

Supporting Information

Periodic Density Functional Calculation on Brønsted Acidity of Modified Y-type Zeolite

Katsuki Suzuki^{1,2}, Takayuki Noda¹, German Sastre³, Naonobu Katada¹ and Miki Niwa^{1*}

¹Department of Chemistry and Biotechnology, Graduate School of Engineering, Tottori University, 4-101 Koyama-cho Minami, Tottori 680-8552 Japan: ²Japan Society for the Promotion of Science (JSPS), Chiyoda-ku, Tokyo 102-8471 Japan: ³Instituto de Tecnología Química U. P. V. – C. S. I. C. Universidad Politécnica de Valencia, Avenida Los Naranjos s/n, 46022 Valencia Spain.

Corresponding author footnote. Miki Niwa, Telephone and fax number, +81-857-31-5256 and e-mail address, mikiniwa@chem.tottori-u.ac.jp

Materials

A series of cation-exchanged Y zeolites were prepared as reported.¹ Na-Y (Si/Al₂ = 5.6, Catalysts & Chemicals Industries Co. Ltd.) was ion-exchanged into NH₄-Y in an aqueous NH₄NO₃ solution, filtered, washed with deionized water and dried at 373 K. The thus prepared NH₄-Y was further exchanged in Ba(NO₃)₂, Ca(NO₃)₂ solution at 353 K for 4 h to prepare an MNH₄-Y (M = Ba or Ca) zeolite. On the other hand, the NH₄-Y was steamed at 823 K for 1 h in a flow of water vapor and nitrogen mixture (H₂O : N₂ molar ratio = 2 : 3). The thus obtained USY was stirred in an Na₂H₂-EDTA solution (0.1 mol dm⁻³) for 24 h at 371 K, followed by ion exchange in NH₄NO₃ solution and drying at 373 K according to Rhodes *et al.*², Gola *et al.*³ and our previous papers.⁴

Ammonia IRMS-TPD measurement

IR (Perkin-Elmer Spectrum-One with a mercury cadmium telluride (MCT) detector kept at 77 K by liquid N₂ during measurements) and MS (Pfeifer QME200) spectrometers were connected with a vacuum line. Self-compressed zeolite wafer (about 10 mg and 10 mm in diameter) was mounted on a holder in an *in situ* IR cell, and evacuated at 773 K for 1 h. IR spectra were recorded before and after ammonia adsorption during the elevation of temperature from 373 to 773 K at a ramp rate of 10 K min⁻¹. Flow rate of helium carrier gas was 82 μmol s⁻¹, the inside of IR cell was kept 25 Torr (1 Torr = 133 Pa), and desorbed ammonia was monitored by MS based on a signal at m/e = 16. After the measurements, the difference IR spectra were calculated, and the differential change of the IR band area with respect to measurement temperature (hereafter called IR-TPD) was compared with

MS-TPD (conventional TPD) to quantify the ammonia species adsorbed on Brønsted or Lewis acid site. It has been known that the wave number of acidic OH band on zeolites shifts to lower frequency with increasing the temperature.⁵ This temperature effect on frequency of OH band (ν_{OH}) is estimated as $\Delta\nu/\Delta T = -0.03$ to $0.052 \text{ cm}^{-1}\text{K}^{-1}$ where $\Delta\nu$ is the shift of ν_{OH} and ΔT is the difference of temperature. Difference spectra of ammonia in the OH stretching region were corrected using this equation. Heat of ammonia adsorption (ΔH) as a parameter to show the strength of the acid site was determined based on the theoretical equation of TPD.⁶

