Electronic Supporting Information

Probing atomic positions of adsorbed ammonia molecules in zeolite†

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1 Experiment Section

1.1 H-ZSM-5pretreatment

H-ZSM-5 (Al:Si=1:19.25) was supplied from Sinopec, China. The elemental analysis of the solid samples was performed using inductively coupled plasma apparatus (P-4010/ICP-AES). It was calcined in air at 480 °C for 2 h with ramp rate of 1 °C min^{-1} before use.

1.2 Ammonia adsorption

H-ZSM-5 was repeatedly heated to 300 °C for 2 hours in vacuum in a 0.7 mm borosilicate capillary pre-attached to a gas cell in order to trace moisture before ammonia adsorption. The sample was then exposed to ammonia vapour in the same gas cell for 30 minutes at room temperature. The capillary was then cut and sealed for Synchrotron PXRD measurements.

2 Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM) of H-ZSM-5

TEM was recorded on a FEI TECNAI-20 instrument with accelerating voltage of 200 kV. TEM specimen was prepared by dispersing the powder in alcohol by ultrasonic treatment and then dropped onto a holey carbon film on a copper grid, and then dried in air.

After coating with a thin layer of gold, the morphologies of the prepared samples were observed using a Philips XL30 FEG SEM equipped with an EDAX energy dispersive X-ray spectrometer (EDS) (Oxford ISIS-Energy).

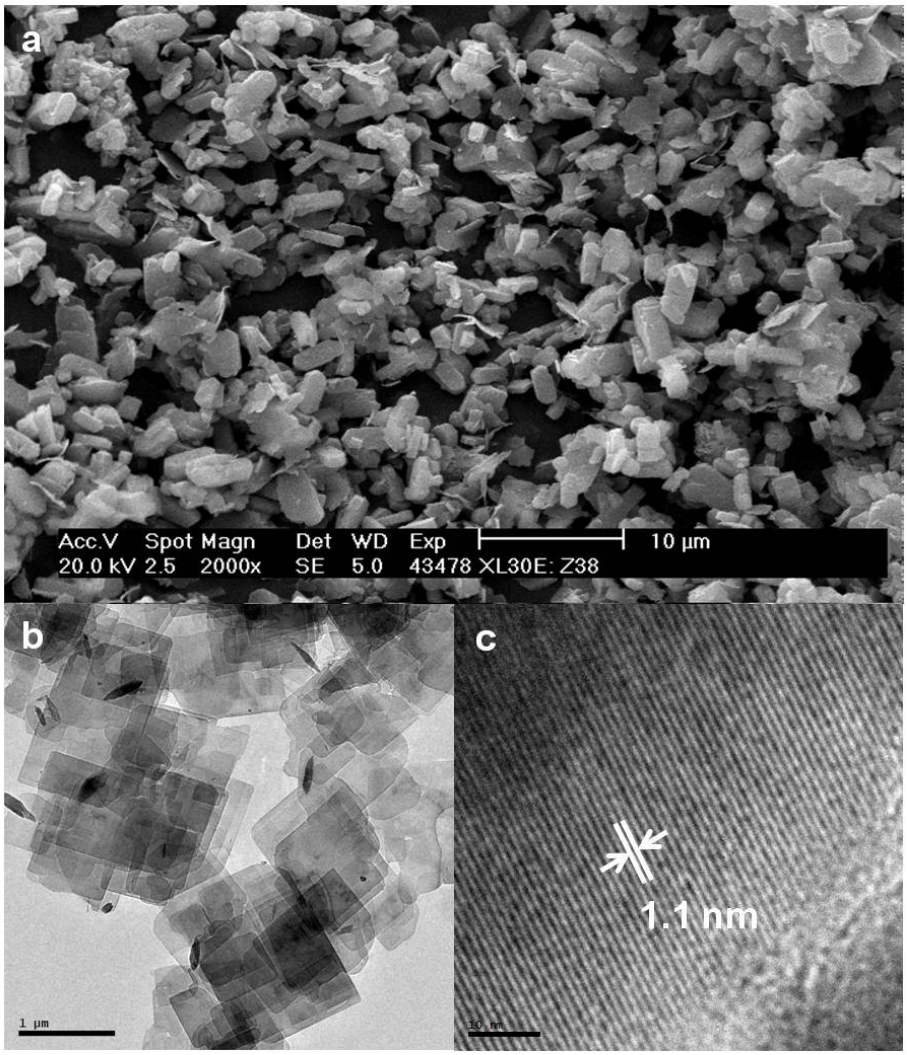


Figure S1. SEM and TEM images of H-ZSM-5. **a**, SEM image shows the particle size of H-ZSM-5 is around 2 µm. Scale bar is 10 µm. **b**, TEM image shows the uniform morphology of H-ZSM-5. Scale bar is 1 µm and **c**, HRTEM of H-ZSM-5. Scale bar is 10 nm.

3 N_2 adsorption and desorption isotherms of H-ZSM-5

N_2 adsorption and desorption isotherms were obtained at 77 K on a Micromeritics Tristar-3000 apparatus. H-ZSM-5 was pretreated under vacuum at 350 °C for 4 h. The specific surface area was calculated using the BET method. The N_2 adsorption and desorption isotherms indicated the typical structure of microporous.

