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Article

Structures and vibrational spectra of Ti-MWW zeolite upon adsorption of H₂O and NH₃: A density functional theory study

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ABSTRACT

The structures and vibrational spectroscopic features of framework Ti(IV) species in Ti-MWW zeolite upon adsorption of H₂O and NH₃ were investigated by density functional theory. The calculations were carried out on cluster models up to 36 tetrahedra at the B3LYP/6-31G(d,p) level of theory. The calculated results indicate that both Ti(OSi)₄ and Ti(OSi)₃OH species can interact with H₂O or NH₃ molecules to form five-coordinated complexes. The Ti(OSi)₃OH species has higher Lewis acidity and adsorbs the ligands more easily than Ti(OSi)₄. The Ti-specific band is attributed to the collective vibration of the antisymmetric stretching of Ti–O–Si bonds. The vibrational frequencies of coordinated Ti species can be divided into two regions: the Ti-specific vibration region and the hydroxyl group vibration region. After adsorption of H₂O, the Ti-specific band of the Ti(OSi)₄ species shifted from 960 to 970 cm^{−1}, and the Ti-specific bands of the Ti(OSi)₃OH species shifted from 990 cm^{−1} (T1 site) and 970 cm^{−1} (T3 site) to 980 cm^{−1}. The frequencies of the corresponding NH₃ adducts were about 5 cm^{−1} higher. The Ti(OSi)₃OH species can also form hydrogen bonded complexes with H₂O and NH₃ through Ti–OH, resulting in the hydroxyl stretching band of Ti–OH red shifting by 500–1100 cm^{−1} and appearing in the 2700–3200 cm^{−1} region.

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1. Introduction

Titanosilicate catalysts are highly active for the selective liquid-phase oxidation of various organic compounds using an aqueous solution of H₂O₂ [1,2]. The well-known TS-1 catalyst is composed of 10-membered ring (10-MR) micropores and is only suitable for the oxidation of substrates and oxidants with small molecular size [3,4]. Ti-MWW zeolite possesses a unique crystalline structure and an attractive pore system consisting of two independent 10-MR channels, 12-MR supercages, and side cups [5,6]. Unlike other zeolites, Ti-MWW exhibits excellent catalytic activity for the selective oxidation of both bulky and small organic molecules [5–9]. The ultraviolet-visible (UV-vis)

and Fourier transform infrared (FTIR) spectra of Ti-MWW samples show characteristic bands at 220 nm and 960 cm^{−1}, respectively [5], which are assigned to the tetrahedral Ti species isolated in the zeolite framework [10–13]. In the presence of H₂O₂ and H₂O, the titanium hydroperoxo complex forms, which is the actual oxidation active center [14–18]. The coordination of Ti(IV) with H₂O and reagent is an essential process for catalysis. The coordination of H₂O and NH₃ with Ti(IV) in TS-1 has been investigated by the extended X-ray absorption fine structure (EXAFS) technique [19,20], which revealed that adsorption of H₂O or NH₃ causes the T–O distances to lengthen by 0.02 or 0.05 Å, respectively, and changes the symmetry of the Ti center from tetrahedral to octahedral. Damin et al.

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[21,22] studied the reactivity of TS-1 towards H_2O and NH_3 , and investigated the geometry of the complexes by the ONIOM method. They found that H_2O or NH_3 attaches to tetrahedral $\text{Ti}(\text{OSi})_4$ at the Ti site and the structure finally reached a bipyramidal geometry. Ricchiardi et al. [23] studied the adsorption of TS-1 and Ti-chabazite with water by a hybrid periodic/embedded molecular mechanical/quantum mechanical cluster approach. They found that one or two H_2O molecules form stable complexes with Ti sites, the oxygen coordination increases from four to five or six, and the binding energies strongly depend on the location of the Ti atom. Bordiga et al. [24] experimentally and theoretically investigated the effect of H_2O and NH_3 adsorption on the vibrational, electronic, and energetic features of Ti(IV) centers in TS-1. They calculated the vibrational frequencies of the tetrapodal Ti(IV) and confirmed that the Ti-specific band at 960 cm^{-1} undergoes a blue shift to 970 cm^{-1} upon contact with H_2O . Zhanpeisov et al. [25] investigated the adsorption features of both “defective” and “nondefective” Ti sites in TS-1 using DFT and 5T (tetrahedron) cluster models. They calculated the energies upon water, methanol, and NH_3 adsorption through either a coordination mechanism or hydrogen-bonding (H-bonding) process, indicating that interaction of ammonia with the Ti species might occur either via H-bonding or coordination mechanisms. Recently, Gallo et al. [26] reported a non-resonant valence-to-core X-ray emission spectroscopic (vtc-XES) investigation and DFT calculations of TS-1 upon molecular adsorption, and confirmed that only one H_2O or NH_3 molecule adsorbs to the Ti center to form a five-coordination structure. Although a number of experimental and theoretical studies have been reported on coordination properties of Ti(IV), most of them are only relevant to TS-1 zeolites.

