Density functional theory calculations on various M/ZSM-5 zeolites: Interaction with probe molecule H$_2$O and relative hydrothermal stability predicted by binding energies

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Abstract

Density functional calculations were carried out on a series of metal-exchanged and H-form ZSM-5 zeolite clusters with or without H$_2$O molecules adsorbed. By comparing the H$_2$O adsorption on H-form and metal exchanged ZSM-5 zeolite clusters, the model for H$_2$O adsorption on M/ZSM-5 zeolites was put forward, confirmed by the consistency of our frequency calculations with previous IR experiments. The binding energies of the metal cations, which decreased as La/ZSM-5 > Ca/ZSM-5 > Mg/ZSM-5 > K/ZSM-5 > Rb/ZSM-5 > Na/ZSM-5 > Zn/ZSM-5 (>H/ZSM-5), determined the relative hydrothermal stabilities of different metal exchanged ZSM-5 zeolites. Detailed analysis on the three parts to the binding energies was performed, concluding that the part between the metal cations and the zeolite framework has played the most important role, which can be reflected by the consistency of the sequences of the elongated of M−O$_f$ distances and the binding energies. Here the mean square deviation Θ was adopted to characterize the [AlO$_4$]$^-$ tetrahedron, which showed that the process of H or M falling off was facilitated at higher water pressure. When the Brϕnsted acidic proton was exchanged with the metal cations or adsorbed with some water, the [AlO$_4$]$^-$ tetrahedron can restore somewhat towards ideal regularity, and this is probably the reason why ^{27}Al MAS NMR signals are illegible in H/ZSM-5 zeolite and will be much improved by the introduction of some water or the exchange with metal cations.
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Keywords: Density functional calculations; Hydrothermal stability; Binding energy; ZSM-5 zeolite

1. Introduction

Recent years have witnessed an explosion of zeolites used as catalysts [1,2], especially those modified by metal cations such as Co^{2+} or Fe^{3+} [3,4]. However, two basic yet crucial problems still remain pending up to date; i.e., why cations such as La^{3+} or Co^{2+} confer greater hydrothermal stability to the same zeolites? Why only certain cations prove active for the specific catalytic reactions, such as extra-framework Fe ion to the reaction of benzene hydroxylation? In this paper, water is chosen as the probe molecule to explore these two problems.

When a single H$_2$O molecule approaches the Brϕnsted acidic site of ZSM-5 zeolite, the neutral complex (hydrogen-bonded) constitutes the sole product, as detected by IR and INS experiments [5–8]. The protonated complex is regarded as the transition state for proton jumping from one framework oxygen to another [5]. Hot debate arose when a second H$_2$O molecule approaches the same Brϕnsted acidic site. By theoretical calculations, Zygmunt et al. [9] considered the protonated complex should be the transition state between the two neutral complexes, as in the case of one adsorbed H$_2$O molecule. Using IR technique, Jentys, Kondo and Buzzoni et al. [6,8,10] found that protonation took place by further adsorbing H$_2$O to the 1:1 hydrogen-bonded system. To mediate the conflict between theoretical and experimental, Zygmunt et al. [9] admitted that the energy barrier between the neutral and protonated complexes is so small (2.9 kcal mol^{-1})

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that can be easily crossed through. Therefore, the neutral and protonated complexes will coexist in H/ZSM-5 zeolites.

Unlike the intensive research on H/ZSM-5 zeolite, the behaviour of adsorbed H_2O molecules on metal-exchanged ZSM-5 zeolites is currently far from understanding [5,6,11,12]. Based on IR experiments, Jentys et al. [6] assumed that H_2O molecules are adsorbed on alkali-metal cations without lateral interaction, which lacks convincing proof from both experiment and theory. On contrary, Zecchina et al. [5] insisted that the latter adsorbed H_2O molecules will not interact directly with the metal cations but form hydrogen-bonded spheres around the previous adsorbed H_2O molecules, just as adsorbed on H/ZSM-5 zeolite. Rice et al. [11] performed density functional calculations on $2H_2O$-Co and Cu/ZSM-5 systems, suggesting that the two adsorbed H_2O molecules are bound directly to the metal cations through their O atoms, stabilized by further forming hydrogen bonds with the zeolite framework.

The manuscript is outlined as follows: First, several series of local ZSM-5 zeolite structures are geometry-optimised: (1) H-form and various metal-exchanged ZSM-5 zeolite clusters (M = Na, K, Rb, Mg, Ca, Zn, Ga or La); (2) one H_2O molecule adsorbed on H-form and metal-exchanged ZSM-5 zeolite clusters (M = Na, K or Ca); (3) two H_2O molecules adsorbed on H-form and metal-exchanged zeolite clusters (M = Na, K); (4) three H_2O molecules adsorbed on H-form and various metal-exchanged ZSM-5 zeolite clusters (M = Na, K, Rb, Mg, Ca, Zn or La). On such basis, the model of water adsorption on M/ZSM-5 zeolites was put forward. Then, the calculated frequencies of OH groups are compared with those from experimental. Secondly, thermodynamic calculations are carried out for M/ZSM-5 zeolite clusters. Here, binding energies of the metal cations are attempted to correlate with the hydrothermal stabilities. Thirdly, the factors related to the binding energies such as the elongation of M−O_f distances here are investigated. And finally, the state of Al site is characterized by the deviation of $[AlO_4]^-$ tetrahedron for all the optimised ZSM-5 zeolite clusters.