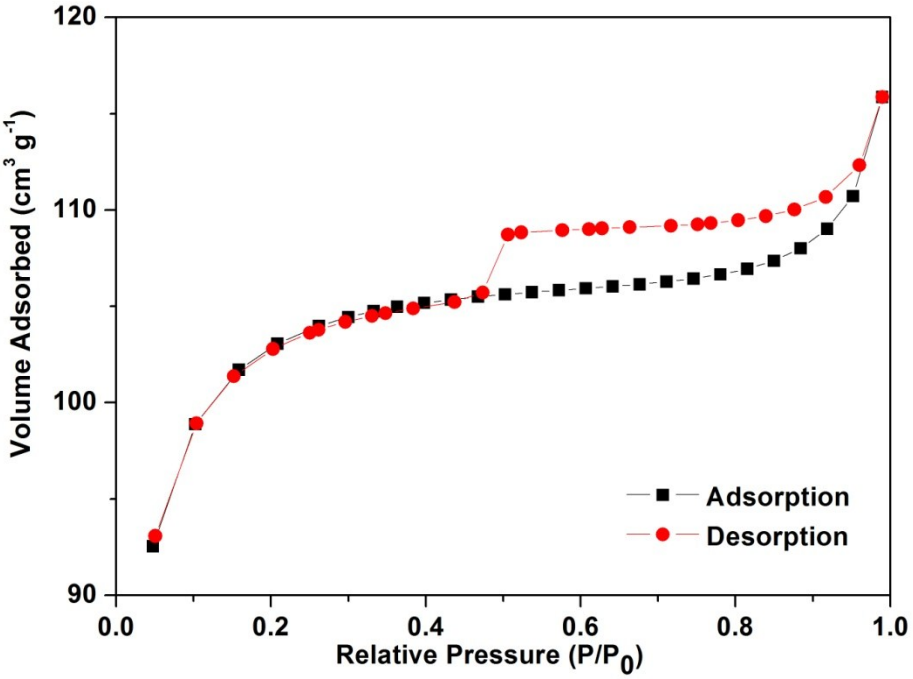


Figure S2. N_2 adsorption and desorption isotherms of H-ZSM-5.

4 Solid state NMR

According to the difference electron density between six and four coordinate Al, ^{27}Al MAS NMR was used to detect the coordination of Al in H-ZSM-5[1]. For the ^{27}Al MAS NMR measurement, the ^{27}Al MAS NMR spectrum was obtained using a 400WB AVANCE III spectrometer, at the Larmor frequency of 104.34 MHz. The one pulse sequence was adopted, with a 10° pulse, a delay time of 0.4 s and a scanning number of 8000. The chemical shift was referenced to 1M $AlCl_3$ aqueous solution. Based on the ^{27}Al MAS NMR spectrum, there are 4.48 Al in the framework of H-ZSM-5. Then the formula of H-ZSM-5 could be written as $H_{4.48}Al_{4.48}Si_{91.52}O_{192}$. Assuming all the four coordinate framework aluminum atoms are exposed on the inner surface, the amount of Brønsted acid sites is calculated to be 0.78 mmol g^{-1}.

Moreover, the acidic properties of solid state catalysts (H-ZSM-5) were characterized through ^{31}P MAS NMR, based on their chemical shift values. For the ^{31}P MAS NMR measurement, the sample was introduced into a glass tube, which was then connected to a vacuum system. The pretreatment was carried out at 573 K for 2 h under vacuum (10^{-1} Pa). After adsorption of gaseous trimethylphosphine (TMP) at room temperature and removal of weakly adsorbed TMP molecules by a brief evacuation (30 min), the glass tube was then isolated and immersed in liquid nitrogen. Then the content of the glass tube was transferred to a glove box. Under dry nitrogen, the sample was packed into a 4 mm ZrO_2 rotor and closed with Kel-F lids. All NMR experiments were performed on 400WB AVANCE III spectrometer at room temperature. ^{31}P high powered decoupling (HPEDC) MAS NMR spectra were acquired at resonance frequency of 161.9 MHz, using 30° pulses with a recycle delay of 15 s at a MAS speed of 12 kHz. $NH_4H_2PO_4$ was used as a standard sample for chemical shift reference and the external intensity standard to quantify the signal in ^{31}P MAS NMR spectra. The error between the amount of Brønsted acid sites that calculated from ^{27}Al MAS NMR measurement and ^{31}P MAS NMR measurement can be explained by the systemic errors in measured peak area and sample weight.

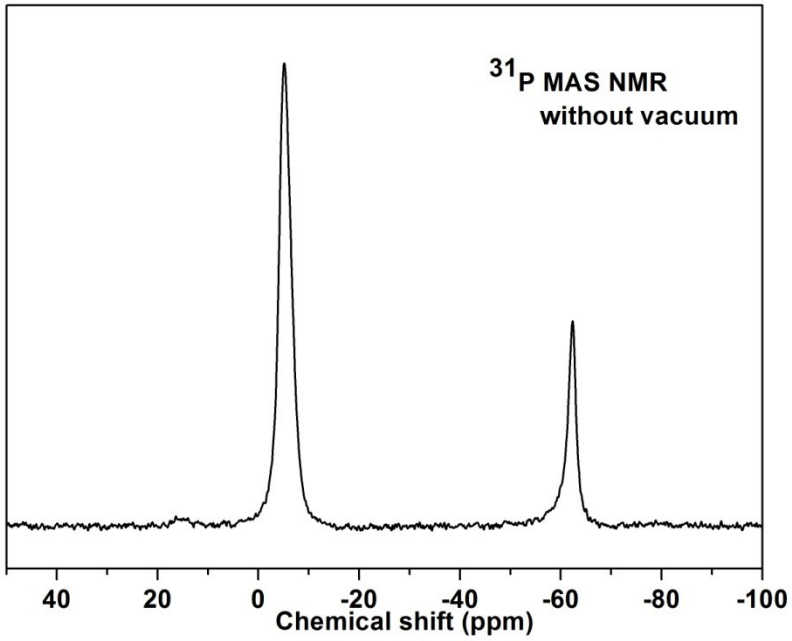


Figure S3. Solid state ^{31}P MAS NMR spectrum of TMP adsorbed H-ZSM-5 without vacuum.

The peak at -5 ppm belonged to the interaction between TMP and the Brønsted acid sites. Another asymmetric peak with lower intensity around -61 ppm was arisen from a very weak interaction between TMP and the Lewis acid sites of non-framework aluminum, and the extra physisorbed TMP [1].

