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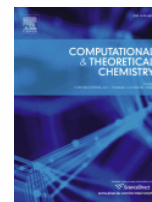
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# DFT study of $\text{Li}^+$ and $\text{Na}^+$ positions in mordenites and hydration stability

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## ABSTRACT

Mordenite is a type of zeolite used in catalysis processes and in the selective adsorption of gases. The properties of this material are related to the presence of aluminium atoms and exchangeable cations in the structure. In this work, we performed DFT periodic calculations of cationic mordenites  $\text{X}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}$  and  $\text{X}_4\text{Al}_4\text{Si}_{44}\text{O}_{96}$  ( $\text{X} = \text{Li}^+$  or  $\text{Na}^+$ ) and the corresponding hydrated species. Calculations of  $\text{Li}^+$  and  $\text{Na}^+$  mordenites indicated preference for the aluminium atoms to occupy T3 and T4 sites. In this configuration, the alkaline cations have preference for the two channels 8MRz and 12MRz along [001] crystallographic axis. In the hydrated structures, the alkaline cations have preference for the side pockets (8MRy along [010] direction). Hydrated structures with high aluminium content have a stability caused by interaction of the alkaline cations with water molecules and oxygen atoms of the framework.

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## 1. Introduction

Zeolites are natural or synthetic microporous materials composed by tetrahedral  $\text{SiO}_4$  and  $(\text{AlO}_4)^-$  sites [1]. They are used in a broad range of processes, from gas separation and purification to ion exchange and catalysis [2-5]. The substitution of silicon  $\text{Si}^{4+}$  for aluminium  $\text{Al}^{3+}$  introduces a negative charge in the structure, which has to be compensated by the presence of exchangeable ions, such as alkaline and transition metal cations [6].

The Si/Al ratio in zeolites can be controlled experimentally, whereas the exact positions of the aluminium atoms in the framework, and consequently the positions of the exchangeable cations, are much more difficult to be determined [6]. The type of exchangeable ions influences the adsorption or catalytic properties of the zeolites, and their positions are related to the aluminium distribution in the structure. Macroscopically, the localization of the aluminium atoms may vary from the centre of the crystal to the outer edges of the structures. At a microscopic level, it is

accepted that two aluminium atoms can never bind to the same oxygen atom, in accordance with the Lowenstein's rule [7].

Mordenite is a type of zeolite used in catalytic processes, such as alkane and olefin cracking, isomerization of hydrocarbons, and in the selective adsorption of gases [8-11]. The framework of mordenites has an one-dimensional channel system, which consists of 12 and 8-membered ring (MR) channels parallel to [001] crystallographic axis. The main channel (12MRz) has dimensions of about  $6.7 \times 7.0 \text{ \AA}$ , while the smaller one (8MRz), in the elliptical shape, has dimensions of  $2.6 \times 5.7 \text{ \AA}$  (Fig. 1a). These channels are interconnected along the [010] direction via 8MRy channel, often referred to as the "side-pockets", formed by a more circular ring ( $3.4 \times 4.8 \text{ \AA}$ ) (Fig. 1b) [12]. Figure 1c shows the unit cell of silica mordenite that contains 48 silicon and 96 oxygen atoms ( $\text{Si}_{48}\text{O}_{96}$ ) and encloses 16 T1, 16 T2, 8 T3 and 8 T4 sites. Any of these T sites can be occupied by aluminium atoms, obeying Lowenstein's rule [7]. Each aluminium atom introduces a negative charge, which is counterbalanced by the presence of exchangeable cations [13,14]. The type of exchangeable cations and their locations strongly influence the physical

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