2. Theoretical methods

In the present work, the local structure of ZSM-5 zeolite is represented by a 5T cluster, somewhat larger than that adopted by Zygmunt et al. [9]. The T_{11} site is occupied by an Al atom [13,14] and thus forms a negative charge in the framework, necessitating a counterion such as H^+, Na^+, $Ca(OH)^+$ or $La(OH)_2^+$ [15,16]. The terminal Si and O atoms were fixed in their Cartesian coordinates and saturated by H atoms, which oriented in the direction of what would normally be the next framework atoms. The corresponding Si−H and O−H bond lengths were set to 1.500 and 1.000 Å, respectively.

All calculations were based on density-functional theory at the gradient corrected approximation level, implemented in the DMOL^3 program, CERIUS 2 of MSI [17]. BP functional was employed due to its superiority over the conventional

B3LYP when treating systems containing heavy elements such as La in this study [18]. As hydrogen bonding; i.e., a weak interaction, plays an important role in the nH_2O-M/ZSM-5 zeolite system, DNP as a high precise basis was applied throughout the work, which proves much more reliable than commonly used 6–31G** basis. For reasonable savings of computational resources, effective core potentials (ECP) were applied to heavy atoms. The core electrons of Zn, Rb and La were replaced by a simple potential, and their valence electrons were treated as 3s3p3d4s4p, 4s4p4d5s5p and 4f5s5p5d6s6p, respectively.

3. Results and discussion

3.1. The adsorbed H_2O molecules in M/ZSM-5 zeolite clusters

The local structures of optimized Na/ZSM-5 zeolite clusters with 0, 1, 2 or 3 H_2O molecules adsorbed are displayed in Fig. 1, and the local structures of optimized Ca and La/ZSM-5 zeolite clusters in Fig. 2. For convenience, the H/ZSM-5 zeolite cluster is referred as Z^-H^+, and the M/ZSM-5 zeolite clusters as $Z^-M^{m+}(OH)_{m-1}$, where m stands for the valence of the metal cation. Adsorbed H_2O molecules are added behind, in the form of $Z^-H^+(H_2O)_n$ or $Z^-M^{m+}(OH)_{m-1}(H_2O)_n$, respectively, with the subscript n representing the number of adsorbed H_2O molecules. It should be noted that all M/ZSM-5 zeolite clusters with the same number of adsorbed H_2O molecules have almost the same configurations if the valence of the exchanged metal cations are equivalent.

From Table 1, it can be clearly made out that direct bonds form between the metal cations and all the O_w atoms, even if the ratio of H_2O/M approaches three (the subscript w means that the corresponding O atoms come from the adsorbed H_2O molecules). However, La is the exception, since the distance between La and O_{w2} is 3.802 Å exceeding the tolerance of direct bonds. The exchanged lanthanum species has two hydroxyls, which obstruct the H_2O molecules approaching the La^{3+} cation, albeit the hydroxyls have shifted greatly to vacate space for the H_2O molecules to be adsorbed, which can be figured out from the changes of the Al–M–O angles upon the addition of H_2O molecules (see Table 2). In Ca/ZSM-5 zeolite, the single hydroxyl can move much more freely as adsorbents are introduced in; however, in La/ZSM-5 zeolite, the two hydroxyls are much more restricted, thus limiting the further interaction with more adsorbents.

In $Z^-M^{m+}(OH)_{m-1}(H_2O)_3$ clusters (M = Na, Ca or La), the O_w atoms in the three H_2O molecules are separated by 3.428, 3.333 and 3.768 Å; 3.461, 3.078 and 3.921 Å; 2.671, 2.673 and 3.242 Å, respectively, indicating that the H_2O molecules in the former two have almost no mutual interaction whereas strong hydrogen bonds are formed in the case of La [19]. The model for H_2O adsorption on M/ZSM-5 zeolites is sketched in Scheme 1. At low H_2O pressures, all the
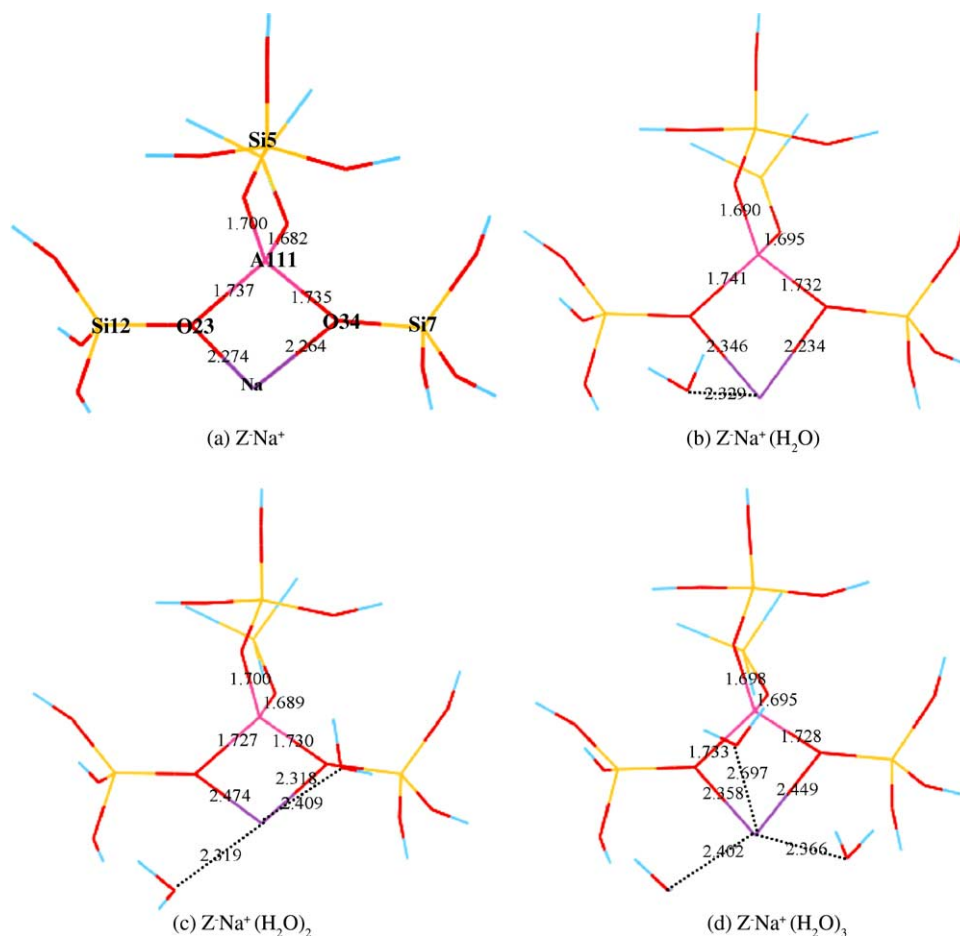
Fig. 1. Na/ZSM-5 clusters adsorbed with 0, 1, 2 or 3 H_2O molecules.