Difference IR spectra during TPD of ammonia in OH stretching region

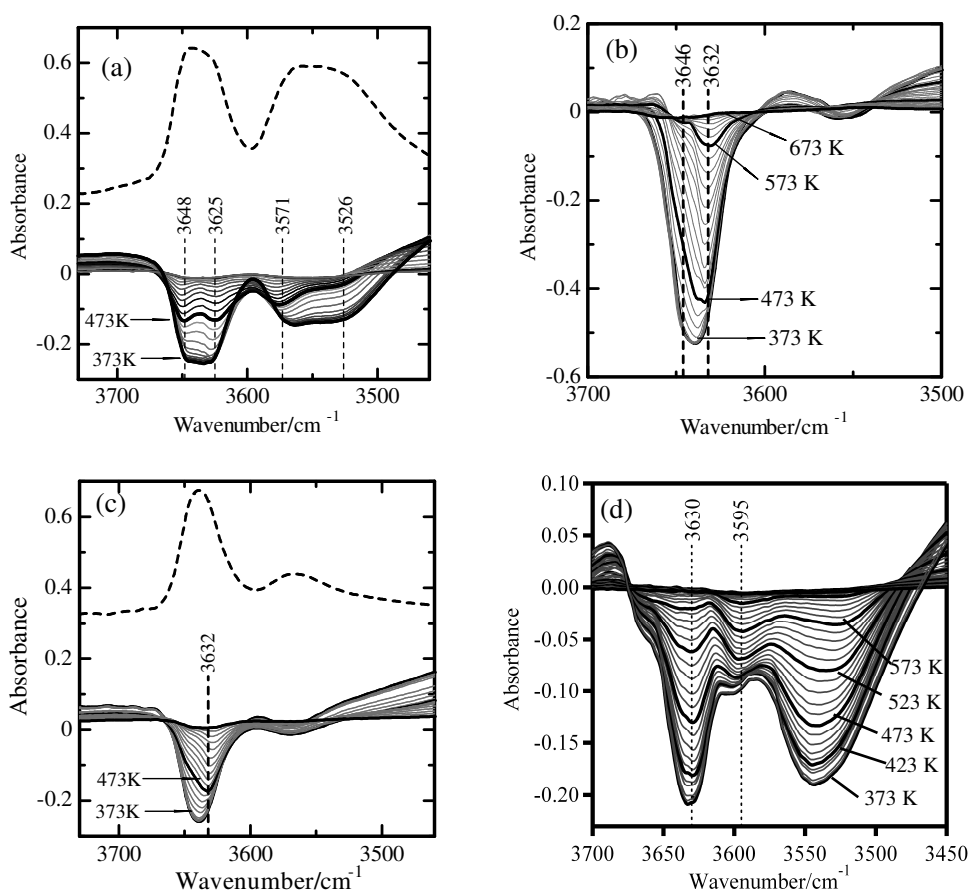


Figure S1. Difference IR spectra during TPD of ammonia on $\text{Na}_2\text{H}_2\text{-EDTA}$ treated USY^7 (a), *in situ* prepared H-Y^8 (b), *in situ* prepared $37\%\text{CaHY}^5$ (c), and *in situ* prepared $35\%\text{BaHY}^1$ (d).

Optimized geometries and energetic parameters of four kinds of nonequivalent SiO(H)Al groups obtained from HCTH/DNP (this work), PW91/PAW⁹ and VWN/DNP¹⁰ periodic DFT calculations are summarized in Table S1. Relative energies of SiO(H)Al groups obtained from HCTH/DNP calculations were in agreement with the values obtained from the other two computational conditions. The T-O bond lengths obtained from HCTH/DNP calculations were slightly longer than those of VWN/DNP calculations. On the other hand, the O-H bond lengths were slightly shorter than those of VWN/DNP calculations. The optimized geometries were slightly different depending on the computational conditions (GGA or LDA approximations); however, the optimized geometries of the H-form FAU in the present calculations is in reasonable agreement with reported geometries.

Table S1. Optimized geometries of isolated SiO(H)Al groups (HAlSi₄₇O₉₆/ u.c.).

	Acid site	E_{rel} / kJ mol ⁻¹	d(AlO) / Å	d(SiO) / Å	d(OH) / Å	d(AlH) / Å	□Si(O)HAl /deg.
HCTH/DNP	1	0	1.927	1.711	0.965	2.484	129.8
	2	8.3	1.934	1.708	0.966	2.431	136.6
	3	1.6	1.972	1.718	0.965	2.495	133.5
	4	6.7	1.918	1.703	0.965	2.455	132.1
PW91/PAW ^a	1	0	1.916	1.716	0.975	2.484	129.0
	2	9.6	1.903	1.710	0.977	2.392	137.7
	3	4.5	1.942	1.711	0.975	2.460	134.5
	4	8.9	1.907	1.712	0.977	2.443	132.5
VWN/DNP ^b	1	0	1.909	1.705	0.980	2.490	128.7
	2	10.8	1.905	1.699	0.985	2.372	140.4
	3	3.4	1.921	1.705	0.984	2.421	136.1
	4	8.6	1.906	1.701	0.982	2.436	134.2

^{a)} Optimized geometries for nonequivalent bridged OH groups (O1-O4) in ref. 9.

