1034 Chemistry Letters Vol.36, No.8 (2007)

Quantitative Measurements of Brønsted Acidity of Zeolites by Ammonia IRMS–TPD Method and Density Functional Calculation

Katsuki Suzuki,[1,2] German Sastre,[3] Naonobu Katada,[1] and Miki Niwa*[1]
[1]*Department of Materials Science, Faculty of Engineering, Tottori University,*
4-101 Koyama-minami, Tottori 680-8552
[2]*Japan Society for the Promotion of Science (JSPS), Chiyoda-ku, Tokyo 102-8471*
[3]*Instituto de Tecnologia Quimica UPV-CSIC, Universidad Politecnica de Valencia,*
Avenida. Los Naranjos s/n, Valencia, Spain

(Received May 29, 2007; CL-070580; E-mail: mikiniwa@chem.tottori-u.ac.jp)

Adsorption energy of ammonia (E_{ads}) on the Brønsted acid center of several zeolites was calculated by an embedded 8T cluster calculation based on the density functional theory. The E_{ads}'s were in good agreement with the ΔU obtained by an ammonia IRMS–TPD method.

Recently, we have proposed a method of infrared-mass spectrometry/temperature-programmed desorption (IRMS–TPD) of ammonia for quantitative measurement of acidity of zeolites.[1] An advantage of this method is "direct measurement" of acidity of Si(OH)Al groups in zeolite framework. By this method, we can measure the acid amount, the acid strength (heat of ammonia adsorption, ΔH) and the location of Si(OH)Al groups.[1,2] This knowledge would be useful for identification of catalytically active center in the zeolite.

Density functional is one of the most flexible methodologies for analyzing those subjects. Adsorption energy of several kinds of base molecules on the acid center has been frequently calculated based on this theory.[3,4] In the present study, we will show the agreement between experimental and theoretical values of heat of ammonia adsorption on Brønsted acid sites on several kinds of zeolites derived by ammonia IRMS–TPD and density functional calculation, respectively.

Embedded 8T cluster calculations were carried out with a Dmol^3 software developed by Accelrys Inc. The geometrical parameters for initial structures of MFI, FER, MWW, MOR, FAU, and BEA were obtained from the Material studio 4.0 library. Embedded 8T cluster models consisting of 8T (Si or Al) sites were cut off from those structures and terminated by H atom to keep the neutrality. The position of proton on zeolite was selected according to previous investigations of quantum chemical calculation or neutron diffraction. The Si(OH)Al groups selected as typical acid center were shown in Table 1. Selected acid centers of MFI are Al(11)–O(11)–Si(12) and Al(7)–O(17)–Si(4); and those bridged OH groups locate in straight and sinusoidal 10 MR (membered ring) channels, respectively.[5] Acid centers of FER selected are Al(4)–O(6)–Si(4) and Al(3)–O(4)–Si(1). In the neutron diffraction,[6] T(4)–O(6)D–T(4) and T(3)–O(4)D–T(1) groups were identified, and those OD groups were reported to locate in the 10 MR channel and ferrierite-cage, respectively. Location of the Al atom was decided also from the quantum chemical calculation.[5] MWW has three kinds of acidic OH groups in the supercage, sinusoidal 10 MR channel and hexagonal prism, and these sites have been attributed to Al(4)–O(3)H–Si(1), Al(3)–O(11)H–Si(2), and Al(2)–O(9)H–Si(5), respectively.[7] Out of 32 OH groups, 17 of them are located in the supercage and 12 MR.[8] Many of the active centers locate in the large cavity; therefore, we selected the Al(4)–O(3)H–Si(1) as typical active center. Acid centers of MOR are selected from our previous study;[1] and Al(1)–O(3)H–Si(2), Al(2)–O(2)H–Si(4), and Al(4)–O(2)H–Si(2) in 12 MR and Al(3)–O(1)H–Si(1) in 8 MR are selected. Acid centers of BEA are Al(1)–O(4)H–Si(8) and Al(9)–O(12)H–Si(4) which locate in the 6 MR and 12 MR, respectively.[9] T site of FAU is only one kind; therefore, nonequivalent oxygen sites are four kinds. Experimental identification of O(1–3)H groups in FAU has been carried out, while O(4)H has not been detected.[2] In this study, we calculated the acidities of O(1–3)H groups as active sites. As examples, cluster models of FAU/O(1)H and MFI/Si(7)–O(17)H–Al(4) groups were shown in Figure 1. Composition formulas of these clusters were $AlSi_{47}O_{78}H_{37}$ and $AlSi_{40}O_{61}H_{43}$, respectively. The Si/Al_2 molar ratio of all cluster models was 18.5–23.5.

