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Trivalent ions modification for high-silica mordenite: A first principles study



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ABSTRACT

Using periodic DFT-D3-U methods, the present work give a mechanistic insight into the high silica B-, Al-, Ga- and Fe-MOR with H, Li, Na, and K as charge balance ions. The acid properties of the zeolite were probed via NH₃ and pyridine adsorption. It is found that the charge balance ions influence the location of the trivalent ions, the cell volumes, as well as the synthesis difficulty of the zeolites. The energy differences for B, Al, Ga and Fe in different T sites are small for the H-form zeolites, while large for the Na- and K-form zeolites. For H-form MOR, the proton of the —OH group prefers to bond to O(7) and O(3) and pointing to the 12MR for trivalent ions in T1 sites. The proton bonds to O(3), O(2), O(2) and O(5), respectively, for B, Al, Ga and Fe in T2 site of MOR, with the —OH group pointing to intersection of 12MR and the side-pocket, except for the B-MOR that —OH group pointing to the 12MR. For trivalent ions located in T3 and T4 sites, the protons prefers to bond to O(1) and O(2), respectively, with the —OH group pointing to the intersection of 8MR and side-pocket as well as the intersection of 12MR and side-pocket. All incorporated B, Al, Ga, and Fe framework ions are tetra-coordinated, except the B atoms are tri-coordinated. The NH₄-form MOR has smaller cell volume than the other form MOR. Na and K are energetically more favored charge balance ions than Li and NH₃ for MOR zeolites synthesis, and the H-form zeolite is the most difficult to be synthesized directly. The strength of the Brønsted acidity follows the order: HBMOR < HFeMOR ≈ HGaMOR < HAlMOR, vs. the Lewis acidity order: HBMOR < HAlMOR < HFeMOR ≈ HGaMOR. NH₃ could be adsorbed inside all kinds of channels, and especially favors in the small 8MR vs. pyridine could only be adsorbed in the main channel of MOR due to the steric effect. It indicates that the acid sites in the side pocket and the small 8-membered ring and the side pocket could not be effectively determined just by the pyridine adsorption experiments. In comparison, the NH₃ adsorption experiments could detect all kinds of Brønsted sites of the MOR zeolites.

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1. Introduction

Zeolites are crystalline porous materials frequently used in many industry processes [1]. The properties of zeolites are determined by their pore structures, and in turn are determined by the preparation conditions [2]. Mordenite (MOR) is one of the important zeolites [3], which could be used as catalyst for many chemical

reactions, such as toluene disproportionation [4], methylation of toluene and benzene with methanol [5], selective catalytic reduction of NO_x and so on [6].

Due to the great importance of mordenite in industry, previous works have intensively investigated into the preparation methods, structures, acid properties and its application in catalytic reactions using both experimental and theoretical methods [7–25]. It is already known that the pure siliceous framework of mordenite is of *Cmcm* space group [26], and the extraframework ions may break the symmetry. The orthorhombic unit cell of nature mordenite has the lattice parameters of $a = 18.09 \text{ \AA}$, $b = 20.52 \text{ \AA}$, and $c = 7.52 \text{ \AA}$ [27,28]. There are two channels parallel to the c axis of the crystal, one is consists of 12-membered with the size of $6.7 \text{ \AA} \times 7.9 \text{ \AA}$ and the other consists of 8-membered ring with the size of $2.6 \text{ \AA} \times 5.7 \text{ \AA}$. These two

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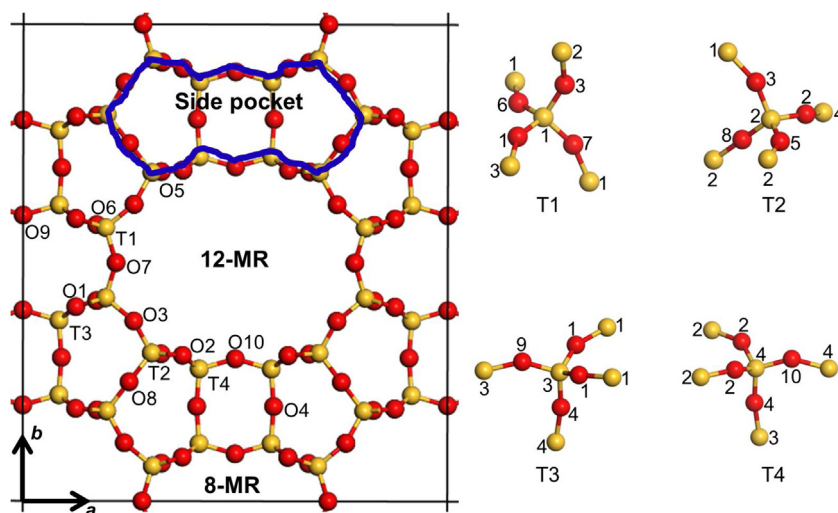