5 Synchrotron PXRD and Rietveld refinement before and after ammonia adsorbed H-ZSM-5.

High resolution Synchrotron PXRD data were collected on Beamline I11, Diamond Light Source, UK. Detailed description of the beamline can be found elsewhere[2]. The energy of the incident X-ray beam was set at 15 keV. The wavelength and the 2θ-zero point correction were refined using a diffraction pattern obtained from a high quality silicon powder (SRM640c). For room temperature, the fine zeolite powder was loaded in a 0.7 mm borosilicate glass capillary. As for *in situ* work, sample was loaded in a capillary gas cell developed by Parker et al[3]. The delivery of NH_3 was provided by a gas panel and the control of temperature was by a Cyberstar hot air blower (RT-1000°C). High resolution PXRD data were obtained from the samples using the multi-analyser crystal (MAC) detectors. The patterns were collected in the 2θ range 0-150 ° with 0.001° data binning. Each pattern was collected for an hour for good statistics. In total, there were more than 4000 *hkl* reflections measured, of which at least 300 independent *hkl* reflections were observed. In a crystallographic point of view, the number of structural variables should not exceed the number of *hkl* reflections in a refinement. In the Rietveld refinements performed in this work, the number of structural parameters has not exceeded 150.

Using the TOPAS software, the diffraction patterns were analysed by Rietveld refinement methods to obtain structural details. The starting coordinates were based on the H-ZSM-5 model by Heo et al. for structural refinement[4]. The Thompson-Cox-Hastings pseudo-Voigt peak function[5] was applied to described the diffraction peaks. The scale factor and lattice parameters were allowed to refine for all the diffraction patterns. The refined structural parameters for pattern were the fractional coordinates (x, y, z) and isotropic displacement factors (B_{eq}) for all atoms, and the site occupancy factors (SOF), translation and rotation axes for the rigid body Z-matrices describing the adsorbed ammonia molecules within the H-ZSM-5 framework. The quality of the Rietveld refinements of synchrotron PXRD data has been assured with a low goodness-of-fit (Gof) factor, a low weighted profile factor (R_{wp}) and a well fitted pattern with acceptable temperature factor (B_{eq}) within experimental errors. During the refinement, all the T-sites (T=Al, Si) of ZSM-5 were set to share the same value of SOF and B_{eq}. All the O-sites of ZSM-5 were set to share the same value SOF and B_{eq}. All the SOFs of the N-sites of ammonia were constrained in 1, which means that the maximum possibility of ammonia molecule in one position is 100%. The values for the H-sites of ammonia were set to share the same SOF and 1.2 times of the B_{eq} for the coordinated N-sites. The B_{eq} of N2 and N3 was set to be 1.3 times of N1, N4 was 1.5 times of N1. The crystallographic data and refinement details are summarised in Tables S2-5 and Tables S11-16 in the Supplementary Information.

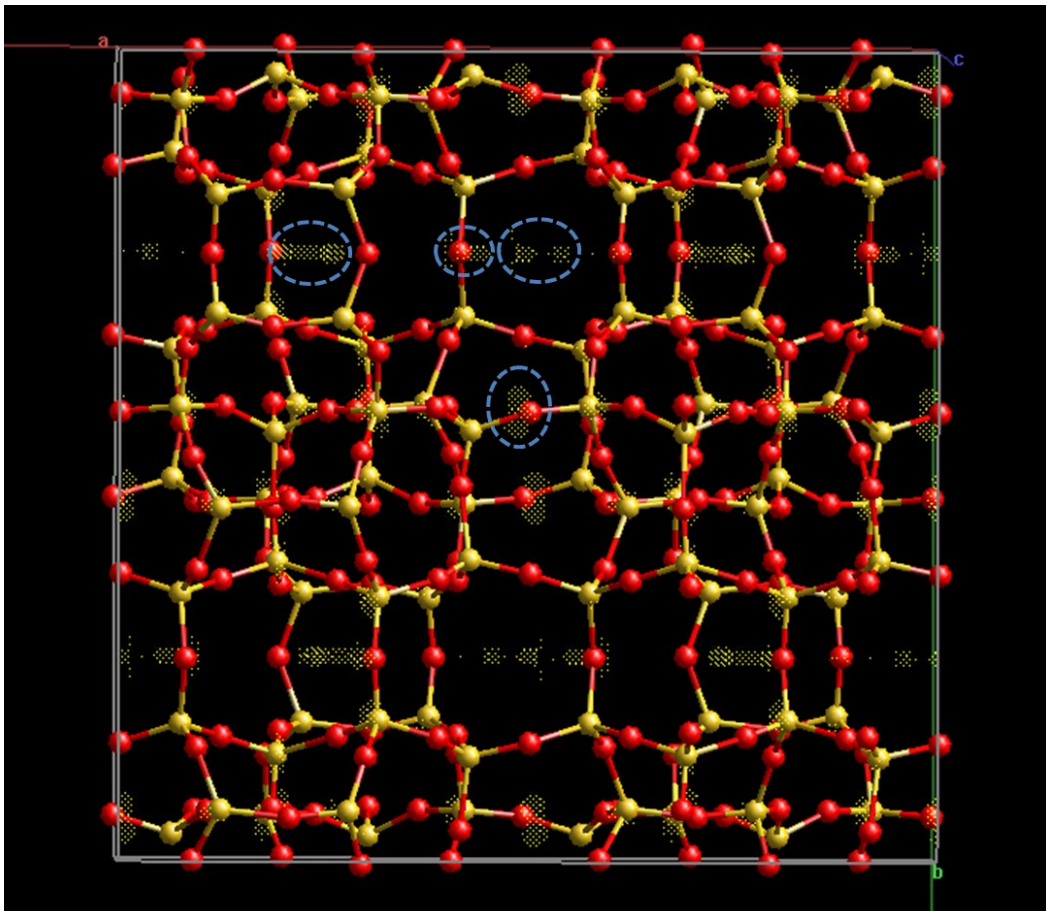


Figure S4. A Fourier map of ammonia molecules pre-adsorbed on H-ZSM-5 at room temperature; the blue circles represent the 4 ammonia positions.