The structure of NH_3, H–Zeolite (H–Z), and NH_3–H–Z were optimized by generalized gradient approximation (GGA) level using Becke–Lee–Yang–Parr (BLYP) exchange and correlation functional. All calculations were performed using the double numerical with polarization (DNP) basis set. The convergence criteria (energy, force, and displacement) were set as 2×10^{-5} Ha, 4×10^{-3} Ha/Å, and 0.005 Å, respectively. The adsorption energy (E_{ads}) was calculated by following equation: $E_{ads} = E_{NH_4\text{–}Z} - (E_{H\text{–}Z} + E_{NH_3})$, where $E_{NH_4\text{–}Z}$, $E_{H\text{–}Z}$, and E_{NH_3} are total energy of each structure. E_{ads} from this equation is calculated as negative parameter.

Table 1 shows parameters of optimized structures of H–Z, E_{ads} of typical acid centers, and experimental parameters obtained by ammonia IRMS–TPD measurements.[1,2,12] Details of experimental method and TPD spectra of ammonia were shown in the Supporting Information. E_{ads} depended on the structural position of acid site, and those were in a range of 93 to 146 kJ/mol.

E_{ads} corresponds to ΔU, and this parameter is equal to $\Delta H - RT_m$, where ΔH is experimentally determined parameter, and R and T_m are gas constant ($8.314\,J\,K^{-1}\,mol^{-1}$) and peak maximum temperature of the TPD experiment, respectively.

For example, ΔU in the 12 MR of MOR was 140 kJ/mol, because ΔH was 145 kJ/mol. Figure 2 shows the correlation between the E_{ads} thus calculated and the ΔU experimentally measured. It is extremely interesting that an agreement between E_{ads} and ΔU was found in the various studied zeolites.

It should be aware that E_{ads} obtained by the quantum chemical calculation is influenced by a calculation method (size of cluster model and/or functional). For example, we reported that

Table 1. Adsorption energy of ammonia and geometry parameter for all calculated cluster models and experimental thermodynamics parameters obtained by ammonia IRMS–TPD measurements

	Acid site/position	Composition	DFT ∠Si(OH)Al /deg	DFT d(OH) /Å	DFT E_{ads} /kJ mol^{-1}	Ammonia IRMS–TPD ΔH /kJ mol^{-1}	Ammonia IRMS–TPD T_m /K	Ammonia IRMS–TPD ΔU /kJ mol^{-1}	ref
MFI	Al(11)–O(11)–Si(12)/straight 10MR	$AlSi_{37}O_{53}H_{47}$	137.4	0.984	129	137	563	132	12
	Al(7)–O(17)–Si(4)/sinusoidal 10MR	$AlSi_{40}O_{61}H_{43}$	136.6	0.981	146				
FER	Al(4)–O(6)–Si(4)/10MR	$AlSi_{43}O_{63}H_{51}$	140.4	0.985	134	142	623	137	12
	Al(3)–O(4)–Si(1)/ferrierite cage	$AlSi_{34}O_{51}H_{39}$	143.7	0.983	145	141	583	136	
MWW	Al(4)–O(3)–Si(1)/super cage	$AlSi_{37}O_{61}H_{31}$	134.4	0.979	133	140	583	135	12
MOR	Al(1)–O(3)–Si(2)/12MR	$AlSi_{48}O_{70}H_{57}$	129.7	0.980	133	145	603	140	1
	Al(2)–O(2)–Si(4)/12MR	$AlSi_{47}O_{72}H_{49}$	135.2	0.978	146				
	Al(4)–O(2)–Si(2)/12MR	$AlSi_{47}O_{72}H_{49}$	139.3	0.982	136				
	Al(3)–O(1)–Si(1)/8MR	$AlSi_{48}O_{70}H_{57}$	140.6	0.982	143	153	673	147	
BEA	Al(9)–O(12)–Si(4)/12MR	$AlSi_{43}O_{67}H_{43}$	130.6	0.979	133	129	533	125	12
	Al(1)–O(4)–Si(8)/6MR	$AlSi_{40}O_{64}H_{37}$	137.0	0.984	119				
FAU	Al(1)–O(1)–Si(1)/super cage	$AlSi_{47}O_{78}H_{37}$	130.4	0.976	100	108	443	104	2
	Al(1)–O(2)–Si(1)/sodalite cage	$AlSi_{47}O_{78}H_{37}$	139.0	0.981	110	119	523	115	
	Al(1)–O(3)–Si(1)/D6R	$AlSi_{47}O_{78}H_{37}$	132.2	0.981	93	105	433	101	