Ti-MWW has unique channel systems with the Ti active centers distributed in both 12-MR supercage and 10-MR intralayer channels. Experimentally, it is difficult to discriminate the coordination features of Ti(IV) at different T site locations. Yang et al. [27] reported a DFT study of the adsorption of NH_3 to Ti(IV) species at the T3 site, and obtained an adsorption energy of 34 kJ/mol , which is comparable with that for TS-1 zeolites [24]. In our previous work [28], DFT calculations of 35T cluster models revealed that Ti(IV) prefers to be located at the T1 and T3 sites in Ti-MWW. The calculated vibrational frequencies include the 960 cm^{-1} band for the tetrapodal $\text{Ti}(\text{OSi})_4$ species. It is believed that the Ti(IV) active centers in both the 10-MR channel and 12-MR supercage in the Ti-MWW catalyst show different catalytic selectivity. Thus, it is important to investigate the interaction of H_2O and NH_3 molecules with Ti(IV) at different framework positions.

In this work, we investigate the coordination of H_2O and NH_3 to tetrapodal and tripodal Ti species located at the T1 and T3 sites in Ti-MWW zeolite using DFT calculations. In the first part of this work, we determine the optimized structures of the coordination complexes of $\text{Ti}(\text{OSi})_4$ and $\text{Ti}(\text{OSi})_3\text{OH}$ species located at the T1 and T3 sites, respectively. Their coordination and H-bonded complexes with H_2O and NH_3 are analyzed. In the second part, we compare the binding energies of H_2O and NH_3 to different Ti species. In the final part, we calculate the IR spectra of the coordination complexes, and provide compre-

hensive and precise insight into the vibrational features of different Ti species.

2. Methodology

2.1. Models

There are eight crystallographically distinct tetrahedral sites in the unit cell of the MWW zeolite lattice [29,30]. The Ti(IV) atoms prefer to be located at the T1 and T3 sites [28]. The cluster models at the T1 and T3 sites (T1@35T and T3@36T, respectively) were truncated from the superlattice of MWW (Fig. 1). The tetrapodal $\text{Ti}(\text{OSi})_4$ and tripodal $\text{Ti}(\text{OSi})_3\text{OH}$ species were constructed and optimized, and the optimized structures were used as the starting models of the bare clusters for the coordination of H_2O and NH_3 molecules. During the calculations, the Ti atom, the four surrounding layers of framework atoms, and the ligand molecule were relaxed, while the Cartesian coordinates of the rest of the framework atoms were fixed [28].

2.2. Calculation method

In this work, we used the B3LYP hybrid functional [31,32] and polarized 6-31G(d,p) basis set, which have been widely used in the studies of Ti-containing zeolites [21–28]. For all of the geometry optimizations, the energy minima were verified by frequency calculations, and no imaginary vibrational frequencies existed for the optimized parts, except for contamination of the imaginary frequencies because of the constrained atoms. For all of the coordination complexes considered in this study, the binding energies were calculated as the total energy difference between the coordination complex and the sum of the isolated initial cluster model and ligand molecule(s):

$$E_b = E_c - (E_L + E_Z)$$

where the subscripts C, L, and Z stand for coordination com-

Fig. 1. T1 and T3 site locations in MWW zeolite and the T1@35T and T3@36T cluster models (balls and lines indicate the relaxed and fixed atoms, respectively).

plex, ligand, and zeolite cluster model, respectively. Note that the energies of C, L, and Z are those estimated at their respective equilibrium geometries. The binding energies thus obtained were then corrected for basis set superposition error (BSSE) using the full Boys-Bernardi counterpoise correction scheme [33]. Negative values of the binding energy mean a favorable interaction. To compare with the experimental IR spectra, the calculated vibrational frequencies were scaled by a factor of 0.961 [34].

To investigate the electronic properties of the adsorption systems, we performed natural bond orbital (NBO) calculation and analysis [35–38]. The second-order perturbation theory analysis can provide an estimate of the donor-acceptor (bond-antibond) interactions in the NBO basis. This analysis is carried out by examining all of the possible interactions between “filled” (donor) Lewis-type NBOs and “empty” (acceptor) non-Lewis NBOs, and estimating their energetic importance by second-order perturbation theory. The larger the second-order perturbation stabilization energy $E(2)$, the stronger the donor-acceptor interaction. All of the calculations were performed with the Gaussian 09 program and included NBO version 3.1 [39].

3. Results and discussion

3.1. Geometric features of the coordination complexes

In Ti-MWW, the $\text{Ti}(\text{OSi})_4$ and $\text{Ti}(\text{OSi})_3\text{OH}$ species have tetrahedral symmetry. A ligand molecule will approach the tetrahedral Ti(IV) center along one of the four Ti–O bond axes from the channel or the cavity direction. In view of the spatial environment, H_2O and NH_3 molecules attack the Ti site along the Ti1–O4 and Ti3–O12 bond axes of the $\text{Ti}(\text{OSi})_4$ species at the T1 and T3 site, respectively. The optimized adducts are shown in Fig. 2, and the geometric parameters and binding energies are summarized in Table 1. For clarity, the local structures of the $\text{Ti}(\text{OSi})_4$ unit are shown in Fig. 3.