adsorbed H_2O molecules are bound directly to the metal cations through the O_w atoms without lateral interaction, which is consistent with the results of earlier IR experiments [7], as seen in model (a). As the H_2O pressure arises, the metal cation will be gradually screened by H_2O molecules [12], as seen in model (b). Jentys et al. [6] observed that model (b) begins to appear when the H_2O pressure climbs from 10^{-3} to 10^{-2} mbar. As the H_2O pressure continues to
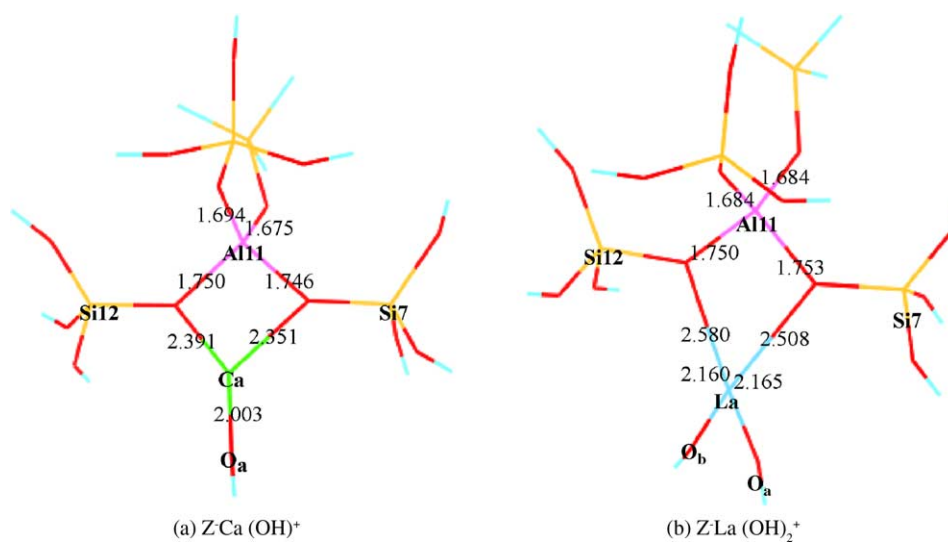

Fig. 2. Ca and La exchanged ZSM-5 clusters.

Table 1
M—O bond lengths in $Z^-M^{m+}(OH)_{m-1}(H_2O)_n$ clusters (units in Å)

	n	Na	K	Rb	Mg	Ca	Zn	La
M[a]		1.020	1.380	1.520	0.720	1.000	0.740	1.032
M—O	0	2.269	2.616	2.790	2.013	2.371	2.023	2.544
	1	2.290	2.653					
	2	2.396	2.743					
	3	2.403	2.777	3.059	2.178	2.449	2.241	2.604
M—O$_{w1}$	1	2.329	2.700					
	2	2.319	2.737					
	3	2.402	2.793	2.957	2.182	2.452	2.374	2.360
M—Ow_2	2	2.409	2.791					
	3	2.697	3.075	2.992	2.286	2.577	2.302	3.802
M—O$_{w3}$	3	2.366	2.786	3.044	2.156	2.425	2.239	2.621

[a] The radius of the metal cation.