Table S1. The electron contrast between ammonia adsorbed H-ZSM-5 and H-ZSM-5.

	Rho	x	y	z
1	2.873	0.2007	0.2500	0.9004
2	2.295	0.0588	0.7500	0.0710
3	2.232	0.0711	0.2500	0.8395
4	2.212	0.0147	0.0499	0.4483
5	1.791	0.2031	0.1634	0.4005
6	1.707	0.1007	0.0435	0.9859
7	1.658	0.1212	0.5445	0.2522
8	1.573	0.0978	0.1325	0.0743
9	1.566	0.0269	0.2500	0.7117
10	1.496	0.0715	0.6077	0.1082

Rho relatives to the electron density.

Refinement Procedure:

The file containing synchrotron PXRD data of ammonia filled H-ZSM-5 was first analysed by GSAS software, using the crystallographic information file from Heo et al[4] with wavelength 0.826617 Å and zero point 0.000254°. The background, scale and cell parameters were provisionally refined (a = 20.104097, b = 19.935268, c = 13.427592) to give a resulting Fourier map which was obtained using a step size of 0.2 Å. Owing to the porous structure of H-ZSM-5, ammonia molecules were expected to take residence in the voids of this solid structure. Since the dynamic size of ammonia molecule is 2.5 Å and the dimension of the H-ZSM-5 channel is 5.5 Å, 4 ammonia positions (1, 3, 4 and 9) were identified in the channel of H-ZSM-5 (Table S1, Fig. S4). Other positions were too close to the framework of H-ZSM-5 to be genuine ammonia species, which were arisen due to the distortion/displacement of the framework atoms.

Le Bail and Rietveld refinements of H-ZSM-5 with and without ammonia are presented in supplementary Section S5 and Table S2. Full cifs in table format and detailed profile fit plots with enlarged ranges are also given in supplementary Section S5 and Section S8.

According to our refinement procedure, ammonia molecule was added into H-ZSM-5 one by one (N1, N2, N3, N4…). Fitting factors (R_{wp} / R_p / R_{exp} / $\chi 2$) were used to gauge the quality of refinement. With the progressive increase in the number of ammonia molecules, the R-factors were found decreasing, which indicates the use of higher number of ammonia is approaching to the real structure (Table S2). It was until the fifth ammonia, the R-factor was almost remained unchanged. However, the pseudo 'fifth' ammonia appeared at the position very close to N3 (within 1.0 Å) which shared the site occupancy of N3. As mentioned above, 4 ammonia positions were actually derived from the Fourier maps with the dynamic diameter of ammonia to be 2.5 Å. Thus, we excluded the ammonia N5 to be a genuine position, which was possibly arisen owing to distortion/displacement of N3 due to thermal motion, etc. As a result, 4 ammonia molecules were used to fitting all the synchrotron PXRD data accordingly.

Table S2. R-factors of H-ZSM-5 samples before and after ammonia adsorbed by Le Bail and Rietveld method.

Samples	Le Bail R_{wp} / R_p / R_{exp} / $\chi 2$	Rietveld R_{wp} / R_p / R_{exp} / $\chi 2$
H-ZSM-5	6.621/5.077/4.958/1.335	8.045/6.343/4.953/1.624
H-ZSM-5· 1NH_3 RT	7.634/5.618/3.271/2.333	13.541/10.784/3.441/3.935
H-ZSM-5· 2NH_3 RT	7.634/5.618/3.271/2.333	12.775/10.190/3.441/3.713
H-ZSM-5· 3NH_3 RT	7.634/5.618/3.271/2.333	10.984/8.709/3.441/3.192
H-ZSM-5· 4NH_3 RT	7.634/5.618/3.271/2.333	9.655/7.499/3.440/2.806
H-ZSM-5· 5NH_3 RT	7.634/5.618/3.271/2.333	9.648/7.529/3.440/2.804

The number (before NH_3) in the sample name column means the number of ammonia positions that have been used.
The fitting factors from Le Bail fit are optimized without any constraint of structure model in contrast to Rietveld-fit, hence accounting for their smaller values.

Table S3. Crystallographic data and details of the H-ZSM-5 samples before and after ammonia adsorbed.

Samples	H-ZSM-5	Ammonia adsorbed H-ZSM-5
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*
Chemical formula	$H_{4.74}Al_{4.74}Si_{91.26}O_{192}$	$H_{4.74}Al_{4.74}Si_{91.26}O_{192} \cdot 18NH_3$
2θ range refinement (°)	3 - 55	3 - 55
Detector	Multi-analyser crystals	Multi-analyser crystals
Number of parameters	139	149
Number of hkls	4191	4169
Refinement methods	Rietveld	Rietveld
a (Å)	20.13636(4)	20.11334(4)
b (Å)	19.95884(4)	19.94432(4)
c (Å)	13.43718(3)	13.43223(3)
V (Å^3)	5400.383(19)	5388.302(20)
R_{wp} / R_p / R_{exp} (%)	8.045/6.343/4.953	9.655/7.499/3.440
Wavelength (Å)	0.825634(2)	0.826617(4)
2θ Zero point (°)	- 0.002500(3)	0.000254(3)
Gof $\chi 2$	1.624	2.806

$H_{4.74}Al_{4.74}Si_{91.26}O_{192} \cdot 18NH_3$ means there are 18 ammonia molecules per unit cell of the H-ZSM-5.