Adsorption of H_2O and NH_3 induces the average Ti–O distance to increase by 0.015–0.028 Å, which qualitatively agrees with the EXAFS and theoretical results of H_2O and NH_3 adsorption to TS-1 zeolite [18,19,24]. The second shell of the $\text{Ti}(\text{OSi})_4$ unit is also affected by the ligand, as indicated by the <O–Si>, <Ti–O–Si>, and <Ti–Si> columns in Table 1, which represent the average bond lengths and bond angles. The <O–Si> bond lengths decrease, and the <Ti–O–Si> bond angles are slightly distorted (<2°), while the <Ti–Si> distances are essentially constant. The distance between the ligand molecules and the Ti atom (Ti–L, L denotes the O and N atoms in H_2O and NH_3 , respectively) is between 2.35 and 2.42 Å, reflecting the strong

Fig. 2. Optimized coordination complexes of the $\text{Ti}(\text{OSi})_4$ species with H_2O and NH_3 (the approached Ti sites are underlined).

Fig. 3. Local structures of the coordination complexes of $\text{Ti}(\text{OSi})_4$ species (bond lengths in Å). (a) Ti1– NH_3 ; (b) Ti3– NH_3 ; (c) Ti1– H_2O ; (d) Ti3– H_2O .

interaction between the ligand and Ti. The perturbation effect of NH_3 is larger than that of H_2O because of its stronger basicity. In addition, the perturbation effect is more prominent at the T1 site. In all cases, ligand adsorption causes a distortion of TiO_4

Table 1

Calculated binding energies and geometric parameters of the coordination complexes of $\text{Ti}(\text{OSi})_4$ species with H_2O and NH_3 .

Complex	E_b (kJ/mol)	<Ti–O> ^a (Å)	<O–Si> ^a (Å)	<Ti–O–Si> (°)	<Ti–Si> (Å)	L–Ti–O (°)	O–Ti–O (°)
Ti1– H_2O	–16.90	1.790 (+0.020)	1.618 (–0.006)	133.0	3.130	165.2	150.3
Ti3– H_2O	–14.85	1.783 (+0.015)	1.614 (–0.008)	135.6	3.114	173.9	150.4
Ti1– NH_3	–34.90	1.801 (+0.028)	1.615 (–0.009)	133.6	3.119	171.0	153.0
Ti3– NH_3	–32.68	1.794 (+0.026)	1.610 (–0.012)	135.3	3.122	170.8	160.2

^a Data in parentheses are the bond length changes induced by H_2O and NH_3 adsorption.

from tetrahedral to distorted triangular bipyramidal symmetry, as indicated by the change of the O–O–Ti–O dihedral angles and L–Ti–O bond angles, which are about 150° – 160° and 165° – 174° (Table 1), respectively, showing the trend toward the ideal value of 180° . Apparently, NH_3 adsorption is more effective to modify the tetrahedral symmetry.

The $\text{Ti}(\text{OSi})_3\text{OH}$ species has distorted tetrahedral symmetry. It can interact with H_2O and NH_3 either via coordination to the central Ti or via H-bonding with the Ti–OH group. The optimized coordination complexes and the local structures of $[\text{Ti}(\text{OSi})_3\text{OH}]\text{--H}_2\text{O}$ are shown in Figs. 4 and 5, respectively. Table 2 summarizes the selected geometric parameters and binding energies of all of the adducts.

At the T1 site, H_2O and NH_3 can attack the Ti site either along the Ti1–O2 or Ti1–O3 bond axes. Compared with the $\text{L}\cdots\text{Ti1--O2}$ adduct, the $\text{L}\cdots\text{Ti1--O3}$ adduct gives rise to longer Ti–O bond lengths and more obvious distortion of the tetrahedral symmetry of TiO_4 , as characterized by the larger O–O–Ti–O dihedral angles of 167° (vs. 145° for $\text{L}\cdots\text{Ti1--O2}$). The Ti–L dis-

tances are also relatively short, indicating that H_2O and NH_3 prefer to approach along Ti1–O3. The structures of the five-coordinated complexes are more analogous to a perfect triangular bipyramid, with L–Ti–O bond angles of 173° – 179° and O–Ti–O–O dihedral angles of 167° – 168° . This further confirms that the tripodal $\text{Ti}(\text{OSi})_3\text{OH}$ species favors the change of the coordination number of Ti(IV) from four to five.

H_2O and NH_3 can also form H-bonds with the Ti–OH group. From Table 2, the Ti–O distances in the H-bonded complexes are less influenced by adsorption than in the coordination complexes. The L–H distances are 1.671–1.760 Å for O–H and 1.609–1.650 Å for N–H, and are longer on Ti1–OH than on Ti3–OH. The O–H distances obtained in this work are considerably shorter than the value (1.817 Å) in Ref. [25], where 5T(oh) models were used, and the terminal Si–OH groups formed H-bonds with H atoms of H_2O , which restrains the oxygen of H_2O to interact with the Ti–OH group. Moreover, the H-bonded complex shows no perturbation of the tetrahedral symmetry of TiO_4 .