Table 2
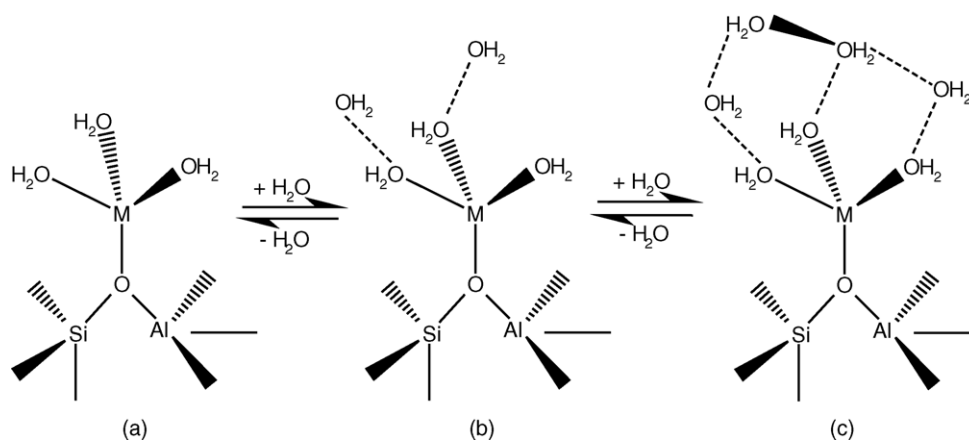Changes on Al—M—O angles in $Z^-M^{m+}(OH)_{m-1}(H_2O)_n$ clusters[a]

n	0	1	3
Ca	172.16^0 (O$_a$)	141.29^0 (O$_a$)	120.11^0 (O$_a$)
La	123.73^0 (O$_a$)		165.81^0 (O$_a$)
	122.04^0 (O$_b$)		106.85^0 (O$_b$)

[a] The O atom in the Al—M—O group is O$_a$ or O$_b$ (see Fig. 2).

go up, the latter adsorbed H_2O molecules will form hydrogen bonds with the inner H_2O molecules instead of forming direct bonds with the metal cations, and finally constitutes a large hydrogen-bonded H_2O sphere [5], as seen in model (c). Jost et al. [20] carried out molecular dynamics simulations on calcium-exchanged chabazite, concluding that the H_2O molecules at low loading have exactly one neighboring cation but at a high loading some of them will have no cations as direct neighbors. Further dynamical calculations on H_2O-M/ZSM-5 zeolite systems are under way. It can be declared that the metal cations tend to gather as many adsorbents around as possible, which is not the case for the Brønsted acidic proton in H/ZSM-5 zeolite. The H/ZSM-5 zeolite cluster with or without adsorbed H_2O molecules are optimized under the same conditions depicted in the part of Theoretical methods. The Brønsted acidic proton can only form one bond (hydrogen bond or covalent bond) to one of the adsorbed H_2O molecules or other adsorbents, determined by the fact that covalent bonds will form between H and many adsorbents. Therefore, the crucial step in catalytic processes; i.e., sufficient contacts among different adsorbents or between reactants and the active sites are severely hindered in H/ZSM-5 zeolite, whereas such a situation can be much improved in M/ZSM-5 zeolites. Accordingly, the exchanged cations behaving as Lewis acidic site become a hot topic recently [21].

IR technique is very powerful to distinguish the vibrations of different OH groups. However, the adsorbed H_2O molecules have exhibited such a large and complex influence that it becomes also unrealistic for experimental researchers to clearly assign all the IR peaks [5,6,12]. Ideally, each peak can be assigned in theoretical calculations by animating the frequencies individually. The vibrational frequency of bridging hydroxyl falls at $3615.11\,cm^{-1}$ after scaled by 0.98 [14], which agrees well with the experimental value at $3616\,cm^{-1}$

Scheme 1. The model for water adsorption on M/ZSM-5 zeolites.

Table 3
Vibrational frequencies for OH groups in $Z^-M^{m+}(OH)_{m-1}(H_2O)_n$ clusters

Metal	n	Vibrational frequencies (units in cm^{-1})
Na	1	3684.5; 3316.0; 1651.6; 3282.0 (O_{32}–H_{11})[a]
	2	3717.2; 3521.1; 3347.0; 1638.7; 1621.9; 3447.4 (O_{19}–H_{22})
	3	3719.8; 3680.2; 3668.9; 1620.2; 1613.9; 1606.1; 3486.3 (O_{32}–H_{11}); 3266.2 (O_{19}–H_{32})
	Exp.	3671 (1, 2, 3)[b]; 3595; 3357 (1, 2); 3278 (1, 3); 1626 (1, 2, 3)
K	1	3683.9; 3329.3; 1633.2; 3292.8 (O_{32}–H_{11})
	2	3728.7; 3508.9; 3412.4; 1641.5; 1620.7; 3412.4 (O_{19}–H_{22})
	3	3723.6; 3666.8; 3657.2; 1644.2; 1615.3; 1594.3; 3506.0 (O_{32}–H_{11}); 3439.2 (O_{19}–H_{32})
	Exp.	3670 (1,3); 3595;3451 (2,3); 3371 (2,3);1630 (1,2,3)
Rb	3	3732.1; 3665.3; 3536.7; 1632.0; 1620.2; 3485.3 (O_{32}–H_{11}); 3461.7 (O_{19}–H_{32})
	Exp.	3668 (3);3595; 3471 (3); 3363; 1633 (3)
Mg	3	3666.3; 3631.1; 3630.4; 3400.0 (O_{32}–H_{21}); 3244.86 (O_{19}–H_{32}); 2432.6 (O_a–H_{12})[c]; 1616.9; 1613.1; 1601.5
Ca	3	3686.3; 3666.6; 3637.7; 1630.4; 1611.2; 1607.0; 3397.2 (O_{32}–H_{21}); 3227.0 (O_{19}–H_{32}); 2684.2 (O_a–H_{12})
Zn	3	3650.1; 3621.6; 3552.3; 1650.9; 1602.0; 1587.6; 3401.9 (O_{32}–H_{21}); 3236.3 (O_{19}–H_{32}); 3024.0 (O_a–H_{12})
La	3	3693.31; 3691.1; 3342.8; 3332.8; 1650.4; 1622.6; 1611.4; 3307.8 (O_{19}–H_{32}); 3182.6 (O_a–H_{12}); 3050.2, 2902.4 (O_3–H_{22}, O_2–H_{12})

