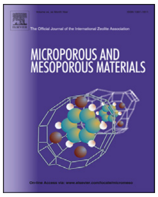
Microporous and Mesoporous Materials 237 (2017) 132–139

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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



Density functional theory investigations into the structures and acidity properties of Ti-doped SSZ-13 zeolite

Lina Han [a, b], Cui Wen [a], Zhiping Wu [c], Jiancheng Wang [b, **], Liping Chang [b], Gang Feng [d, e], Rongbin Zhang [d], Dejin Kong [e], Jianwen Liu [f, *]

[a] *College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, PR China*
[b] *Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, PR China*
[c] *Jiangxi Institute of Computing Technology, Nanchang 330003, PR China*
[d] *Institute of Applied Chemistry, College of Chemistry, Nanchang University, Nanchang 330031, PR China*
[e] *Shanghai Research Institute of Petrochemical Technology SINOPEC, Shanghai 201208, PR China*
[f] *National Supercomputing Center in Shenzhen, Shenzhen 518055, PR China*

ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form
10 September 2016
Accepted 14 September 2016
Available online 15 September 2016

Keywords:
SSZ-13 zeolites
Titanium
Substitution effect
First principle
DFT

ABSTRACT

The tetra-coordinated titanium incorporated SSZ-13 zeolites has been investigated using the dispersion-corrected periodic density functional theory. The adsorption of H_2O inside the channels of the Ti-SSZ-13 zeolites were systematically studied. The most stable adsorption site was found in the main channel of the Ti-SSZ-13 zeolites for the water molecule adsorption. The water molecule could react with the Ti sites yielding partial hydrolysis of the Ti—O—Si bridges to produce two independent Brønsted acid sites, i.e. the O_wH and bridge OH group. The latter shows stronger Brønsted acidity, which can potentially act as a catalytic site. The hydrolysis reaction of the Lewis acidic sites make the tetra-coordinated Ti penta-coordinated. The tetrahedral Ti^{IV} ions in zeolite lattices could be reduced to Ti^{III} ions via H atom adsorption. The Ti^{III}-SSZ-13 zeolites exhibit stronger Lewis and Brønsted acidity than Ti^{IV}-SSZ-13 zeolites. The adsorption of NH_3 and pyridine inside the channels of both Ti-SSZ-13 and H-Ti-SSZ-13 zeolites were also studied. The results show that the NH_3 and pyridine could physisorb in the Lewis acid sites of these zeolites, indicating the weak Lewis acidity for the substituted Ti sites. Deprotonation energy analysis indicates that the Brønsted acidity of the bridge OH in the Ti-SSZ-13 hydrolysis follows the order of O_wH—Ti—OH—Si > Ti—2(OH)—Si > Ti—O_wH,Si—OH, which is opposite to the stability of the structures. The results provide new insights for synthesis for the SSZ-13-type zeolites and fundamental information for the zeolitic catalyst designation to enhance the catalytic performance.

1. Introduction

Considerable effort has been devoted to the synthesis and characterization of the titanium silicalite molecular sieve due to its unique catalytic properties in selective oxidation reactions [1–5]. TS-1 is a mild catalyst, which was the first synthesized titanosilicate zeolites and applied in 1980s [3,6]. The active sites of TS-1 zeolite are produced via the addition of hydrogen peroxide (H_2O_2) [3,7,8]. The TS-1 zeolite was found high catalytic activity since the Ti^{IV} sites have vacant *d* orbitals and show Lewis acidity toward adsorbates [9–12]. Except for TS-1, many other molecular sieves containing isolated Ti atoms in tetrahedral coordination have been synthesized with diverse pore architectures such as Ti-MWW [13–15], Ti-Beta [16–19] and Ti^{IV}-MCM-22 [20,21].

The SSZ-13 zeolite has attracted much attention due to its outstanding acidity and catalytic properties [22–25]. The framework of SSZ-13 owns a 3-dimensional interconnected pore system with 8-membered ring windows (3.8 Å × 3.8 Å) and a relatively low framework density (15.1 T/1000 $Å^3$) [26,27], which was first discovered by Zones et al. [28,29]. Because of its unique pore configuration as well as acidity properties, SSZ-13 has been applied for the separation of CO_2 [30,31], methanol-to-olefin (MTO) reactions [24,32], and selective catalytic reduction (SCR) of NO_x in the presence of NH_3 [33–35]. Many previous works have investigated the synthesis and acidities of M^{3+}-doped ($M = $ B, Al, Ga) SSZ-13

---

* Corresponding author.
** Corresponding author.
E-mail addresses: wangjiancheng@tyut.edu.cn (J. Wang), liujw@nsccsz.gov.cn (J. Liu).

http://dx.doi.org/10.1016/j.micromeso.2016.09.028

zeolites [32,36–38]. The computational results show that the Brønsted acidities increase following the order: B < Fe < Ga < Al-doped zeolites [39–41]. While, the incorporation of tetra-valent Ti^{4+} into SSZ-13 zeolites are not well known.

