Structural and physico-chemical properties of high-silica mordenite

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Abstract

The structural and physico-chemical properties of high-silica mordenite (MOR) zeolite were investigated using chemical computational techniques and then the results obtained were compared with our experimental data. With an increase in the size of structure model in which each four non-equivalent crystallographic tetrahedral site (T site) was substituted by Al atom, the order of stabilization energy varied. However, T3 site present in side pocket was energetically the most stable one among these four sites regardless of the model employed, namely it was found that Al atom is preferentially sitting in the T3 site of MOR zeolite.
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1. Introduction

Mordenite (MOR) zeolite is one of industrially important zeolites due to its good catalytic activity and thermal stability and used as a solid acid catalyst in refining and petrochemical catalytic processes [1–3]. MOR zeolite framework has 1-D channel system, which consists of 12- and 8-membered ring (MR) channels parallel to [001] direction, 6.5×7.0 Å and 2.6×5.7 Å in diameter, respectively. These channels are interconnected along [010] direction via 8-MR channel (side pocket, 3.4×4.8 Å in diameter). In the structure of MOR zeolite with the *Cmcm* space group, there are four non-equivalent crystallographic tetrahedral sites (T: Si or Al atoms), usually called T1, T2, T3 and T4 sites, and 10 different crystallographic oxygen sites, O1 – O10 sites (Fig. 1) [4,5]. T1 and T2 sites are located in the 5-MR while T3 and T4 sites in the 4-MR.

In particular, T1 site faces toward both the 12-MR main channel and the 8-MR channel. T2 and T4 sites face toward both the main channel and the side pocket. T3 site is located between the 8-MR channel and the side pocket. O2, O3, O7 and O10 sites face toward the center of main channel. O1 and O9 sites face toward the center of side pocket. O5 and O6 sites are located near the intersection of the main channel and the side pocket. O4 and O8 sites point toward the chains of 5-MR, which are linked laterally to form the MOR zeolite framework. Namely, six of the 10 oxygen sites (O5–O10) lie between equivalent tetrahedral atoms while the other four sites (O1–O4) lie between non-equivalent tetrahedral atoms. Consequently, 10 different Al–(OH)–Si groups can be produced.

It is well recognized that the amount and distribution of framework aluminum as well as the framework structure itself are related to the thermal stability and the acid strength of a particular zeolite. Therefore, a lot of researchers have investigated the Al distribution in MOR zeolite using crystallographical and spectroscopic data [6–15]. In literature reported so far, however, only the distribution of Al atoms in MOR zeolite with Si/Al ratio below 10 has been studied because of a lack of high-silica zeolite.
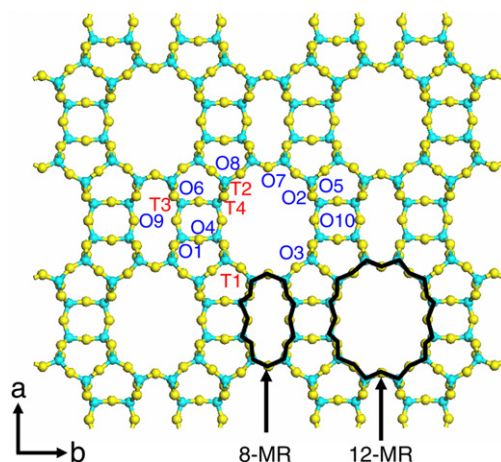
Fig. 1. MOR zeolite framework viewed along the *c*-axis. T1–T4 and O1–O10 indicate four and ten non-equivalent crystallographic sites of Al and O atoms, respectively.

Although the high-silica MOR zeolite can be produced by dealumination treatment, an existence of extra framework aluminum makes the clarification of Al distribution more complicated. Therefore, quantum chemical technique has also been employed for the investigation of Al distribution in MOR zeolite framework. However, the stable Al site depended on the model and method employed [16–18]. Brändle et al. reported that there are only a slight difference in the stabilization energy among T sites, indicating that either the probability of Al atoms or Si atoms in T sites is almost equiprobable [17].

We have studied the direct hydrothermal synthesis of high-silica MOR zeolite by various methods. Very recently, the highly crystalline MOR zeolite with a bulk Si/Al ratio of ≈30 was successfully prepared using both tetraethylammonium hydroxide as a structure-directing agent and NaF as a fluoride source, when $Al(NO_3)_3$ was employed as an aluminum source [19,20]. The addition of seed crystals or NH_4NO_3 as a mineralizer was also found to be very effective for direct synthesis of high-silica MOR zeolite [21,22]. However, characteristic of the as-synthesized MOR zeolites such as Al distribution corresponded to physico-chemical property has not been clarified yet.

From such viewpoints, we investigated the structural and physico-chemical properties of high-silica MOR zeolite using theoretical techniques and compared with experimental data, which have been already reported in recent article [23].

2. Experimental

2.1. The models for simulation

The geometry of the models for the simulation was derived from the crystal structure of MOR zeolite determined by X-ray diffraction [4]. There are four symmetrically independent tetrahedral sites (labeled T1–T4) in the

unit cell of MOR zeolite structure, as shown in Fig. 1. To clarify a difference in framework stability, one Al atom was substituted for one Si atom at each T site. Proton atom was used as compensating cation. The stoichiometry of the models is listed in Table 1. To reduce calculation time, many researchers have used cluster models as the adequate one which represents basic features of a local electronic structure on an active center in the zeolitic framework. However, selecting the proper cluster for zeolitic structure is itself a subject of many studies. Si atoms at the periphery of the cluster model were replaced by H atoms. Even the methodology is obviously not perfect but frequently used to saturate dangling bonds in cluster boundaries. Then, the model with periodic boundary condition was also used to eliminate an influence of saturating dangling bonds.

2.2. Simulation methodology

Density functional theory (DFT) quantum chemical calculation was performed using DMol^3 package in Materials Studio (version 3.2) developed by Accelrys, Inc. on Appro HyperBlade Cluster integrated by Best Systems, Inc. [24,25]. The geometry optimization and total energy calculations of the final optimized geometry were carried out using double numerical polarization basis set with polarization functions (DNP), whose accuracy is comparable to Gaussian 6-31G^{++} with Perdew Burke Ernzerhof (PBE) type non-local gradient correction functional for exchange and correlation terms [26,27]. The stabilization energy after substitution of Al atom for Si atom was calculated by subtracting the energies of gas-phase atoms and the siliceous model from the energy of the optimized system. The stabilization energy of Al substituted model was calculated as follows [28]:

$$dE = \{E(\text{Al substituted model}) + E(\text{Si atom})\}$$
$$- \{E(\text{siliceous model}) + E(\text{Al atom}) + E(\text{H atom})\}$$

where dE: stabilization energy, E(Al substituted model): total energy for optimized model, E(Si atom): total energy for Si atom, E(siliceous model): total energy for parent siliceous model, E(Al atom): total energy for Al atom, E(H atom): total energy for H atom. With this definition, a negative dE corresponds to the stable substitution of Al in the MOR zeolite framework.

The adsorption simulation was carried out using Grand Canonical Monte Carlo (GCMC) method. The GCMC calculations were performed using sorption module in Cerius2 developed by Accelrys Inc., USA. The burchart-UNIVERSAL potentials parameter set was employed for calculating the interaction between molecules [29–31]. All GCMC calculations were performed for 5,000,000 cycle steps at 298 K. The stabilized models for the GCMC calculations were obtained by molecular dynamics (MD) calculations. The MD calculations were carried out with the MXDTRICL program developed by Kawamura et al. [32]. The Verlet algorithm [33] was used for calculation of