[a] The frequency for the hydrogen bond between O_{32} and H_{11}.
[b] The value of $n(H_2O)$ where calculated values in clusters are comparable to experimental from Ref. [7].

[22]. The vibrational frequencies related to adsorbed H_2O molecules are scaled by 0.98 and then listed in Table 3. Albeit our best effort, some of the frequencies are still illegible and thereof beyond discussion. In $Z^-Na^+(H_2O)_3$ cluster, the asymmetric stretching vibrations of three adsorbed H_2O molecules lie at 3668.9, 3680.2 and 3719.8 cm^{-1}, respectively, in good agreement with the results of Sárkány (a strong band at 3668 cm^{-1} together with a weak one at 3698 cm^{-1}) [12]. The peak at 3486.3 cm^{-1} is the product of hydrogen bond formed between O_{32} and H_{w1}, as pointed out by Zecchina et al. [5] that at relatively high H_2O pressure a broad band appears at 3480–3430 cm^{-1}. Hydrogen bonds increase in amount and intensity with the increase of adsorbed H_2O molecules, and some of them are listed in the brackets of Table 3. In Na, K and Rb/ZSM-5 zeolites, the good consistence of IR experiments [6] with our frequency calculations prove the reliability of our optimized structures and the rationality of our proposed H_2O adsorption models, settling the earlier conflicts between Zecchina and Jentys mentioned in the introduction [5,6]. In our opinion, the IR peak at 3595 cm^{-1} [6] doesn't relate to the metal-exchanged sites due to two reasons: (1) its position does not shift even slightly as the metal cation changes from Na to Rb; (2) it has no corresponding value in our calculated results.

3.2. Evaluation of hydrothermal stability for various M/ZSM-5 zeolites

Steamed at high temperatures, the introduced metal cations will be gradually displaced away from the exchanged sites, leaving the framework Al atoms exposed to the attack of water. Different exchanged cations have different effects on the hydrothermal stability of ZSM-5 zeolites, and the overall process of demetalation can be represented by the following reaction

$$Z^-M^{m+}(OH)_{m-1}(H_2O)_n$$
$$\rightarrow Z^-H^+ + (n-1)H_2O + M(OH)_m \tag{1}$$

Thermodynamic calculations are carried out utilizing statistical mechanics [23]. Conventionally, thermodynamic data available in experiments are used [24]. By calculating the enthalpy changes according to reaction (1), the hydrothermal stabilities of various metal exchanged ZSM-5 zeolites are obtained, which decrease as Na/ZSM-5 > K/ZSM-5 > Zn/ZSM-5 > Ca/ZSM-5 (see Table 4), in obvious contradiction with the experimental results (La/ZSM-5 > Ca/ZSM-5 > Na/ZSM-5 > H/ZSM-5 [25]; Ca/ZSM-5 ≫ Zn/ZSM-5 > H/ZSM-5 [26]). If the thermodynamic data are taken

Table 4
Enthalpy change for reaction (1) (units in kJ mol^{-1})[a]

Na			K			Ca	Zn	La
1[b]	2	3	1	2	3	3	3	3
		−1112.0			−1124.2	−1720.2	−1375.9	
−7.9	−25.4	−26.0	−7.5	−19.9	−31.9	−27.5	−34.7	−27.4

[a] All data are taken from calculations except those for H_2O and $M(OH)_m$ in the upper line.
[b] n.

exclusively from the theoretical calculations, the sequence is changed to Na/ZSM-5 > La/ZSM-5 > Ca/ZSM-5 > K/ZSM-5 > Zn/ZSM-5, with Na/ZSM-5 zeolite as the only exception with the experimental sequence. The failure of thermodynamic prediction may lie in that the thermodynamic computation of solids is based on the assumption of ideal gases, where the enthalpy $H(T) = E_{vib}(T) + E_{rot}(T) + E_{trans}(T) + RT$, with subscripts vib, rot and trans standing for vibrational, rotational and translational contributions, respectively. In fact, the conversion of one substance from gas to solid needs to adsorb a great deal of energy, which may differ a lot for two different materials. Moreover, the lattice energies of two different solids may also vary greatly. Both these two factors will cause the calculated results of ideal gases deviated severely from the experimental results of solids. Accordingly, it is no wonder that the calculated enthalpy difference between zinc and calcium hydroxides is about 5.6 kJ/mol, whereas the experimental value reaches almost 550 kJ/mol. For a specific exchanged metal cation such as Na or K, the hydrothermal stability of M/ZSM-5 zeolites descend as the water pressure arises, which can be accurately predicted by thermodynamic calculations. Unfortunately, it fails once more when trying to reach a conclusion on the relative hydrothermal stabilities on Na and K/ZSM-5 zeolites at each level of water pressures (see Table 4 to compare the values of Na and K/ZSM-5 zeolite clusters adsorbed with 1, 2 or 3 H_2O molecules, respectively). Therefore, to accurately obtain the relative hydrothermal stabilities of different metal exchanged zeolites, a novel and effective method becomes of high necessity.