5.1 The Rietveld refinement and details of ammonia-free and ammonia adsorbed H-ZSM-5 at room temperature.

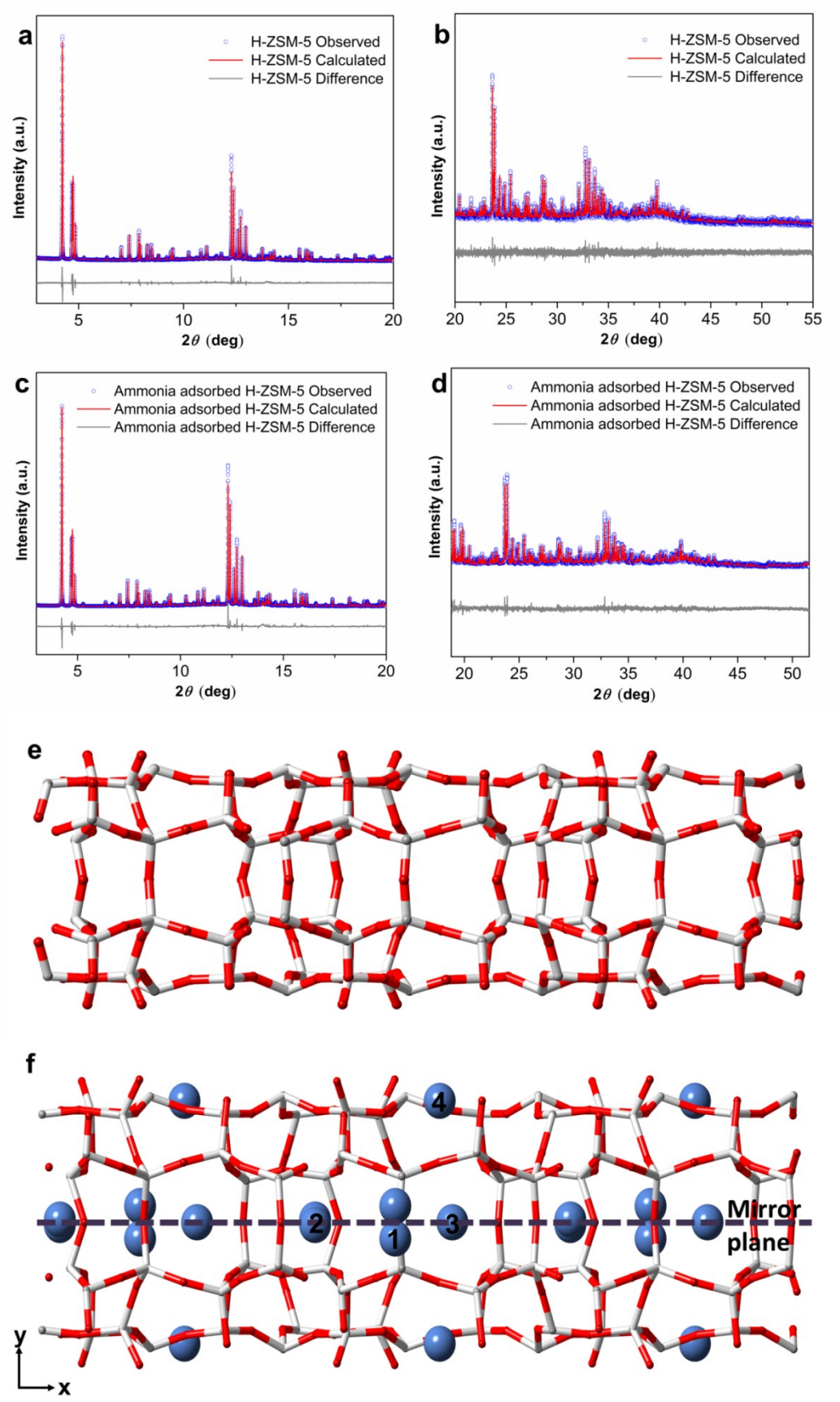


Figure S5. Synchrotron PXRD refinement and the structure of H-ZSM-5 and ammonia adsorbed H-ZSM-5 at room temperature. Comparison of the experiment data (blue circle) and Rietveld refinement (red line) and the difference between them (grey line) for synchrotron PXRD patterns (a) before ammonia adsorbed H-ZSM-5 at room temperature range from 3 ~ 20°, (b) range from 3 ~ 55°. (c) After ammonia adsorbed H-ZSM-5 at room

temperature range from 3 ~ 20°, (d) range from 3 ~ 55°. The refined structure of before (e) and after (f) ammonia adsorbed H-ZSM-5 (viewed from z-axis). The framework of H-ZSM-5 is using the stick mode, red stick is O and grey stick is Si. The N of NH_3 is blue ball. The symmetric ammonia N-sites between mirror plane are illustrated. (dark grape dot line).

Table S4. Crystallographic information files from the Rietveld refinement of H-ZSM-5 at room temperature.