Fig. 4. Optimized coordination complexes of $\text{Ti}(\text{OSi})_3\text{OH}$ species with H_2O (the approached sites are underlined).

Fig. 5. Local structures of the coordination complexes of H_2O with the $\text{Ti}(\text{OSi})_3\text{OH}$ species. (a) $\text{Ti1(O2)OH--H}_2\text{O}$; (b) $\text{Ti1(O3)OH--H}_2\text{O}$; (c) $\text{Ti1OH--H}_2\text{O}$; (d) $\text{Ti3OH--H}_2\text{O}$; (e) $\text{Ti3OH--H}_2\text{O}$.

Table 2Calculated binding energies and selected geometric data of the coordination complexes of the $\text{Ti}(\text{OSi})_3\text{OH}$ species with H_2O and NH_3 .

Complex ^a	E_b (kJ/mol)	$\langle\text{Ti}-\text{O}\rangle^b$ (Å)	$\langle\text{Si}-\text{O}\rangle^b$ (Å)	L-Ti-O (°)	O-Ti-O (°)
<u>Ti1</u> (O ₂)OH-H ₂ O	-30.71	1.799 (+0.022)	1.613 (-0.007)	176.1	145.6
<u>Ti1</u> (O ₃)OH-H ₂ O	-51.97	1.813 (+0.036)	1.610 (-0.010)	179.0	167.6
<u>Ti3</u> OH-H ₂ O	-43.60	1.818 (+0.024)	1.613 (-0.003)	176.0	159.1
<u>Ti1</u> (O ₂)OH-NH ₃	-41.67	1.807 (+0.030)	1.669 (+0.049)	167.7	156.9
<u>Ti1</u> (O ₃)OH-NH ₃	-75.86	1.813 (+0.036)	1.606 (-0.014)	177.4	168.3
<u>Ti3</u> OH-NH ₃	-61.97	1.828 (+0.034)	1.609 (-0.007)	173.4	166.8
Ti1 <u>OH</u> -H ₂ O	-38.07	1.793 (+0.016)	1.613 (-0.007)	—	—
Ti3 <u>OH</u> -H ₂ O	-40.59	1.804 (+0.010)	1.612 (-0.004)	—	—
Ti1 <u>OH</u> -NH ₃	-52.76	1.791 (+0.014)	1.610 (-0.010)	—	—
Ti3 <u>OH</u> -NH ₃	-52.72	1.808 (+0.014)	1.609 (-0.007)	—	—

^a Underlined atoms are the sites approached by the ligand.^b $\langle\text{Ti}-\text{O}\rangle$ and $\langle\text{Si}-\text{O}\rangle$ denote the average values of three Ti-O and three Si-O bond lengths, respectively, and the data in parentheses are the changes of the bond length upon H_2O and NH_3 adsorption.

3.2. Comparison of the adsorption energies

The BSSE-corrected binding energies for all of the coordinated and H-bonded complexes are listed in Tables 1 and 2, respectively. For the $\text{Ti}(\text{OSi})_4$ species, the binding energies of NH_3 are significantly higher (more than 100%) than those of H_2O . This is not unexpected because of the higher basicity of NH_3 . The $\text{Ti}(\text{OSi})_4$ species show slightly higher binding energies for H_2O and NH_3 at the T1 site than at the T3 site. For the $\text{Ti}(\text{OSi})_3\text{OH}$ species, the Ti-OH group noticeably enhances the Lewis acidity of Ti(IV), resulting in higher binding energies. The H-bonding strength is weaker than the coordination interaction, suggesting that H_2O and NH_3 molecules prefer to adsorb to the central Ti atom to form coordination complexes. The energetics are generally consistent with the geometric features that the shorter the L-Ti distances, the higher the binding energies. It is noteworthy that the binding energies of the tripodal Ti(IV) species are 2–3 times higher than the tetrapodal Ti(IV) species, indicating that the $\text{Ti}(\text{OSi})_3\text{OH}$ species favors the formation of a coordination complex with the ligand. This is in agreement with the hypothesis for the change of the coordination number of Ti(IV). It has been assumed that the coordination expansion takes place with partial hydrolysis of the Ti-O-Si bridges and that hydrolysis increases the accessibility of the Ti center for additional ligands. This assumption is supported by IR and ^{17}O NMR spectroscopic observations [40].