In various M/ZSM-5 zeolites, the improved stability by the metal cations can be evaluated through the following equation

$$E_b^0 = E[Z^-M^{m+}(OH)_{m-1}] - E(Z^-) - E[(m-1)(OH)] \quad (2)$$

where $E[Z^-M^{m+}(OH)_{m-1}]$ is the electronic energy of M/ZSM-5 cluster, $E(Z^-)$ is the electronic energy of the zeolite cluster optimised without metal cations, and $E[(m-1)(OH)]$ is the electronic energy of hydroxyls bound to the metal cations. H/ZSM-5 zeolite is also considered here by replacing M with H in Eq. (2). Accordingly, the enhancement on the hydrothermal stability of metal exchanged ZSM-5 zeolites over H/ZSM-5 zeolite can be obtained by the equation below

$$E_e^0 = E_b(M) - E_b(H) - E[(m-1)(OH)] \quad (3)$$

In the same way, we can learn how much the hydrothermal stability of M/ZSM-5 zeolites is enhanced compared to

H/ZSM-5 zeolite at a certain water pressure. For instance, the enhanced hydrothermal stabilities of our M/ZSM-5 zeolite clusters with three H_2O molecules adsorbed are obtained through the following equation with a similar formalism to Eq. (3)

$$E_e^3 = E_b^3(M) - E_b^3(H) - E[(m-1)(OH)] \quad (4)$$

More negative values of binding energies (E_b) mean stronger binding to the zeolite framework. The data of E_b^0, E_e^0 and E_b^3 are listed in Table 5. The binding energies of E_b^0 (or E_e^0) decrease in the sequence as La/ZSM-5 > Ga/ZSM-5 > Ca/ZSM-5 > Mg/ZSM-5 > K/ZSM-5 > Rb/ZSM-5 > Na/ZSM-5 > Zn/ZSM-5 (>H/ZSM-5), in fine agreement with the experimental results [25,26]. Lanthanide elements such as La and Ce have been well acknowledged as the effective additives on improving the hydrothermal stability of zeolites. In the previous paper [14] we have elaborated on the Brϕnsted acidic proton associated with the framework Al atoms, which are the most fragile part of the whole zeolite. The sequence of E_e^3 is almost a duplicate to that of E_e^0 (or E_b^0), with the exception of Zn. Accordingly, the hydrothermal stability of M/ZSM-5 zeolites seems to have been determined by the binding energies; i.e., the nature of the exchanged metal cations. The consistency of E_e^3 and E_e^0 (or E_b^0) in sequence further confirms this conclusion since the added H_2O molecules have shown little influence. As discussed in part 3.1, the exchanged metal cations rather than the Brϕnsted acidic proton form direct bonds with as many as O_w atoms, decreasing the chance of water attacking the Al sites and thus retarding the dealumination process.

3.3. Elongation of $M-O_f$ distances by adsorbed H_2O molecules

The binding energies of metal cations can be divided into three parts: (1) with the hydroxyl in M(OH)$_{m-1}$, which is almost unaffected during the demetalation process. (2) With the adsorbed H_2O molecules, which show little influence on the sequence of binding energies of different metal exchanged ZSM-5 zeolites as depicted in part 3.2. (3) With the zeolite framework, which will be discussed in this part. The average lengths of $M-O_{23}$ and $M-O_{34}$ bonds; i.e., $M-O_f$ distances are collected and listed in Table 1. $M-O_f$ locates at 2.269 Å for M = Na and 2.013 Å for M = Mg, respectively, which shows a relatively large deviation from the data of Ferrari et al. [27] (2.302 and 1.970 Å for Na and Mg, respectively). Probably the small cluster AlH(OH)$_3$$^-$ they have chosen is incompetent for correctly describing the local ZSM-5 zeolite

Table 5
Binding energies according to Eqs. (2)–(4) (units in kJ mol^{-1})

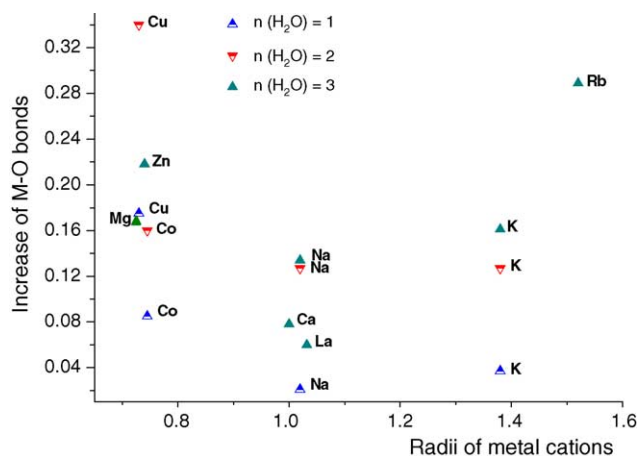|	H	Na	K	Rb	Mg	Ca	Zn	Ga	La
E_b^0	34.1	−33.2	−61.5	−38.6	−292.5	−418.0	−13.2	−451.9	−1026.1
E_e^0		−69.7	−95.7	−72.8	−326.6	−452.1	−47.4	−486.1	−1060.3
E_e^3		−22.0	−42.2	−17.5	−342.9	−469.0	−22.8		−1019.0

