Further, although zeolites with large porosity generally don't present important affinities for aromatics adsorption [21], the presence of charge compensating cations arises an electric field within the supercage (containing an average of 7.5 Na<sup>+</sup> cations), drastically modifying both affinity and selectivity for the adsorbate molecules. We concentrated exclusively on the sodium cation, since it corresponds to the standard as-synthesized composition [22]. Finally, from the textural point of view, Faujasite belongs among zeolites with the highest adsorption capacity due to both its surface area and microporous volume respectively of ~800 m<sup>2</sup> g<sup>-1</sup> and 0.33 cm<sup>3</sup> g<sup>-1</sup> [23].

## 2. Computational details

### 2.1. Microscopic models

#### 2.1.1. The Faujasite structures

In order to investigate the role of the Na<sup>+</sup> cations in adsorption process, we considered separately the FAU zeolite in two chemical compositions: the hypothetical - purely siliceous one and the aluminosilicate one containing Na<sup>+</sup> charge compensating cations. Whereas, for the pure silica FAU zeolite, we placed the Si and O atoms on the crystallographic positions according to the model reported by Colligan et al. [24], the cationic NaX system with the chemical composition Si<sub>100</sub>Al<sub>92</sub>Na<sub>92</sub>O<sub>384</sub>, which reproduces the experimental Si:Al ratio of 1.1, was modeled using the experimental

data reported by Zhu et al. [25]. Both systems have a cubic unit cell with lattice parameters respectively of 24.26 Å and 25.08 Å. For the NaX model, the distribution of Al atoms strictly respects the Löwenstein's Al–O–Al avoidance rule [26]. The extra-framework cations were distributed in accordance with the model experimentally determined by Zhu et al. [25]. The distribution is defined as follows: 32 cations in sites I' (SI') located within the sodalite cages, in front of a 6-membered ring, 32 cations in sites II (SII) and 28 in sites III' (SIII') (both of the latter sites are located within the supercage, respectively coordinated by the 6-membered ring and situated in the plan of the 12-membered ring separating 2 supercages).

For the Monte Carlo simulation part, the Faujasite system is assumed to be semi-ionic with atoms carrying the following partial charges (in electron units): Si (+2.4), Al (+1.4), O(z) (–1.2) and Na (+1) [27].

#### 2.1.2. Adsorbate molecules

The DFT optimized molecular geometries of the investigated bis-chlorinated aromatic molecules were taken from Rai et al. [28]. For the purpose of the subsequent Gibbs ensemble Monte Carlo (GEMC) simulation the adsorbate molecules were described via the explicit hydrogen model where each atom constitutes a single, partial charge bearing, interaction site. Both the aromatic cycle and attached exocyclic atoms were considered as rigid entities, consequently no intramolecular interactions were taken into account. The partial charges carried by each atom are presented in the Table 1.

#### 2.1.3. The FAU zeolite/adsorbate molecules interaction potential

The intermolecular sorbate/sorbate and sorbate/zeolite interactions were modeled using a sum of repulsion–dispersion and the electrostatic potential expressed via the Lennard-Jones (LJ) and the Coulombic terms, as described in Equation (1):

$$U_{ij}^{Inter} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \quad (1)$$

In Equation (1)  $q_i$  and  $q_j$  are the atoms partial charges,  $r_{ij}$  is the distance separating two atoms and  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the corresponding LJ interatomic potential parameters. The parameters for adsorbates corresponding to those terms have been taken from the Transferable Potential for the Phase Equilibrium (TraPPE) [28] force field, initially fitted to reproduce the liquid/vapor coexistence curves. Additionally, the parameters for zeolite were extracted from the Clay force field [27]. The whole set of all applied parameters is reported in Table 1. The Lennard-Jones cross-terms were calculated through the Lorentz-Berthelot combination rule.

### 2.2. GEMC simulation

Absolute adsorption isotherms of ortho- and meta-dichlorobenzene (ortho- and meta- DCIB) were computed at 298 K in both the purely siliceous and aluminosilicate, charge compensating cations (Na<sup>+</sup>) containing Faujasite, applying the Configurational-bias Monte Carlo simulation within isobaric–isothermal (NpT) version of the Gibbs ensemble [29], implemented within the code Towhee [30]. We have applied the osmotic version of the Gibbs ensemble, where only the adsorbate molecules are allowed to transfer between gas phase reservoir and zeolite. Major advantages of such simulation set are a close imitation of the experimental set up and no need of the chemical potential calculation. The system used for all simulations contained a total of 500 adsorbate molecules (in the gas phase reservoir or

Download English Version:

<https://daneshyari.com/en/article/4758151>

Download Persian Version:

<https://daneshyari.com/article/4758151>

[Daneshyari.com](https://daneshyari.com)