It is commonly believed that the Lewis acidity of Ti-zeolite can be defined considering the lowest unoccupied molecular orbital (LUMO) energies of the clusters. Based on the molecular orbital analysis, it was found that the LUMO and LUMO + 1 in Ti-zeolite clusters have degenerate energy levels and belong to the unoccupied d orbitals of Ti, which are used to coordinate with the framework oxygens through electron density donation of $p(\text{O}) \rightarrow d^*(\text{Ti})$. The energy levels of the LUMOs in the Ti-clusters have no definite relationship with the Lewis acidity. To investigate the Lewis acid-base interaction, NBO analyses were carried out. It was found that the bonding between the Ti center and the H_2O molecule comes from electron density donation of $sp^2(\text{O}_w) \rightarrow 4p^*(\text{Ti})$ (Fig. 6), indicating that the Lewis acidity of the Ti site is related to the LUMO + 2 and LUMO + 3

but not to the LUMO of the Ti-clusters. Similar electronic properties were found in a theoretical study of TS-1 zeolite [41]. The $E(2)$ energies for H_2O adsorption decrease in the order $\text{Ti1OH} > \text{Ti3OH} > \text{Ti1} > \text{Ti3}$ species, which is consistent with the adsorption energies of H_2O .

3.3. Vibrational spectra of coordination complexes

3.3.1. Vibrational features upon H_2O adsorption

The calculated vibrational frequencies of Ti(IV) species upon H_2O adsorption are summarized in Table 3. For the bare tetrapodal Ti species, there are three vibrational modes related to tetrahedral $\text{Ti}(\text{OSi})_4$, among these the strongest ones are at 963 cm^{-1} (at the Ti1 site) and 958 cm^{-1} (at the Ti3 site), which are attributed to a combination of the antisymmetric stretching vibrations of four Ti-O-Si [19,28]. Coordination of the $\text{Ti}(\text{OSi})_4$ species with H_2O induces the characteristic Ti band to undergo a slight hypsochromic shift from 963 to 971 cm^{-1} (at the Ti1 site) and from 958 to 960 cm^{-1} (at the Ti3 site). The O-H vibrational frequencies of the adsorbed H_2O show a bathochromic shift of $20\text{--}50\text{ cm}^{-1}$ to the $3600\text{--}3730\text{ cm}^{-1}$ region, indicating

Fig. 6. NBO contours accounting for the Lewis acidity of the Ti center in different coordination complexes with H_2O . (a) Ti ($4p_z^*$) in $\text{Ti1-H}_2\text{O}$; (b) Ti ($4p_y^*$) in $\text{Ti1(O3)OH-H}_2\text{O}$; (c) Ti ($4p_z^*$) in $\text{Ti3-H}_2\text{O}$; (d) Ti ($4p_y^*$) in $\text{Ti3OH-H}_2\text{O}$.

Table 3

Vibrational frequencies (cm^{-1}) of the different coordination complexes of Ti species with H_2O calculated at the B3LYP/6-31(d,p) level of theory (scaled by a factor of 0.961).

Vibration	H_2O	Ti1	Ti3	Ti1OH	Ti3OH	Ti1(O2)OH	Ti1(O3)OH	Ti3OH
$\nu(\text{O-H})_{\text{sym}}$	3654	3606	3631	3592	3610	3611	<u>3467</u>	<u>3461</u>
$\nu(\text{O-H})_{\text{asym}}$	3763	3730	3738	3728	3730	3720	3709	3700
$\delta(\text{O-H})$	1600	1564	1551	1606	1597	1582	1587	1555
$\nu(\text{Ti-O-Si})$	—	971 (963)	960 (958)	996 (990)	979 (970)	972 (990)	982 (990)	981 (970)
$\Delta\nu(\text{Ti-O-Si})$	—	+8	+2	+6	+9	-18	-8	+11
$\nu(\text{TiO-H})$	—	—	—	3222 (3747)	3151 (3720)	3700 (3747)	3683 (3747)	3712 (3720)
$\Delta\nu(\text{TiO-H})$	—	—	—	-525	-569	-47	-64	-8
$\nu(\text{SiO-H})$	—	—	—	3572 (3598)	3697 (3702)	3594 (3598)	<u>3480</u> (3598)	<u>3543</u> (3702)
$\Delta\nu(\text{SiO-H})$	—	—	—	-26	-5	-4	-118	-159

Note: The underlined atoms are the sites approached by H_2O ; the data in parentheses are the vibrational frequencies without H_2O adsorption; and the underlined data are the stretching vibrational frequencies of the hydroxyl group forming a H-bond with the framework oxygen.

that the adsorption of H_2O to the $\text{Ti}(\text{OSi})_4$ species is quite weak, which is in agreement with the low binding energies of H_2O .

For the coordination complexes of $\text{Ti}(\text{OSi})_3\text{OH}$ species with H_2O , the Ti-specific bands for Ti1OH (990 cm^{-1}) and Ti3OH (970 cm^{-1}) both shift to 980 cm^{-1} . For the H-bonded complexes, the Ti-specific bands blue shift by about $5\text{--}9\text{ cm}^{-1}$, and the TiO-H stretching vibrational frequencies show a bathochromic shift of about $525\text{--}570\text{ cm}^{-1}$. Furthermore, when H_2O adsorbs to the Ti center, the adjacent Si-OH forms a H-bond with one of the bridging oxygen atoms, resulting in the SiO-H stretching vibration showing a bathochromic shift of about $110\text{--}160\text{ cm}^{-1}$. Fig. 7 shows the calculated vibrational spectra of $\text{Ti}(\text{OSi})_4$ and $\text{Ti}(\text{OSi})_3\text{OH}$ species (at the T1 site) before and after coordination with H_2O .