Fig. 3. Length elongation of M−O$_f$ distances in Z$^-$M^{m+}(OH)$_{m-1}$(H$_2$O)$_n$ clusters after adsorption of H$_2$O molecules (units in Å).

structure. As to the Z$^-$Zn^{2+}(OH) cluster, the average length of Zn−O$_{23}$ and Zn−O$_{34}$ bonds; i.e., Zn−O$_f$ distance falls at 2.023 Å, in good consistency to that reported by Barbosa et al. [28]. For M/ZSM-5 zeolites with M of the same valence, M−O$_f$ distance increases as the increase of M's radius, as can be seen from the group Na, K and Rb or Mg, Zn and Ca (in Table 1). For M of close radii such as Na, Ca and La, M−O$_f$ distance increases as the increase of the valence, owing to the larger electrostatic repulsion between the framework Al and the metal cation of higher valence.

Na−O$_f$ distance is elongated from 2.269 to 2.290, 2.396, 2.403 Å as the first, second and then third H$_2$O molecules approach the Na/ZSM-5 zeolite cluster. The elongation of M−O$_f$ distance by adsorbed H$_2$O molecules has been observed in all the other M/ZSM-5 zeolite clusters studied by us as well as those of Cu$^+$, Cu^{2+} and Co^{2+} exchanged ZSM-5 zeolite clusters studied by Rice et al. [11], indicating that the interaction between the metal cations and the zeolite framework is gradually weakened by the addition of the adsorbed H$_2$O molecules. As a result, the metal cations will become easier to be the extracted from the ZSM-5 zeolites. The elongated distances of M−O$_f$ distances by one, two and three adsorbed H$_2$O molecules are colleted and illustrated in Fig. 3. The less elongated M−O$_f$ distances imply

less influence by adsorbed H$_2$O molecules on the exchanged metal cations, and such metal cations will be bound more firmly to the zeolite framework. In consequence, the metal cations will protect the Al sites more effectively from the attack of H$_2$O molecules, thus enhancing the hydrothermal stability of ZSM-5 zeolites to a better degree [14,25,26]. Here we used the optimised M−O$_f$ distances in Cu^{2+} and Co^{2+} exchanged ZSM-5 zeolite clusters with or without adsorbed H$_2$O molecules by Rice et al. [11] to calculate the elongated M−O$_f$ distances. It is obvious that Co−O$_f$ bonds are elongated much less than Cu−O$_f$ bonds when adsorbed by one or two H$_2$O molecules (see Fig. 3), which accords finely with the well-known fact that Co^{2+} is much superior to Cu^{2+} on the improvement of the hydrothermal stability of ZSM-5 zeolites [29]. It can be declared from Fig. 3 that the elongation is slighter in the cases of M = Na, K, Ca and La, especially Ca and La, which agrees with the better hydrothermal stabilities of these metal exchanged ZSM-5 zeolites obtained by Liu et al. [30] and other researchers [25,26]. With the radius of the metal cation considered, the elongated M−O$_f$ distance is consistent well in sequence with the binding energy (E_e^0 or E_e^3).

3.4. [AlO$_4$]$^-$ tetrahedron in H and M/ZSM-5 zeolite clusters

The ZSM-5 zeolite framework is influenced indirectly by adsorbed H$_2$O molecules; i.e., through the metal cation. Therefore, the metal cation acts as the protector of the Al sites against the hydrothermal treatments. Here the deviation of [AlO$_4$]$^-$ tetrahedrons from ideal regularity is parameterized by the mean square deviation (Θ) instead of the shear strain parameter (Ψ) previously used by Engelhardt and Koller et al. [31,32]. Their definitions are $\Theta = \sqrt{\frac{1}{6}\sum_{i=1}^{6}(\alpha_i - \bar{\alpha})^2}$ and $\Psi = \sum_{i=1}^{6}|\tan(\alpha_i - 109.47°)|$, respectively, where α_i is the ith of the six O−Al−O angles, and $\bar{\alpha}$ is the average of the six angles (units in degrees). Both parameters Θ and Ψ in Table 6 show that the [AlO$_4$]$^-$ tetrahedron in the bare ZSM-5 cluster is in nearly perfect regularity whereas severely destroyed by the Brønsted acidic proton (see Fig. 4 for these two optimized clusters). The Brønsted acidic proton destroys the [AlO$_4$]$^-$

Table 6
Deviation of [AlO$_4$]$^{3-}$ tetrahedrons from ideal regularity

	Θ					Ψ				
	0[a]	1	2	3		0	1	2	3	
H	9.30	6.81	6.36	5.94	2.55[b]	0.86	0.58	0.55	0.49	0.23[b]
Na	6.38	5.86	5.63	5.61		0.58	0.53	0.51	0.51	
K	5.49	5.30	4.57	5.04		0.51	0.46	0.42	0.46	
Rb	5.08			4.57		0.47			0.44	
Mg	8.73			7.28						
Ca	7.17	7.00		6.82		0.62	0.61		0.62	
Zn	8.29			6.62						
La	6.64			7.29						

