Periodic DFT Calculation of the Energy of Ammonia Adsorption on Zeolite Brønsted Acid Sites to Support the Ammonia IRMS–TPD Experiment

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Periodic DFT calculation supports quantitatively the energy of ammonia adsorption on zeolite Brønsted acid sites, which was measured by ammonia IRMS–TPD experiment as an index of the acid strength.

We have studied the acidities of various zeolites by means of ammonia infrared spectroscopy/mass spectroscopy–temperature-programmed desorption (IRMS–TPD).[1] Simultaneous measurements of IR and MS spectroscopy during the ammonia TPD allow us to quantitatively determine the number and strength of the Brønsted OH. The structure of the OH also can be estimated from the band position. Thus, we have detailed information of the distribution of Brønsted acid sites in zeolites.

In addition, our previous paper reported that the measured strengths of acid sites (ΔH) were supported well by DFT calculation, because the calculated values were in good agreement with the experimentally measured values.[2] However, the calculation reported was performed with an embedded 8T (T = Si or Al) cluster model, and, therefore, the constructed zeolite model may not be enough to confirm the experimentally measured heat of ammonia adsorption.

In order to obtain a more precise and correct value of ammonia adsorption, we have studied a DFT calculation based on periodic boundary conditions. In the present study, four kinds of zeolite species, i.e., FAU, CHA, BEA, and MOR, were selected. Both FAU and CHA have one equivalent T site in the framework, and there are only four kinds of Brønsted acid sites. A study of the ammonia adsorption on the four sites of CHA was reported by us.[3] On FAU, three OHs which have been experimentally identified were studied.[4] MOR and BEA have four and nine kinds of nonequivalent T sites; consequently, it can be considered that those have 14 and 32 kinds of Brønsted SiO(H)Al groups, respectively. Because the unit cell of zeolite systems contains large numbers of framework atoms, the computational cost of periodic calculation is very high. In this work, therefore, we selected the typical protonated sites in MOR and BEA according to previous findings of neutron diffraction[5] and quantum chemical calculations.[6] Locations of Brønsted OH groups in each zeolite framework are shown in Figure 1.

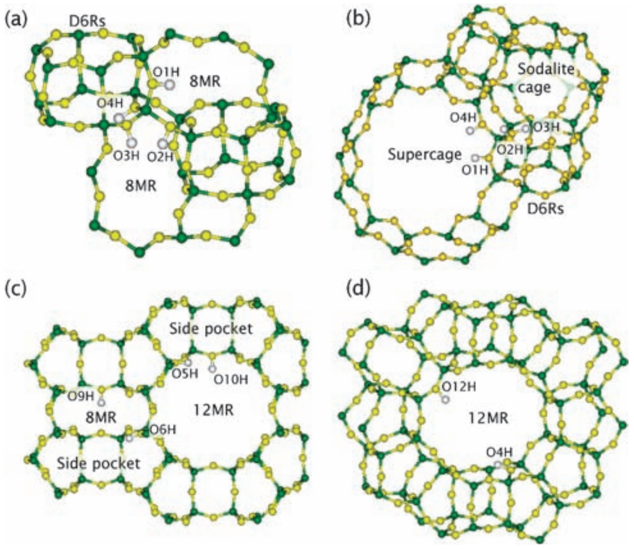

Figure 1. Locations of bridged acidic OH groups in CHA (a), FAU (b), MOR (c), and BEA (d) zeolites.

Periodic DFT calculations were performed by using the Dmol^3 software developed by Accelrys Co. Initial structures of purely siliceous CHA, MOR, and BEA were obtained from the Material studio 4.0 library. For MOR, however, the lattice constant in *c* direction was set to be double, because the *c* lattice was so short that adsorbed ammonia molecules in each cell may have some interaction. Thus, we assumed a supercell whose lattice constants were $a = 19.094$ Å, $b = 20.516$ Å, $c = 15.048$ Å, and $\alpha = \beta = \gamma = 90.0°$. For the FAU system, a rhombohedral unit cell was assumed.[7] Geometry optimization and energy calculations were made based on the generalized gradient approximation (GGA) level using the Hamprecht–Cohen–Tozer–Handy (HCTH) exchange and correlation functional. All calculations were performed using a double numerical polarization (DNP) basis set. The adsorption energy of ammonia (E_{ads}) was calculated on the basis of the following equation: $E_{\text{ads}} = (E_{\text{H-Z}} + E_{\text{NH}_3}) - E_{\text{NH}_4\text{-Z}}$, where $E_{\text{NH}_4\text{-Z}}$, $E_{\text{H-Z}}$ and E_{NH_3} are the total energies of NH_4-zeolite, H-zeolite, and gaseous ammonia, respectively.