Species	Atom	*x*	*y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37757(55)	0.05862(78)	0.75307(71)	1	2.120(42)	8d
	O2	0.30556(67)	0.06097(56)	0.92349(71)	1	2.120(42)	8d
	O3	0.20414(50)	0.05533(59)	0.02567(54)	1	2.120(42)	8d
	O4	0.09531(50)	0.06501(58)	0.91389(78)	1	2.120(42)	8d
	O5	0.12132(55)	0.05524(77)	0.73035(71)	1	2.120(42)	8d
	O6	0.24917(52)	0.05586(86)	0.75503(74)	1	2.120(42)	8d
	O7	0.37103(57)	0.84182(57)	0.77139(73)	1	2.120(42)	8d
	O8	0.30680(72)	0.84622(45)	0.92436(72)	1	2.120(42)	8d
	O9	0.18966(58)	0.83908(40)	0.02996(59)	1	2.120(42)	8d
	O10	0.09336(57)	0.84283(52)	0.92226(87)	1	2.120(42)	8d
	O11	0.11023(58)	0.85036(55)	0.75493(72)	1	2.120(42)	8d
	O12	0.23740(52)	0.84657(56)	0.73886(76)	1	2.120(42)	8d
	O13	0.30915(59)	0.94191(50)	0.81841(54)	1	2.120(42)	8d
	O14	0.07653(46)	0.95782(56)	0.82133(67)	1	2.120(42)	8d
	O15	0.41696(57)	0.12334(55)	0.61718(85)	1	2.120(42)	8d
	O16	0.40430(59)	0.99566(54)	0.58554(82)	1	2.120(42)	8d
	O17	0.40448(63)	0.86160(52)	0.56403(82)	1	2.120(42)	8d
	O18	0.18845(70)	0.13345(49)	0.61659(73)	1	2.120(42)	8d
	O19	0.20172(73)	0.00425(51)	0.60632(73)	1	2.120(42)	8d
	O20	0.20248(79)	0.87324(50)	0.57508(74)	1	2.120(42)	8d
	O21	0.99880(55)	0.05258(77)	0.79710(68)	1	2.120(42)	8d
	O22	0.99186(56)	0.84965(60)	0.79639(73)	1	2.120(42)	8d
	O23	0.41871(84)	0.75	0.64062(08)	1	2.120(42)	4c
	O24	0.19282(106)	0.75	0.64730(94)	1	2.120(42)	4c
	O25	0.28988(89)	0.75	0.07010(104)	1	2.120(42)	4c
	O26	0.10102(82)	0.75	0.08102(111)	1	2.120(42)	4c
	Si1	0.42397(31)	0.05522(40)	0.66598(47)	1	1.323(22)	8d
	Si2	0.31051(39)	0.03073(26)	0.81382(49)	1	1.323(22)	8d
	Si3	0.27963(27)	0.06024(37)	0.03550(45)	1	1.323(22)	8d
	Si4	0.12022(29)	0.06094(38)	0.02894(47)	1	1.323(22)	8d
	Si5	0.07061(31)	0.03104(30)	0.81345(52)	1	1.323(22)	8d
	Si6	0.18976(35)	0.05776(34)	0.67650(43)	1	1.323(22)	8d
	Si7	0.42394(32)	0.82882(32)	0.67498(54)	1	1.323(22)	8d
	Si8	0.30705(39)	0.86969(29)	0.81726(44)	1	1.323(22)	8d
	Si9	0.27479(30)	0.82838(29)	0.03230(51)	1	1.323(22)	8d
	Si10	0.11939(33)	0.82277(31)	0.03025(54)	1	1.323(22)	8d
	Si11	0.07124(32)	0.87098(34)	0.82122(52)	1	1.323(22)	8d
	Si12	0.18486(35)	0.82600(27)	0.68190(51)	1	1.323(22)	8d

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

Table S5. Crystallographic information files from the Rietveld refinement of ammonia adsorbed H-ZSM-5 at room temperature.

Species	Atom	*x*	*y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37106(48)	0.06090(56)	0.74470(59)	1	1.877(36)	8d
	O2	0.31000(46)	0.06347(43)	0.91358(59)	1	1.877(36)	8d
	O3	0.20862(39)	0.05412(49)	0.02069(50)	1	1.877(36)	8d
	O4	0.09804(38)	0.05954(50)	0.91695(64)	1	1.877(36)	8d
	O5	0.11306(46)	0.05958(53)	0.72027(56)	1	1.877(36)	8d
	O6	0.24425(42)	0.05515(59)	0.76389(57)	1	1.877(36)	8d
	O7	0.37373(50)	0.84657(46)	0.76543(61)	1	1.877(36)	8d
	O8	0.30159(51)	0.84015(39)	0.93420(57)	1	1.877(36)	8d
	O9	0.18744(48)	0.84026(36)	0.02999(54)	1	1.877(36)	8d
	O10	0.08503(46)	0.84543(44)	0.90458(70)	1	1.877(36)	8d
	O11	0.10906(49)	0.84794(46)	0.74325(65)	1	1.877(36)	8d
	O12	0.23246(45)	0.84591(44)	0.73573(60)	1	1.877(36)	8d
	O13	0.31036(46)	0.93561(38)	0.82142(50)	1	1.877(36)	8d
	O14	0.08096(39)	0.96190(41)	0.82020(61)	1	1.877(36)	8d
	O15	0.41725(45)	0.13254(47)	0.62589(65)	1	1.877(36)	8d
	O16	0.40971(48)	0.99862(45)	0.57365(71)	1	1.877(36)	8d
	O17	0.40470(45)	0.85947(44)	0.57875(74)	1	1.877(36)	8d
	O18	0.18366(48)	0.12940(43)	0.61252(58)	1	1.877(36)	8d
	O19	0.20337(55)	0.00425(44)	0.59728(61)	1	1.877(36)	8d
	O20	0.19781(56)	0.87059(45)	0.58130(58)	1	1.877(36)	8d
	O21	0.99735(45)	0.05377(59)	0.79390(62)	1	1.877(36)	8d
	O22	0.99647(48)	0.85442(54)	0.78290(63)	1	1.877(36)	8d
	O23	0.41803(63)	0.7500	0.61083(91)	1	1.877(36)	4c
	O24	0.18734(74)	0.7500	0.66036(81)	1	1.877(36)	4c
	O25	0.30194(76)	0.7500	0.05113(79)	1	1.877(36)	4c
	O26	0.11273(66)	0.7500	0.05157(92)	1	1.877(36)	4c
	Si1	0.42493(25)	0.06096(27)	0.65598(35)	1	0.573(19)	8d
	Si2	0.30857(31)	0.02900(22)	0.80426(35)	1	0.573(19)	8d
	Si3	0.28099(21)	0.06188(26)	0.02860(35)	1	0.573(19)	8d
	Si4	0.12394(22)	0.06377(28)	0.02571(36)	1	0.573(19)	8d
	Si5	0.06917(26)	0.03097(23)	0.81672(37)	1	0.573(19)	8d
	Si6	0.18494(25)	0.05581(27)	0.67156(34)	1	0.573(19)	8d
	Si7	0.42372(26)	0.83032(26)	0.67094(41)	1	0.573(19)	8d
	Si8	0.30558(30)	0.86851(24)	0.81529(34)	1	0.573(19)	8d
	Si9	0.27343(24)	0.83005(24)	0.03067(37)	1	0.573(19)	8d
	Si10	0.11854(26)	0.82310(24)	0.02289(39)	1	0.573(19)	8d
	Si11	0.07060(26)	0.87152(28)	0.81007(39)	1	0.573(19)	8d
	Si12	0.18214(27)	0.82621(22)	0.67780(39)	1	0.573(19)	8d
Ammonia 1	Translate	0.9110(10)	0.7215(15)	0.2215(16)			
	N1	0.9110	0.7215	0.2215	0.89(1)	1.49(20)	4c
	H12	0.9540	0.7340	0.1900	0.89(1)	1.79(24)	4c
	H13	0.9130	0.7360	0.2930	0.89(1)	1.79(24)	4c
	H14	0.8750	0.7450	0.1840	0.89(1)	1.79(24)	4c

