Microporous and Mesoporous Materials 195 (2014) 216–226

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Density functional theory investigations into the structure and spectroscopic properties of the Ti^{4+} species in Ti-MWW zeolite

Danhong Zhou [a,*], Huijuan Zhang [a], Jiajia Zhang [a], Xiuming Sun [a], Haichao Li [b], Ning He [b], Weiping Zhang [b]

[a] *College of Chemistry and Chemical Engineering, Liaoning Normal University, 850 Huanghe Road, Dalian 116029, People's Republic of China*
[b] *State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, Dalian 116024, People's Republic of China*

ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form 18 April 2014
Accepted 19 April 2014
Available online 26 April 2014

Keywords:
Titanosilicate
Ti location
Calculated IR spectra
Vibrational mode
Excitation state

ABSTRACT

The location and structure of the framework Ti^{4+} species in Ti-MWW zeolites were studied by density functional theory (DFT) based on the cluster models mimicking the Ti-MWW zeolite with a Si/Ti ratio of 35. The geometry, spectroscopic properties and energies of substitution for the Ti^{4+} species at different T sites were investigated. The results indicated that the Ti^{4+} species in form of $Ti(OSi)_4$ prefers to locate at the T1 and T3 sites, positioning on the edge of 12-membered ring cavity and the intersection of the 10-membered ring intralayer channels in MWW, respectively. In their calculated infrared (IR) spectra, the vibrational mode at 960 cm^{-1} band is actually a collective vibration of the antisymmetric stretching of $Ti(–O–Si)_4$ in a deformed tetrahedral geometry. The totally symmetric $Ti(OSi)_4$ tetrahedron at the Ti4 site is absent from the 960 cm^{-1} band because the vibrational mode is infrared inactive. Hydrolysis of a Ti–O–Si bridge was thermodynamically favorable and resulted in a tripodal defect Ti species with an inversed Ti–OH group and a remaining Si–OH in the adjacent T site. The calculated IR spectra of the tripodal Ti species have a blue shift in the characteristic IR band to 990–1000 cm^{-1}. The UV–vis spectra of the Ti^{4+} species were calculated by the time-dependent DFT method. The calculated IR and UV–vis spectra are in very good agreement with the experimental measurements, and provide microscopic features for the identification of the structure of framework titanium in Ti-MWW zeolites.

1. Introduction

TS-1 is the first synthetic titanosilicate [1] and has been the most active and commercially successful catalyst for the selective liquid-phase oxidation of various organic compounds via aqueous solution of hydrogen peroxide (H_2O_2) [2–5]. However, TS-1 with MFI topology [6] comprises 10-membered ring (10-MR) micropores that limit its application in the oxidation of substrates and oxidants with bulky molecular sizes. A novel titanosilicate Ti-MWW zeolite has been successfully synthesized by Wu et al. [7], which displayed excellent catalytic properties for both bulky and small molecules [8]. The MWW zeolite has a unique pore system composed of 12-MR side cups and two independent interlayer and intralayer 10-MR channels, one of which contains the 12-MR supercages [9,10]. Versus TS-1, the Ti-MWW zeolites exhibit superior catalytic performances in selected epoxidation reactions using H_2O_2 as an oxidant, as well as a distinct solvent effect and catalytic selectivity [11–17]. Clerici et al. [18] reported that TS-1 is more active for *cis*-but-2-ene than for *trans*-but-2-ene, which makes TS-1 applicable in the production of epoxy derivatives with *cis*-configuration by starting from a mixture of alkenes containing *cis*/*trans* isomers. Tatsumi et al. [19] reported that TS-1 is more selective for the *cis*-isomers in the epoxidation of a *cis*/*trans* mixture of hex-2-enes. However, Ti-MWW has a totally opposite catalytic selectivity for the epoxidation of olefinic stereoisomers with unusual solvent effect [11–15]. Here it is extremely selective for the epoxide in the *trans*-configuration. It shows the best catalytic activity in CH_3CN as well as higher efficiency in H_2O_2 utilization [13]. This may bring about reconsideration of the stereoselectivity of titanosilicates in olefin epoxidation and offers a tool to study the relationship between shape selectivity and the microstructure of Ti active sites.

The microstructure of Ti active sites depends on the synthesis processes. The Ti-MWW were prepared by methods different from that of TS-1 [7,11,16,17]. In direct hydrothermal synthesis of Ti-MWW, boric acid was required as a structure-supporting agent. In post-synthesis, B-MWW was used as precursor, and Ti was inserted in the silanol nest produced by deboronation. In the final prepared Ti-MWW zeolite with Si/Ti >40, the framework Ti^{4+} probably locates within the supercages on the exterior pockets and in the 10-MR channels [11].

---

* Corresponding author. Tel.: +86 411 82158088; fax: +86 411 82156858.
E-mail address: zhoudh662@163.com (D. Zhou).