Calculated E_{ads} and the corresponding experimental values ΔU are summarized in Table 1. The optimized geometries of H- and NH_4-formed periodic systems are shown in Supporting Information.[8]

Among the four kinds nonequivalent SiOAl linkages in FAU, only O(1–3) sites can be protonated.[4] Ammonium cations on the bridged O(2 and 3) linkages were stabilized in sites II and I′ by forming tridentate species. Those adsorption configurations are in agreement with ammonia-adsorbed complex models indicated by Zecchina et al.[9] E_{ads}'s on O(1–3) groups were 122, 110, and 101 kJ mol^{-1}, respectively. The theoretical values for O2H and O3H were comparable to the experimental values (115 and 101 kJ mol^{-1}), while the E_{ads} on O1H was overestimated. The reason for a small deviation from the experimental value could originate from the computational conditions; i.e., consid-

Table 1. Calculated E_{ads} and measured ΔU on isolated Brønsted OH groups

IZA Code	Acid site	Location (MR)	E_{ads} /kJ mol^{-1}	ΔU^{b} /kJ mol^{-1}
CHA[a]	Al1–O1–Si1	8	127.9	131
	Al1–O2–Si1		129.3	134
	Al1–O3–Si1		131.3	128
	Al1–O4–Si1	6	110.1	101
FAU	Al1–O1–Si1	12	121.9	105
	Al1–O2–Si1	6	110.2	115
	Al1–O3–Si1		100.8	101
MOR	Al2–O5–Si2	12	135.1	142
	Al4–O10–Si4		140.9	
	Al1–O6–Si1	8	136.3	147
	Al3–O9–Si3		149.8	
BEA	Al9–O12–Si4	12	126.9	125
	Al1–O4–Si8	6	122.3	

[a]E_{ads} and ΔU were summarized in ref 3. [b]E_{ads} obtained from DFT calculation corresponds to $\Delta U = \Delta H - RT_{\mathrm{m}}$ where T_{m} is the peak maximum temperature (K) of the TPD measurement, and R is gas constant (8.314 J K^{-1} mol^{-1}). ΔU's of FAU, MOR, and BEA were summarized in ref 2.

ered level of approximation and/or lattice parameter of the periodic system. However, the calculated E_{ads} on FAU structure, except for the O1H, agreed with the experimental values.

The ΔU on bridged OH groups in 12 and 8MRs of MOR were 142 and 147 kJ mol^{-1}, respectively; therefore, the Brønsted acid site in 8MR was stronger than that in 12MR. The calculated E_{ads} on acidic OH groups in 12MR (Al2–O5–Si2 and Al4–O10–Si4 centers) were 135.1 and 140.9 kJ mol^{-1} which were in good agreement with the experimental value (142 kJ mol^{-1}). On the other hand, the E_{ads} on 8MR (Al1–O6–Si1 and Al3–O9–Si3 centers) were 136.3 and 149.8 kJ mol^{-1}, respectively. Al3–O9–Si3 center showed the strongest E_{ads}, and it was comparable to the experimental value (147 kJ mol^{-1}).

Like a previously reported study on CHA,[3] the thermodynamic parameters of heterogeneous Brønsted acid sites in FAU and MOR obtained from IRMS–TPD measurements were quantitatively supported by means of periodic DFT calculations. In addition, the Al1–O4–Si8 and Al9–O12–Si4 centers in BEA showed reasonable E_{ads} (122 and 127 kJ mol^{-1}) corresponding to the experimental value (125 kJ mol^{-1}). Figure 2 shows the plots of calculated E_{ads} against the corresponding ΔU. The agreement between the experimental and theoretical adsorption energies of ammonia can be confirmed.

In summary, adsorption energies of ammonia on Brønsted acid sites in zeolites obtained from ammonia IRMS–TPD measurements were quantitatively supported by periodic DFT calculations. In a previous paper, we have identified that the DFT calculation with the embedded cluster model also provided us an E_{ads} value which was in agreement with the ΔU measured by the experiment.[2] Those findings suggest that the adsorption energy of ammonia is mainly influenced by the local environment of active site; i.e., T–O–T bond angle, T–O bond length, and spatial arrangement of surrounding framework atoms. These consistencies tell us that the combined study of IRMS–TPD and DFT calculation will be utilized as a powerful technique to study zeolite acidity in detail.[7,10,11]

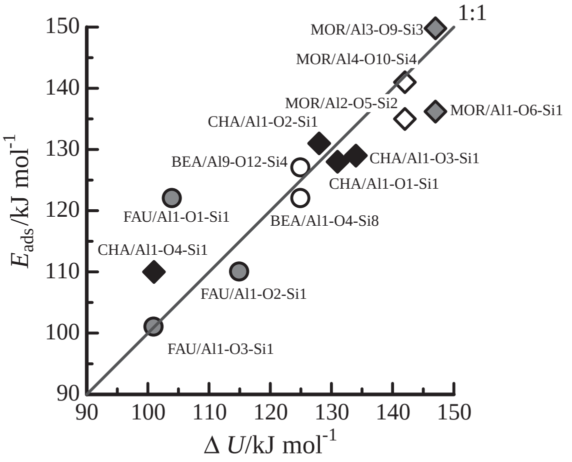

Figure 2. Relationship between ΔU and E_{ads}.

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