Ammonia 2	Translate	0.7462(20)	0.2549(10)	-0.3643(29)			
	N2	0.7462	0.2549	0.6390	0.76(1)	1.94(26)	4c
	H22	0.7400	0.2100	-0.3300	0.76(1)	2.33(31)	4c
	H23	0.7400	0.2900	-0.3120	0.76(1)	2.33(31)	4c
	H24	0.7920	0.2500	-0.3930	0.76(1)	2.33(31)	4c
Ammonia 3	Translate	0.9774(21)	0.2499(25)	0.5509(26)			
	N3	0.9800	0.2700	0.5460	0.97(1)	1.94(26)	4c
	H32	1.0000	0.2570	0.4860	0.97(1)	2.33(31)	4c
	H33	0.9370	0.2790	0.5520	0.97(1)	2.33(31)	4c
	H34	0.9650	0.2014	0.5550	0.97(1)	2.33(31)	4c
Ammonia 4	Translate	0.5021(20)	0.4616(18)	0.0215(32)			
	N4	0.4980	0.4660	0.0190	0.94(1)	2.24(30)	8d
	H42	0.4910	0.4990	-0.0260	0.94(1)	2.69(46)	8d
	H43	0.4780	0.4710	0.0850	0.94(1)	2.69(46)	8d
	H44	0.4870	0.4190	-0.0090	0.94(1)	2.69(46)	8d

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

All the SOFs of the N-sites of ammonia are constrained in 1.

The values for the H-sites of ammonia are share the same SOF and 1.2 times of the B_{eq} for the coordinated N-sites.

The B_{eq} of N2 and N3 is 1.3 times of N1, N4 is 1.5 times of N1.

5.2 The positions of Al sites and Brønsted acid sites in H-ZSM-5

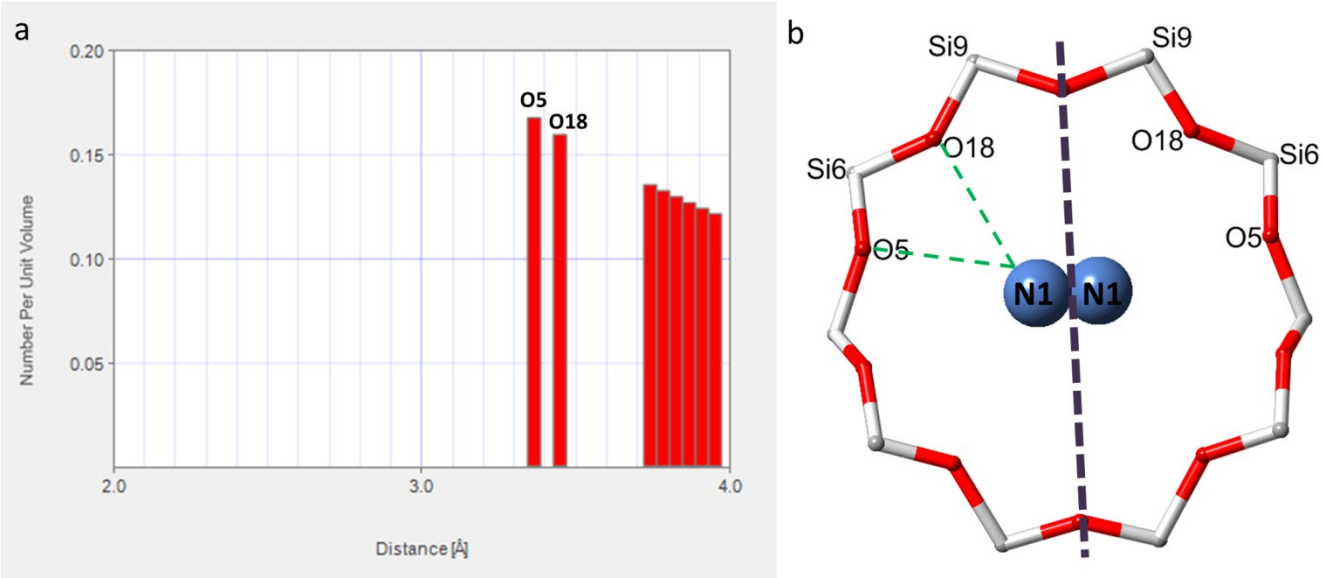


Figure S6. The deduced distances of the framework oxygen and ammonia adsorbed H-ZSM-5 at room temperature. (a) The N-$O_{(framework)}$ distances in range 2.0 to 4.0 Å, which exports from CrystalMaker. The closest distances of N-$O_{(framework)}$ are 3.358 Å (N-O5) and 3.460 Å (N-O18). (b) The position of Si6, Si9, O5 and O18. All of the symmetrical ammonia molecules and T6 sites are illustrated with labels. The framework atoms in H-ZSM-5 are presented in stick mode: red stick is O and grey stick is Si. The N of NH_3 is blue ball. Dark grape dot line is a mirror plane.