Many experimental studies have reported the IR spectra of Ti-silicate zeolites upon H_2O adsorption. Bordiga et al. [24] reported that at low $p_{\text{H}_2\text{O}}$ the formation of the $\text{Ti}(\text{IV})\text{--H}_2\text{O}$ adduct is not able to cause a significant perturbation of the 960 cm^{-1} band. The Ti-specific band only undergoes a hypsochromic shift at higher $p_{\text{H}_2\text{O}}$ when more than one H_2O molecule is adsorbed per Ti site (shifting from 959 to 973 cm^{-1}). If H_2O is dosed directly from the liquid phase, the 960 cm^{-1} band undergoes a further shift to 990 cm^{-1} . They also performed DFT calculations and confirmed that adsorption of one H_2O molecule only slightly affects the vibrational spectrum of the $\text{Ti}(\text{OSi})_4$ species. Nevertheless, a reasonable interpretation of the 973 and 990 cm^{-1} bands is still absent. Although Ti-MWW is structurally different from TS-1, isolated $\text{Ti}(\text{IV})$ is also characterized by the 960 cm^{-1} band. Therefore, we might compare the

calculated results with the experimental data for TS-1. In Ti-MWW, the Ti species at the T1 and T3 sites showed different vibrational features. For the Ti3 site, when the $\text{Ti}(\text{OSi})_4$ species adsorbs one H_2O molecule, hydrolyzes, and then adsorbs another H_2O , the Ti-specific band changes from 958 to 960 , then to 970 , and finally to 981 cm^{-1} . Whereas, for the Ti1 site, the Ti-specific band changes from 963 to 971 , then to 990 , and finally to 982 cm^{-1} , corresponding to the $\text{Ti}(\text{OSi})_4$ species, $[\text{Ti}(\text{OSi})_4]\text{--H}_2\text{O}$ adduct, $\text{Ti}(\text{OSi})_3\text{OH}$ species, and $[\text{Ti}(\text{OSi})_3\text{OH}]\text{--H}_2\text{O}$ adduct, respectively. Our results indicate that if the $\text{Ti}(\text{OSi})_4$ species adsorbs one H_2O molecule, the Ti-specific frequency shows minor changes ($2\text{--}8\text{ cm}^{-1}$). When the tetrapodal $\text{Ti}(\text{OSi})_4$ species hydrolyzes to the tripodal $\text{Ti}(\text{OSi})_3\text{OH}$ species, the Ti-specific frequency shows a clear shift ($12\text{--}27\text{ cm}^{-1}$).

In the hydroxyl stretching vibration region, the $\nu(\text{O-H})$ stretching modes of gaseous H_2O , the internal silanol groups, and the Ti-OH groups appear in the $3600\text{--}3760\text{ cm}^{-1}$ region. Upon H_2O adsorption, the bands shift to the $3150\text{--}3460\text{ cm}^{-1}$ region, where the H-bonded Ti-OH groups in the $\text{H}_2\text{O}\text{--TiOH}$ adduct show a vibration at around 3150 cm^{-1} , and the H-bonded silanol groups as well as H_2O molecules in the $\text{H}_2\text{O}\text{--TiOH}$ adduct show a vibration at around 3460 cm^{-1} . All of the results are comparable with the experimental IR spectra of TS-1 [24].

3.3.2. Vibrational features upon NH_3 adsorption

In the presence of a protonic acid, NH_3 can easily form NH_4^+ , which shows a characteristic IR absorption band of the N-H

Fig. 7. Calculated vibrational spectra of $\text{Ti}(\text{OSi})_4$ (a) and $\text{Ti}(\text{OSi})_3\text{OH}$ (b) species at the T1 site before and after coordination with H_2O .

Table 4

Vibrational frequencies (cm^{-1}) of the different adsorption complexes with NH_3 calculated at the B3LYP/6-31(d,p) level of theory (scaled by a factor of 0.961).

