

DFT study of Li, Na and K positions in mordenites: implication for the adsorption properties

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INTRODUCTION

Zeolites are natural or synthetic microporous materials composed of tetrahedral $[\text{SiO}_4]$ and $[\text{AlO}_4]$ unities used in a broad range of processes¹. The substitution of silicon (Si^{4+}) for aluminium (Al^{3+}) causes a negative charge in the structures which is compensated by the presence of exchangeable cations. An important parameter in zeolites is the Si/Al ratio which is easy to control experimentally, whereas the exact position of Al atoms in the framework and, consequently, of the cations is much more difficult. The alkaline cations in the zeolites influences the adsorption properties and their positions are strongly related to the Al distribution. In this work we performed periodic calculations of Li, Na and K mordenites with Si/Al ratio of 5 and 11. The aim of this work is to describe the preferential positions of the alkaline cations and their effects on the adsorption properties.

METHODS

A hydrated crystalline mordenite structure was obtained from the database of zeolites². Two homogeneous Al distribution were assumed, according to the Lowenstein rule. Optimizations of the $\text{X}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot 8\text{H}_2\text{O}$, $\text{X}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}$ and $\text{X}_4\text{Al}_4\text{Si}_{44}\text{O}_{96}$ ($\text{X} = \text{Li}^+$, Na^+ and K^+) structures were performed using the cp2k program at periodical level (1x1x1) with the cell parameters $a = 18.256$; $b = 20.534$; $c = 7.542$ Å and $\alpha = \beta = \gamma = 90^\circ$. The plane wave method (PAW) with PBE exchange-correlation functional and the Ahlrichs-VDZ basis set was used.

RESULTS AND DISCUSSION

Optimization of Li^+ -MOR, Na^+ -MOR and K^+ -MOR (Si/Al=5) showed three preferential positions for the alkaline cations. In the hydrated mordenites the cations surrounded by solvating water molecules prefer the small channel (Fig. 1a). In the absence of water the alkaline cations

moved to the main channel leading to a third position (Fig. 1b).

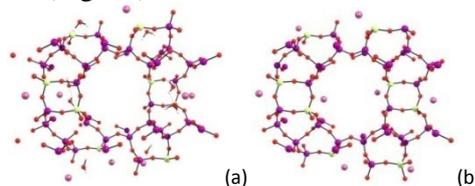


Figure 1. Periodical optimization (1x1x1) of Na^+ -MOR: (a) $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}\cdot 8\text{H}_2\text{O}$ and (b) $\text{Na}_8\text{Al}_8\text{Si}_{40}\text{O}_{96}$ (PAW/PBE/Ahlrichs-VDZ basis set).

The K^+ -MOR showed a higher degree of structural deformations and an alignment of the K atoms with the oxygen in the small channel.

In the Na^+ -MOR, the $[\text{AlO}_4]$ site at the small channel has higher negative charge (-0.58) compared to the corresponding hydrated structure (-0.38).

Although it has been suggested that the Al positions are controlled by experimental conditions¹ our theoretical calculation of $\text{Li}_4\text{Al}_4\text{Si}_{44}\text{O}_{96}$ and $\text{Na}_4\text{Al}_4\text{Si}_{44}\text{O}_{96}$ (Si/Al=11) showed that alkaline cations prefer the small channel by 27.3 and 39.0 kcal mol⁻¹, respectively.

CONCLUSIONS

In the hydrated mordenites the cations surrounded by solvating water molecules prefer the small channel. In the absence of water the hydrated cations moved to the main channel. K^+ -MOR showed a more structure distortion and an alignment of K atoms with the oxygen atom in the small channel.

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¹J. Dedecek, B. Wichterlova, Z. Sobalik. *J. Phys. Chem. b.* 103, 1462, (1999).

²Database of Zeolite Structures, <http://www.iza-structure.org/databases>.