Fig. 1. The $p(1 \times 1 \times 2)$ cell of mordenite and the local structures of the building units of T sites. (Si and O atoms are shown in yellow (indexed with numbers 1–4) and red (indexed with 1–10), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

channels are interconnected along the b axis via 8-membered side pockets with the size of $3.4\text{\AA} \times 4.8\text{\AA}$ [29]. As shown in Fig. 1, the structure of mordenite has four non-equivalent crystallographic tetrahedral sites which were usually called as T1, T2, T3, and T4 sites, and ten different crystallographic oxygen sites, which were labeled as O(1–10). T1 connects to the nearby T1, T2, T1, and T3 sites via O(6), O(3), O(7) and O(1), respectively vs. T2 connects to the nearby T1, T4, T2, and T2 sites via O(3), O(2), O(8) and O(5); T3 connects to the nearby T1, T1, T3, and T4 sites via O(1), O(1), O(9) and O(4); and T4 connects to the nearby T2, T2, T4, and T3 sites via O(2), O(2), O(10) and O(4). T1 and T2 sites are in the 5-membered ring and O(3) and O(4) sites in the 4-membered ring. T1 faces to the 12-membered main channel and 8-membered channel, vs. T2 and T4 face to the 12-membered main channel and the side pocket, and T3 faces to the 8-membered channel and side pocket [29].

For the widely used aluminosilicate mordenite, the location of the framework Al had been extensively studied. The experiments results of Alberti indicates that T3 is the preferential position for framework Al atom and followed by the T4 [28]. However, the theoretical results differ in the assignment of the most stable T sites for Al location [30], since the computational results depends on the mordenite model as well as the computational methods. Sauer and Brändle studied the location of Al in mordenite using Hartree-Fock (HF) methods and a model potential to mimic the periodic structures of the zeolite [22], and found the Al preferential position in mordenite following the order: $T4 > T2 > T1 > T3$, with the energy differences between T3 and T4 as small as 4.4 kJ/mol. Demuth et al. employed the local-density approximation and gradient-corrected functional with a periodic mordenite model, found that the stability order: $T1 > T2 > T4$ [31]. The HF calculation of Yuan *et al.* using the single pentameric cluster to represent each crystallographic tetrahedral sites shows that Al prefers the T3 and T4 sites over T1 and T2 [32]. On the basis of density functional theory (DFT) calculations, Oumi *et al.* found that the stability order for the Al location depends on the size of the cluster. For the smaller clusters, the order is: $T3 > T4 > T1 > T2$ [29], while, as the cluster size increases the order changes to $T3 > T1 > T4 > T2$. When periodic boundary conditions are used, the stability follows the order: $T3 > T2 > T1 > T4$.

It should be mentioned that the substitution of one tetravalent Si^{4+} by one trivalent cation (M^{3+}) could generate one negative charge for a supercell under the periodic boundary conditions. Theoretically, the charge can be distributed in the whole supercell. However, it is usually distributed on the more electronegative

oxygen atoms which connect the substituted atoms, and can be compensated by H^+ in the same supercell, generating the Brønsted site. After the substitution process, the M^{3+} stays in the framework of the zeolites should have vacant orbitals that can accept electrons. Following the view of Lewis, the framework M^{3+} can also work as Lewis sites in the zeolites [33].

The acid property of mordenite also attracts great attention in catalysis, due to it influences the catalytic performance of the zeolites. The location of protons in H-form Al incorporated mordenite has been extensively studied by a variety of methods [9], including X-ray/neutron diffraction, FTIR spectroscopy, and *ab initio* calculations. However, conflicting results had been reported. Early X-ray diffraction studies on dehydrated H-form Al incorporated mordenite indicates that the probability of proton attachment to the different oxygen sites was equal [34]. On the basis of FTIR studies, the low frequency and high frequency $\nu(\text{OH})$ bands have been assigned to OH groups in the 8-membered and 12-membered rings, respectively [35]. Martucci *et al.* studied the deuterated mordenite using neutron diffraction and found that there are four different Brønsted acid sites [36]. One is on O(6) site, at the entrance of the side pocket; another is on O(9), in the center of the 8-membered ring channel; the other two are on the O(5) and O(10) sites, pointing into the center of the 12-membered ring. Bevilacqua and co-workers further proposed that the low frequency OH group corresponds to the O(6) site, while the high frequency OH groups are due to Brønsted acid at O(2), O(5), O(3), O(7) and O(10) sites [37,38]. Marie *et al.* reported that there is a third type of Brønsted acid site corresponding to a $\nu(\text{OH})$ band at an intermediate frequency, which suggests three types of OH groups located at O(2)–O(7)–O(9) [16]. DFT calculations of zeolites H-form mordenite gave similar results that OH groups locate at O(2)–O(7)–O(9) or O(2)–O(7)–O(9)–O(10) [31,39]. Alberti also concluded that the most likely sites for the Brønsted acid protons are O(2)–O(7)–O(9) [28]. However, DFT calculations found that the main channel and side pocket OH groups are actually similar in energy and the experimentally observed low frequency band should not be simply ascribed to Brønsted acid sites located in the side pockets that have additional hydrogen-bonding interactions with the framework [40]. Solid-state MAS NMR studies on the H-form mordenite show that there are four most plausible locations for Brønsted acid sites in mordenite (a) O(1)/O(9), pointing into the center of the 8-ring channel; (b) adjacent pair of O(2) sharing one proton through hydrogen-bonding; (c) O(5), which points slightly toward the side pocket;

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