Vibration	NH_3	<u>Ti1</u>	<u>Ti3</u>	<u>Ti10H</u>	<u>Ti30H</u>	<u>Ti1(O2)OH</u>	<u>Ti1(O3)OH</u>	<u>Ti3OH</u>
$\nu(\text{N-H})_{\text{sym}}$	3326	3332	3323	3333	3336	3335	3310	3327
$\nu(\text{N-H})_{\text{asym}}$	3450	3451, 3472	3433, 3458	3446, 3470	3459, 3480	3453, 3463	3428, 3466	3446, 3471
$\delta(\text{N-H})$	1628	1612	1627	1630	1620	1617	1622	1615
$\nu(\text{Ti-O-Si})$	—	972 (963)	964 (958)	1019 (990)	981 (969)	984 (990)	987 (990)	985 (970)
$\Delta\nu(\text{Ti-O-Si})$	—	+9	+6	+29	+12	-6	-3	+15
$\nu(\text{SiO-H})$	—	—	—	3546 (3598)	3702 (3702)	3498 (3598)	3466 (3598)	3485 (3702)
$\Delta\nu(\text{SiO-H})$	—	—	—	-52	0	-100	-132	-217
$\nu(\text{TiO-H})$	—	—	—	2700 (3747)	2548 (3720)	3757 (3747)	3674 (3747)	3690 (3720)
$\Delta\nu(\text{TiO-H})$	—	—	—	-1047	-1172	+10	-73	-30

Note: The underlined atoms are the sites approached by NH_3 , and the data in parentheses are the vibrational frequencies without adsorbed NH_3 .

bending vibration at 1450 cm^{-1} . With a Lewis acid ligand, it can also form the $\text{L}\cdots\text{NH}_3$ adduct, which shows an IR absorption band near 1630 cm^{-1} . Therefore, it is possible to distinguish between protonic and Lewis acids: upon NH_3 adsorption, the absorption bands at 1450 and 1630 cm^{-1} are characterized as protonic and Lewis acids, respectively.

The calculated vibrational frequencies of the Ti species upon NH_3 adsorption are summarized in Table 4. Coordination of NH_3 to the $\text{Ti}(\text{OSi})_4$ species induces the Ti-specific band to undergo a slight hypochromatic shift from 963 to 972 cm^{-1} (at the Ti1 site) and from 958 to 964 cm^{-1} (at the Ti3 site). These shifts can be attributed to framework distortion from tetrahedral to triangular bipyramidal symmetry, which leads to lengthening of the Ti-O distances and shortening of the O-Si distances. Regarding the vibrational features of the adsorbed NH_3 molecule, the N-H asymmetric and symmetric stretching vibrational frequencies vary by $\pm 30\text{ cm}^{-1}$, and the N-H bending vibrational frequency appears near 1630 cm^{-1} , indicating that the $\text{Ti}(\text{OSi})_4$ species has Lewis acidity.

For the coordination complexes of the $\text{Ti}(\text{OSi})_3\text{OH}$ species with NH_3 , the Ti-specific band shifts by $<15\text{ cm}^{-1}$ for all of the models, with the exception of the Ti1OH-NH_3 adduct where a H-bond forms between NH_3 and the bridging oxygen in Ti-O-Si, resulting in a blue shift of 29 cm^{-1} for $\nu(\text{Ti-O-Si})$. The most remarkable variations are the hydroxyl stretching vibrational frequencies of the Ti-OH group and the adjacent Si-OH group. When the Ti-OH group interacts with NH_3 through H-bonding, the TiO-H stretching vibration shows a bathochromic shift of $>1000\text{ cm}^{-1}$, which is stronger than the change induced by H-bonded H_2O . Furthermore, with adsorption of NH_3 to the Ti center, the adjacent Si-OH forms a H-bond with one of the bridging oxygen atoms, resulting in the SiO-H stretching vibration undergoing a bathochromic shift of about $100\text{--}200\text{ cm}^{-1}$.

4. Conclusions

In this work, we report theoretical calculations of the geometric and vibrational features of tetrapodal and tripodal Ti(IV) species in Ti-MWW with coordination of H_2O and NH_3 . The DFT method was used with large cluster models, in which four shells of framework atoms surrounding the central Ti were relaxed. The computational results confirm that NH_3 interacts with the central Ti(IV) atom to a greater extent than H_2O . Adsorption of one H_2O or NH_3 molecule to the tetrahedral

Ti(IV) center induces formation of a five-coordinated complex with triangular bipyramidal symmetry. The binding energy to $\text{Ti}(\text{OSi})_3\text{OH}$ species is larger than to $\text{Ti}(\text{OSi})_4$ species, and the Ti(IV) species at the T1 site show slightly stronger Lewis acidity than at the T3 site. The tripodal $\text{Ti}(\text{OSi})_3\text{OH}$ species can also form H-bonded complexes with H_2O and NH_3 through Ti-OH. The calculated vibrational frequencies of the adsorption complexes are divided into two regions: the hydroxyl group vibrational region and the Ti-specific region. The $\nu(\text{O-H})$ and $\nu(\text{N-H})$ vibrational modes show slight blue shifts, reflecting the Lewis acidity of the Ti species. The H-bonded Ti-OH group shows an obvious red shift of $500\text{--}1100\text{ cm}^{-1}$ and appears in the $2700\text{--}3200\text{ cm}^{-1}$ region. The Ti-specific band of the $[\text{Ti}(\text{OSi})_4]\text{-H}_2\text{O}$ adduct is at $960\text{--}970\text{ cm}^{-1}$, and that of the $[\text{Ti}(\text{OSi})_3\text{OH}]\text{-H}_2\text{O}$ adduct is at 980 cm^{-1} . The calculated results are comparable with the experimental IR spectra of TS-1, indicating that Ti-MWW zeolites have similar coordination properties to TS-1 zeolites.