Eilertsen and coworker [42] have synthesized Titanium Chabazite with and without aluminum (Ti-CHA with Si/Ti = 246 and Ti–Al-CHA with Si/Ti = 95 and Si/Al = 17). The high Si/Ti ratio indicated that the isomorphous substitution of Si by Ti is more difficult than the trivalent cations (Si/B = 6.9–11.8 [43] and Si/Al = 2). About 2–3% of the framework tetrahedral positions could be occupied by Ti, which are tetra-coordinated in anhydrous conditions [44,45]. Because of the very mild conditions with aqueous H_2O_2 as the oxidant, the Ti–Al-CHA was applied for the production of methyl with methanol as feed. It exhibited high H_2O_2 conversion as well as high selectivity towards methyl formate [42]. Recently, Titanated chabazites (Ti-CHA) with various Si/Ti ratios was synthesized by hydrothermal conversion of titanated faujasite [46]. The peak of the UV–vis was clearly observed at ~220 nm and the FT-IR spectra was observed at ~960 cm^{-1} for Ti-CHA, indicating the incorporation of Ti into the zeolite framework. The thermal stability of the Ti-CHA was better than that of non-modified CHA. *Ab initio* calculation was carried out to investigate the interaction of water molecules with Ti sites in Ti-CHA zeolites with an equal number of framework Ti and Si atoms per cell [47]. It was found that the physical adsorption energy of water is −34.4 kJ mol^{-1} and the hydrolysis of the Ti–O–Si bridge is endothermic.

The activity of Ti sites of the zeolites was found related to the interactions between Ti and the water molecules [11,47,48]. In the catalytic reaction and the crystallization process, water molecules could adsorb or react with the Ti sites yielding partial hydrolysis of the Ti–O–Si bridges [47]. Spectroscopy studies on Ti-zeolites also found that Ti centers are not completely linked to the framework, some of the Ti–O–Si bridges around the center are broken into Ti–OH and Si–OH groups and the Ti–OH–Si groups after hydrolysis, which are the actual catalytic sites in Ti-silica catalysts [49]. Moreover, the hydrolysis reaction leads to the coordination number changes of Ti^{IV} between tetra- and hexa-coordination [11]. The Ti^{IV} is the Lewis acid sites of the Ti^{IV}-doped zeolites while the Brønsted acid sites are the hydrolysis products of the Lewis acid sites.

Since Ti-CHA catalysts could work for different reactions, the Ti^{IV} in framework could be reduced. The experiment results show that the Ti^{III} sites in the zeolites exhibited unique photocatalytic reactivity for a variety of reactions, such as the decompositions of NO_x to N_2 and O_2 and partial oxidation of hydrocarbons with O_2. Moreover, the cyclic voltammetry experiments revealed that the tetrahedral Ti ions in zeolite lattices are easily reduced to Ti^{III} ions [50]. Thus, it is necessary to investigate the distribution of Ti and the transformation between Ti^{III} and Ti^{IV} in the Ti-doped zeolite.

In this work, the structures as well as the Lewis and Brønsted acid sites of the Ti-doped SSZ-13 zeolites were studied using the dispersion-corrected density functional theory. The unit cell of Ti-SSZ-13 lattice with a very low content of Ti (Ti/Si = 1/35) were chosen as the computational model, which is similar to the real titanosilicates microporous materials (Ti/Si is lower than 1/30) [48]. The adsorption of hydrogen and water as well as the acid properties of the zeolites as indicated by the adsorption of NH_3 and pyridine were systematically investigated.