http://dx.doi.org/10.1016/j.micromeso.2014.04.037

Various experimental techniques have been applied to characterize the structures of Ti-MWW, including X-ray diffraction (XRD), scanning electron microscopy (SEM), inductively coupled plasma (ICP), FT-IR, and UV–vis spectroscopy [7,8,11,17]. The UV–vis absorption spectra of Ti-MWW samples showed characteristic absorption bands at 210–220 nm [7], which is assigned to the tetrahedral Ti species isolated in the zeolite framework [20] and corresponds to a charge transfer from the oxygen ligands to the Ti centre in TiO_4 unit [21,22]. The FT-IR spectra of Ti-MWW samples showed the characteristic IR band at 960–970 cm^{-1} that is usually regarded as the fingerprint region of Ti species in the tetrahedral coordination in titanosilicates [2,3,7]. However, the exact assignment of the 960 cm^{-1} band has been a matter of debate. It was first attributed to the Si–O stretching vibration perturbed by the neighboring Ti^{4+} ions [23]. It was later attributed to the stretching vibration of the Si–O bond in Si–O–Ti bridges or to the Ti–O–Si stretch [24]. The assignments of this band are also complicated by the fact that hydroxyls and Si–OH groups of defect sites absorb in the same range. Camblor et al. [25] proposed that the 960 cm^{-1} band is a Si–O vibration associated with framework defects. Scarano et al. [26] investigated the IR spectra of defective silicalites and TS-1 containing variable amounts of hydroxyls and found a broad absorption in the 970 cm^{-1} region related to the Si–O vibrations in silanols. In practice, a mixture of $Ti(OSi)_4$, $Ti(OSi)_3OH$, and $Ti(OSi)_2(OH)_2$ species is probable in titanosilicates, as proposed by the theoretical calculations that partial hydrolysis of the Ti–O–Si bridges in framework-substituted silicas is energetically feasible [27].

A number of theoretical calculations have been performed to investigate the Ti location and vibrational features of TS-1 zeolite [28–31]. Quantum mechanical calculations not only provide vibrational frequencies to be compared with the experimental ones, but also describe the electronic structure of the clusters for interpretation of the UV–vis spectra. Sauer and deMan [30] calculated the vibrational spectra of a variety of small clusters, demonstrating that antisymmetric Ti–O–Si vibrations may appear at frequencies near 960 cm^{-1}. Ricchiardi et al. [31] performed the vibrational frequency calculations with B3LYP/6-31(d) method, using a “shell-3” cluster model containing one shell of the complete tetrahedron surrounded on a central T atom for modeling a non-defective titanosilicate. In the calculated spectra, no single mode has been associated individually with the 960 cm^{-1} band. However, using the QM/MM embedding method they have reproduced the transparency gap of silicate and the appearance of asymmetric TiO_4 vibrations at 960 cm^{-1} in TS-1. Nevertheless, the occurrence and exact frequency of these vibrations vary widely with model size and connectivity, in a manner that has not yet been explained.

The 960 cm^{-1} band of Ti-MWW is not as sharp as that of TS-1, especially at low Ti content. This phenomenon is because Ti-MWW contains a crystallographically isomeric framework of Ti species due to its unique crystalline structure [16]. The assignment of the spectroscopic bands and the distribution of Ti^{4+} sites still need to be addressed. To our knowledge, theoretical calculations on the vibrational spectra of Ti-MWW zerolite have not been reported. Yang et al. [32] investigated the distribution of Ti^{4+} and Ti^{3+} ions in Ti-MWW by DFT method and suggested that the T3 site is most probable for the location of framework Ti in MWW zeolite. However, the T3 site situates inside the intralayer 10-MR channels, which alone cannot account for the experimentally observed catalytic performance characterized by the 12-MR supercage in Ti-MWW. The adopted cluster models by the authors may be inadequate to identify the individual framework Ti sites.

Here, we report DFT investigations into the location and structure of Ti^{4+} species in Ti-MWW zeolite. The larger cluster models including seven shells of framework atoms surrounding the central T site are used, and different constrain strategies are tested. Our studies focus on the fully coordinated Ti species in form of $Ti(OSi)_4$ and defect Ti species of $Ti(OSi)_3OH$. The preferred location of Ti^{4+} is predicted by calculating the substitution energy of the Ti/Si replacement, combined with consideration of the deboronation procedures. The vibrational frequencies and excitation states of structurally different Ti species are calculated and compared with the experimental IR and UV–vis spectra available for Ti-MWW catalysts. The vibrational modes for the characteristic 960 cm^{-1} band in IR spectra are discriminated. The energetics and spectroscopic results provide important evidence into the location of Ti^{4+} at the T1 and T3 sites in Ti-MWW.

2. Models and computational details

2.1. Models

In the unit cell of the MWW lattice [9,10] there are eight crystallographically distinct tetrahedral sites (Fig. 1), denoted as T1, T2, T3, T4, T5, T6, T7, and T8. The cluster models of different sizes with a central T atom at T1–T5 and T8 sites were truncated from the framework of MWW, respectively. The T6 and T7 sites were

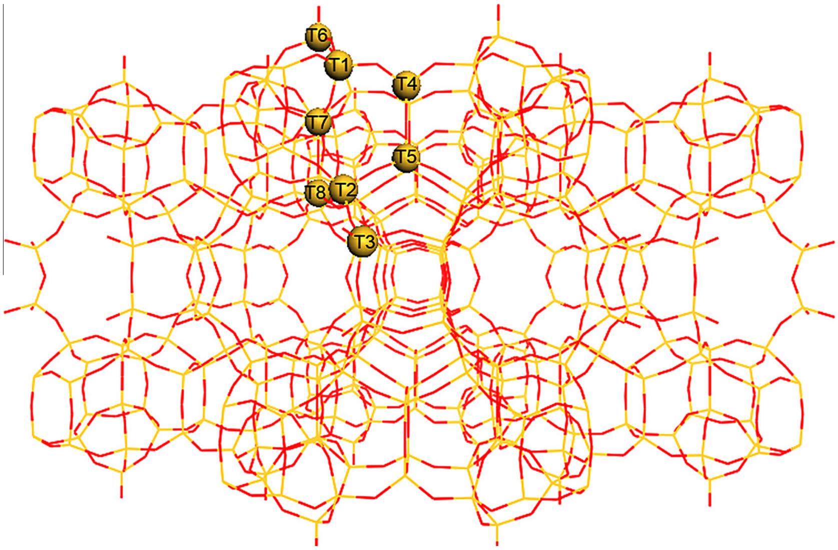

Fig. 1. The structure of MWW zeolite and the positions of different T sites.