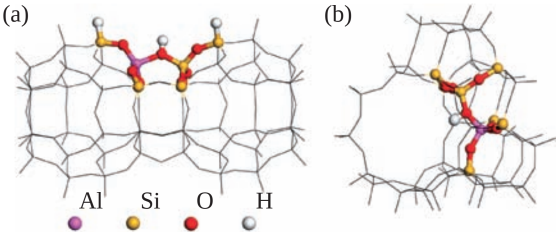

Figure 1. Embedded 8T clusters of (a) FAU/Al(1)–O(1)H–Si(1) ($AlSi_{47}O_{78}H_{37}$) and (b) MFI/Al(7)–O(17)H–Si(4) ($AlSi_{40}O_{61}H_{43}$).

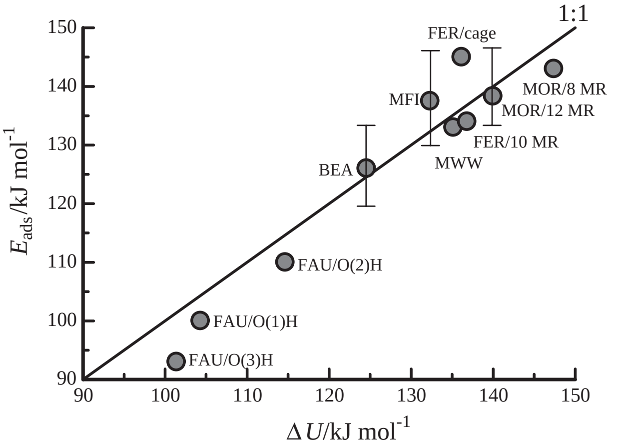

Figure 2. Correlation between ΔU and E_{ads}.

E_{ads} of acid sites of 12 MR in MOR was 213–220 kJ/mol (from periodic calculation using LDA[1]), whereas these were reported 142.2–147.9 kJ/mol (from periodic cluster calculation using GGA[10]) and 119 kJ/mol (from embedded cluster calculation[11]), respectively. Therefore, the embedded 8T cluster models using GGA approximation is a good method to show accurate values for ammonia adsorption energies on zeolite structures.

In conclusion, the E_{ads}'s calculated by DFT were in good agreement with ΔU of ammonia adsorption on acid sites in various H-form zeolites. This agreement indicates that both methods provide us the acid strength of the zeolite correctly. Therefore, Brønsted acidity, i.e., number, strength, and structure, will be studied more profoundly by combining these advantages of the experiment and the theory.

The relationship between the Brønsted acidity and the crystal structure will be discussed in a forthcoming study. Advantage of the embedded 8T cluster method for the Brønsted acidity also will be studied furthermore.

This present work is supported by the Grant-in-Aid for Scientific Research (A) (No. 18206082) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 M. Niwa, K. Suzuki, N. Katada, T. Kanougi, T. Atoguchi, *J. Phys. Chem. B* **2005**, *109*, 18749.
2 K. Suzuki, N. Katada, M. Niwa, *J. Phys. Chem. C* **2007**, *111*, 894.
3 C. Lo, B. L. Trout, *J. Catal.* **2004**, *227*, 77.
4 J. Lomratsiri, M. Probst, J. Limtrakul, *J. Mol. Graphics Modell.* **2006**, *25*, 219.
5 A. Simperler, R. G. Bell, M. D. Foster, A. E. Gray, D. W. Lewis, M. W. Anderson, *J. Phys. Chem. B* **2004**, *108*, 7152.
6 A. Martucci, A. Alberti, G. Cruciani, P. Radaelli, P. Ciambelli, M. Rapacciulo, *Microporous Mesoporous Mater.* **1999**, *30*, 95.
7 D. Zhou, Y. Bao, M. Yang, N. He, G. Yang, *J. Mol. Catal. A: Chem.* **2006**, *244*, 11.
8 G. Sastre, V. Fornes, A. Corma, *J. Phys. Chem. B* **2000**, *104*, 4349.
9 H. Fujita, T. Kanougi, T. Atoguchi, *Appl. Catal. A: Gen.* **2006**, *313*, 160.
10 M. Elanany, D. P. Vercauteren, M. Koyama, M. Kubo, P. Selvam, E. Broclawik, A. Miyamoto, *J. Mol. Catal. A: Chem.* **2006**, *243*, 1.
11 M. Brändle, J. Sauer, *J. Am. Chem. Soc.* **1998**, *120*, 1556.
12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 14, 2007; doi:10.1246/cl.2007.1034