2. Models and calculation details

As reported in our previous work [51], the periodic $p\,(1 \times 1 \times 1)$ SSZ-13-type zeolites model was chosen to represent the structures of SSZ-13-type zeolite (Fig. 1), the unit cell ($Si_{36}O_{72}$) composes with D6Rs (double six-rings), which are connected with tilted 4MRs, and its main channel is 8MR. All tetrahedral (T) sites of the SSZ-13 framework are equivalent; while there are four kinds of inequivalent oxygen sites [22]. The unit cell parameters of SSZ-13 zeolite (CHA-type) is in the monoclinic space group R/3m with the lattice parameters of $a = b = 13.675$ Å, $c = 14.767$ Å, $\alpha = \beta = 90.000°$, $\gamma = 120.000°$. In order to investigate the local structures and acid properties of the zeolite, one Si atom was substituted by Ti atom in the unit cell to get the Si/Ti ratio of 35.

The dispersion-corrected periodic density functional method as implemented in the Vienna *ab initio* Simulation Package (VASP) was applied in all calculations [52,53]. The DFT-D2 method of Grimme was used to take into account the dispersive interactions [54,55], as previously reported that the dispersion correction have very important influence to the relative energies for the MTW-type zeolites [40,56]. The exchange and correlation energies were calculated by the generalized gradient approximation (GGA) formulation with the PBE functional [57]. The Kohn-Sham one-electron states were extended in accordance with plane-wave basis sets with a kinetic energy of 400 eV. The projector augmented wave (PAW) method was applied to describe the electron-ion interactions [58,59]. DFT + U calculations were performed for the strong on-site Coulomb repulsion of the Ti *d* electrons with the U–J = 2.5 eV [51]. The Brillouin zone was sampled with a 3 × 3 × 3 *k*-points mesh, generated by the Monkhorst-Pack algorithm, for the unit cell of SSZ-13. The convergence criteria were 1.0×10^{-4} eV for the SCF energy, 1×10^{-3} eV and 0.05 eV/Å for the total energy and the atomic forces, respectively. For structure optimizations, the atoms and the cell parameters of SSZ-13 lattice were fully relaxed. All the calculations were performed on high performance computer clusters.

In order to study the influences of the substituted trivalent Ti to the thermochemistry of the zeolites synthesis reactions, the reaction of 36 $Si(OH)_4$ molecules was calculated to produce a $p\,(1 \times 1 \times 1)$ SSZ-13-type zeolites cell ($Si_{36}O_{72}$) and 72 H_2O molecules. The energy change for the pure silica SSZ-13 zeolites synthesis reaction is −29 kJ mol^{-1}, which indicates an exothermic reaction similar to that for the pure silica MTW zeolites [40]. The incorporation of one Ti atom into the SSZ-13 framework could be considered as the substitution of one Si atom of the pure silica zeolites by one Ti atom, which could be described as the following reaction:

$$(\mathrm{O{-}Si{-}O})_n^{\mathrm{SSZ-13}} + n\mathrm{Ti(OH)_4} \rightarrow n\mathrm{Si(OH)_4} + (\mathrm{O{-}Ti{-}O})_n^{\mathrm{SSZ-13}} \qquad \text{(a)}$$

The associated substitution energy could be calculated as following:

$$E_{sub} = nE[\mathrm{Si(OH)_4}] + E[(\mathrm{O{-}Ti{-}O})_n^{\mathrm{SSZ-13}}] - E[(\mathrm{O{-}Si{-}O})_n^{\mathrm{SSZ-13}}] - nE[\mathrm{Ti(OH)_4}] \qquad \text{(b)}$$

where E [$Si(OH)_4$], E [$(O{-}Ti{-}O)_n^{SSZ-13}$], E [$(O{-}Si{-}O)_n^{SSZ-13}$], E [$Ti(OH)_4$] are the total energies of the free $Si(OH)_4$, Ti-SSZ-13 zeolite cell, pure silica SSZ-13-type zeolite cell, free $Ti(OH)_4$ molecules, respectively.

The adsorption energies (E_{ads}) for the adsorption of H, H_2, H_2O, NH_3 and pyridine in the zeolite were calculated by:

$$E_{ads} = E(\text{molecule@SSZ-13}) - [E(\text{molecule}) + E(\text{SSZ-13})] \qquad \text{(c)}$$

where E (molecule@SSZ-13), E (molecule) and E (SSZ-13) are the total energies of the SSZ-13-type zeolite cell with adsorbed molecule in the pore, the gas phase H, H_2, H_2O, NH_3 and pyridine molecules and the SSZ-13-type zeolite, respectively. The larger adsorption energy indicates the stronger adsorption of the molecules on the acid sites.