[a] n.
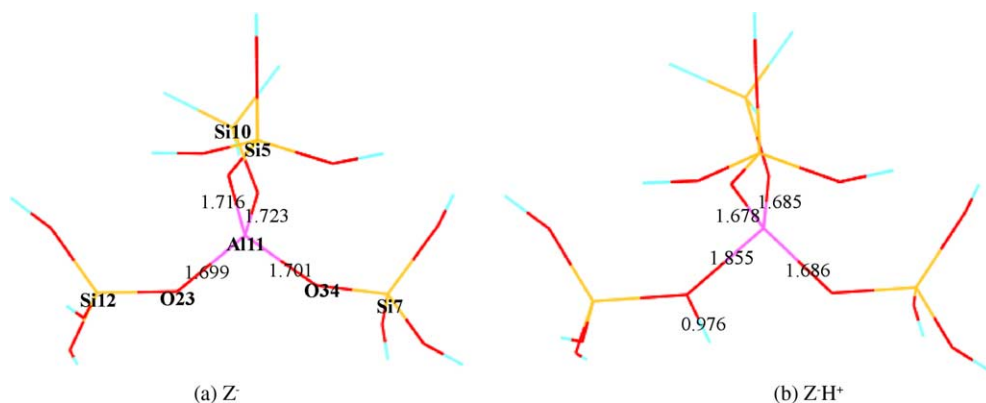[b] The bare ZSM-5 cluster without the acidic proton (see Fig. 4a).

Fig. 4. Structures of H/ZSM-5 clusters with or without acidic proton.

tetrahedron greatly from regular and thus the corresponding H/ZSM-5 zeolite shows much less stability than its deprotonated form. The advantage of Θ over Ψ can be seen from the case of the Ca/ZSM-5 zeolite clusters. The $[AlO_4]^-$ tetrahedron in Ca/ZSM-5 zeolite gradually approaches regularity as more water is gradually introduced, which can be reflected correctly by the parameter Θ rather than Ψ. Accordingly, the parameter Θ is used for the subsequent calculations. The parameter Θ in the bare ZSM-5 zeolite cluster is the smallest (see Table 6), and the configuration of $[AlO_4]^-$ tetrahedron in this cluster can be regarded as the one with the Brønsted acidic proton or the metal cations completely falling away from the zeolite framework. When the Brønsted acidic proton is exchanged by the metal cations, the $[AlO_4]^-$ tetrahedron can restore somewhat towards ideally regular even without adsorbing H_2O molecules. When the H or M/ZSM-5 zeolites adsorb more and more water, the $[AlO_4]^-$ tetrahedron will gradually approach ideal regularity, implying the facilitation of H or M falling off by the higher water pressure. It is probably the reason that the ^{27}Al MAS NMR signal of tetrahedral Al sites in H-form zeolites is almost illegible, whereas such a situation can be much improved by exchanging with the metal cations or adsorbing some water. The parameter Θ in $Z^-M^{m+}(OH)_{m-1}(H_2O)_3$ clusters (M = Ca or La) is much larger than those with exchanged with Na, K or Rb. It drops much more slowly than those exchanged with Mg or Zn (8.73–7.28 and 8.29–6.62 for Mg and Zn ($n = 0$–3), respectively). Therefore, the ZSM-5 zeolites exchanged with Ca or La can endure more severe hydrothermal treatments.

4. Conclusions

In the present paper, density functional calculations were carried out on a series of metal-exchanged and H-form ZSM-5 zeolite clusters. The major findings are summarized below.

The equilibrium structures are obtained for H and M/ZSM-5 zeolites adsorbed with 0, 1, 2 or 3 H_2O molecules (M = Na, K, Rb, Mg, Ca, Zn or La). The metal cations tend to gather as many adsorbents around as possible, which is not the case for the Brønsted acidic proton in H/ZSM-5 zeolite. The model for H_2O adsorption on M/ZSM-5 zeolites is put forward, confirmed by the agreement of our frequency calculations with previous IR experiments.

The hydrothermal stabilities of M/ZSM-5 zeolites seem to be determined by the binding energies of the metal cations, which decrease as La/ZSM-5 > Ca/ZSM-5 > Mg/ZSM-5 > K/ZSM-5 > Rb/ZSM-5 > Na/ZSM-5 > Zn/ZSM-5 (>H/ZSM-5), in good accordance with experimental results.

The binding energy of the metal cation is divided into three parts: (1) with the hydroxyl in $M(OH)_{m-1}$, unaffected during the demetalation process; (2) with adsorbed H_2O molecules, which show little influence by the consistency in the sequences between E_e^3 and E_e^0 (or E_b^0); (3) with the zeolite framework, which is reflected by the elongation of $M-O_f$ distances. The sequence of the elongated $M-O_f$ distances agrees well with those of the binding energies and the hydrothermal stabilities, further confirming that the hydrothermal stabilities are determined by the nature of the exchanged metal cations; i.e., their binding energies.

The mean square deviation Θ is adopted to characterize the $[AlO_4]^-$ tetrahedron, which shows that the process of H or M falling off is facilitated at higher water pressure. Meanwhile, the problem is settled why ^{27}Al MAS NMR signals are illegible in H/ZSM-5 zeolite and can be much improved by the introduction of some water or the exchange by certain metal cations.

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