^{b)} in ref. 10.

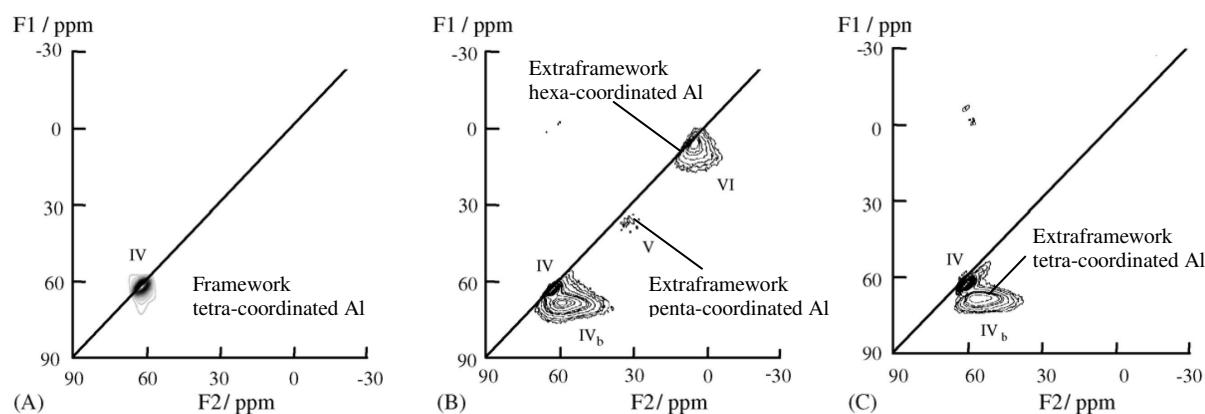


Figure S2. ^{27}Al MQMAS NMR spectra (16T) of NaY (A), USY (B) and Na₂H₂-EDTA treated USY (C). Reproduced from ref. 11.

References

- S1. Noda, T.; Suzuki, K.; Katada, N.; Niwa, M. *J. Catal.* **2008**, *259*, 203-210.
- S2. Rhodes, N. P.; Rudham, R. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2551-2557.
- S3. Gola, A.; Rebours, B.; Milazzo, E.; Lynch, J.; Benazzi, E.; Lacombe, S.; Delevoye, L.; Fernandez, C. *Microp. Mesop. Mater.* **2000**, *40*, 73-83.
- S4. Katada, N.; Kageyama, Y.; Takahara, T.; Kanai, T.; Begum, H. A.; Niwa, M. *J. Mol. Catal., A: Chem.* **2004**, *211*, 119-130.
- S5. Suzuki, K.; Noda, T.; Katada, N.; Niwa, M. *J. Catal.* **2007**, *250*, 151-160.
- S6. Niwa, M.; Katada, N.; Sawa, M.; Murakami, Y. *J. Phys. Chem.* **1995**, *99*, 8812-8816.
- S7. Niwa, M.; Suzuki, K.; Isamoto, K.; Katada, N. *J. Phys. Chem. B* **2006**, *110*, 264-269.
- S8. Suzuki, K.; Niwa, M.; Katada, N. *J. Phys. Chem. C* **2007**, *111*, 894-900.
- S9. Sastre, G.; Katada, N.; Suzuki, K.; Niwa, M. *J. Phys. Chem. C* **2008**, *112*, 19293-19301.
- S10. Hill, J. -R.; Freeman, C. M.; Delley, B. *J. Phys. Chem. A* **1999**, *103*, 3772-3777.
- S11. Katada, N.; Nakata, S.; Kato, S.; Kanehashi, K.; Saito, K.; Niwa, M. *J. Mol. Catal. A: Chem.* **2005**, *236*, 239-245.