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Graphical Abstract

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Structures and vibrational spectra of Ti-MWW zeolite upon adsorption of H₂O and NH₃: A density functional theory study

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The vibrational spectra of Ti-MWW upon adsorption of H₂O and NH₃ are investigated by density functional theory. The Ti(OSi)₄ and Ti(OSi)₃OH species interact with H₂O to form five-coordinated complexes, with the Ti-specific bands at 971 and 982 cm⁻¹, respectively.

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Ti-MWW分子筛吸附H₂O和NH₃的结构和振动光谱的密度泛函理论计算

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摘要: Ti-MWW分子筛具有10元环(10MR)孔道体系和12MR超笼以及外表面杯状空穴, 在以H₂O₂水溶液为氧化剂的催化氧化反应中表现出不同于其他钛硅分子筛的特殊溶剂效应和立体选择性。已有的实验和密度泛函理论(DFT)计算研究表明, 骨架Ti(IV)可能分布在10MR孔道和12MR超笼中。最近, 我们采用DFT计算研究了Ti-MWW分子筛中骨架钛落位, 通过比较Ti/Si替代能和红外振动光谱, 提出Ti(IV)最可能落位在T1和T3位, 并以[Ti(OSi)₄]形态存在, 显示960 cm⁻¹钛特征振动峰。[Ti(OSi)₄]物种水解时Ti-O键

发生选择性断裂,生成具有翻转Ti–OH的[Ti(OSi)₃OH]物种。由于Ti中心具有Lewis酸性,与配体分子络合后使Ti(IV)的配位状态改变。Ti-MWW分子筛中不同的骨架Ti(IV)落位和形态可能呈现不同的催化选择性。本文应用DFT研究了Ti-MWW分子筛中T1和T3位上不同钛物种与H₂O和NH₃的吸附作用,考察了其几何结构、吸附能以及红外振动光谱性质,为深入理解骨架Ti(IV)的微观结构及实验红外光谱表征提供参考数据。

计算采用36T簇模型,从MWW分子筛晶体结构中分别以T1和T3为中心截取七层骨架原子,末端设为Si–H键并固定为1.46 Å。结构优化时松弛内部四层骨架原子并固定最外三层骨架原子。所有计算在B3LYP/6-31G(d,p)理论水平完成,计算的吸附能都经过BSSE校正,计算的频率以约化因子0.961校正。所有计算在Gaussian 09软件包完成。

计算结果表明,四配位的[Ti(OSi)₄]和[Ti(OSi)₃OH]物种都能与H₂O或NH₃分子作用生成三角双锥的五配位络合物。H₂O或NH₃分子有选择性地进攻Ti–O键的Ti端,形成近乎直线的L–Ti–O键, L–Ti距离可达2.2–2.4 Å。T1位钛物种的Lewis酸性比T3位的略高。对于[Ti(OSi)₃OH]物种, Ti–OH的存在使得Ti(IV)的酸性大大增强,表现出很强的吸附作用。此外, [Ti(OSi)₃OH]物种也能通过Ti–OH基团与H₂O和NH₃形成氢键络合物,但是其吸附能比形成配位络合物的能量更小,说明配体分子更趋向于吸附在Ti中心形成配位络合物。自然键轨道分析表明, Ti(IV)中心的Lewis酸性归因于Ti的空4*p*轨道接受配体提供的孤对电子,并且属于LUMO+3。所有吸附络合物的特征振动频率分布在两个区域,即钛特征振动区域和羟基振动区域。T1和T3位的[Ti(OSi)₄]物种的钛特征振动频率都在960 cm⁻¹,与H₂O形成五配位的吸附络合物之后,钛特征振动频率位移到970 cm⁻¹。[Ti(OSi)₃OH]物种的钛特征振动频率分别为990 cm⁻¹ (T1位)和970 cm⁻¹ (T3位),吸附H₂O分子后都位移到980 cm⁻¹。相应的NH₃吸附络合物的钛特征振动峰频率都高出5 cm⁻¹。分析表明,钛特征振动模式归属于Ti–O–Si键的不对称伸缩振动的协同振动。

在羟基伸缩振动区域,气相H₂O、末端Si–OH基团以及Ti–OH基团的羟基伸缩振动在3600–3760 cm⁻¹。吸附H₂O后,羟基伸缩振动移到3460–3150 cm⁻¹区域。[Ti(OSi)₃OH]物种与NH₃和H₂O形成氢键络合物后,钛羟基的伸缩振动频率分别红移500和1100 cm⁻¹,出现在2700和3200 cm⁻¹区域。吸附分子的O–H和N–H的伸缩振动频率略微蓝移,这反映了Ti物种具有Lewis酸性。

关键词: 密度泛函理论; 钛硅分子筛; 络合; 振动频率; 红外光谱

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