Table S6. Refined N1-O5 and N1-O18 distances from ammonia desorption by *in situ* synchrotron PXRD. (see the details in section 8 of Supplementary Information)

Bond	RT	100 °C	200 °C
N1-O5 (Å)	3.358(12)	3.856(15)	4.068(23)
N1-O18 (Å)	3.460(12)	3.817(15)	3.891(21)

According to the ICP characterization above, there was 4.48 Al per unit cell. The same number of Brønsted acid sites in H-ZSM-5 is expected. This means when Al replaces one symmetric Si position, it will create one charge unbalance for each substitution. Thus, a compensation proton will distribute at the O positions of with equivalent negatively charge in the H-ZSM-5. From the strong interaction and distance between adsorbed ammonia molecule and $O_{(framework)}$ of H-ZSM-5, according to our refinement, the periodic Al site at T6 site with O5 and O18 are clearly inferred. Thus, the NH_4^+ binds to O5 and O18 of almost equivalent negative charge as a bidentate mode (Figure S6). From Table S6 and Figure S6, the bidentate geometry of ammonium ion in sinusoidal channel with the two neighboring oxygens as N1-O5 and N1-O18 persists until 200 °C, agreeing with a theoretical prediction in the literature.[6]

6 Force field calculation

The framework energy for ammonia adsorbed H-ZSM-5 was calculated by the Forcite modules in Materials Studio v6.0. The H-ZSM-5 framework was calculated in a pure silica form (20.140×19.921×13.431 Å), with one T6 site set as the Al site, based on the deduction from the refined positions from Rietveld refinement. Due to the acidic nature of Brønsted site, the basic NH_3 would take up the proton to form NH_4^+. So, the force field calculation was initiated using one NH_4^+, three NH_3 and a negative charged oxygen framework. The force field of COMPASS27 was used with parameters of o2z and si4z for oxygen and silicon, respectively. The Smart algorithm, by calculating the potential energy overlaps, was used to optimise the geometry and unit cell parameters.

Table S7. Force field calculation of ammonia ion adsorbed H-ZSM-5.

Bond	Force field (N···H···O)	Atom FF(SXRD)	x	y	z
N1-O18 (Å)	4.493				
N1-O5 (Å)	3.814	N1(N1)	-8.4694(-8.5336)	-6.7020(-6.4580)	11.0160(12.2708)
N2-N1 (Å)	2.737	N2(N2)	-11.0537(-11.8939)	-5.8072(-5.7836)	11.0271(12.1300)
N3-N1 (Å)	2.624	N3(N3)	-6.6952(-5.5007)	-6.0414(-6.0504)	12.8331(14.5839)
N4-N3 (Å)	3.031	N4(N4)	-5.7382(-5.6987)	-3.9599(-1.9195)	14.8195(15.9582)

FF(SXRD): the N atoms positions from force field (the N atoms positions from synchrotron XRD).

7 TG-DTG analysis of desorption energy of ammonia in H-ZSM-5

Thermogravimetric (TG) and differential Thermogravimetric analysis (DTG) of ammonia adsorbed H-ZSM-5 was heated to 600 °C in air by using an TA Instruments TGA Q50 at 1 °C min^{-1}, 7.5 °C min^{-1}, 10 °C min^{-1}, 15 °C min^{-1} and 20 °C min^{-1}. The desorption energy for ammonia desorbed from H-ZSM-5 was calculated according to the following equation, which was deformed from the Arrhenius equation[7] based on the assumption of the first order desorption:

$$2\ln T_m - \ln\beta = E_{des}/RT_m + \ln E_{des}/AR$$

T_m is the temperature that the rate of desorption get maximum in the desorption DTG curve. β is the temperature ramp rate. E_d is the desorption energy and A is a constant. Plotting ($2\ln T_m - \ln\beta$) versus $1/T_m$ for a series of β values allows the determination of E_{des}.

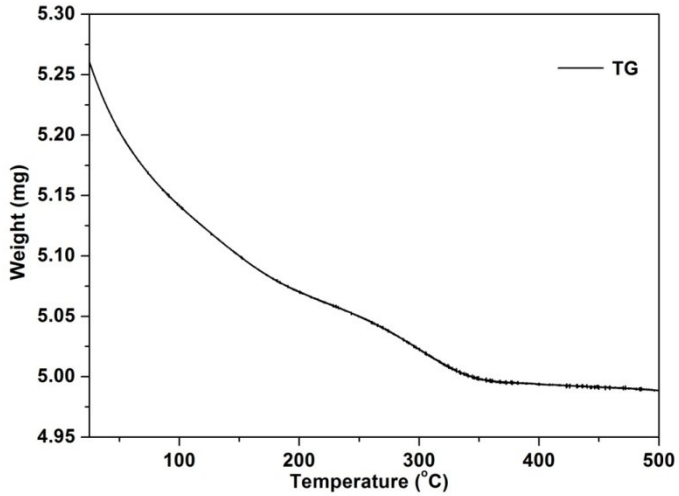


Figure S7. TG measurement of ammonia adsorbed H-ZSM-5 at 1 °C min^{-1}. The weight loss levels before 400 °C and the steady final weight is 4.9914 mg. Thus, there are 0.265 mg ammonia molecules desorbed from 25 °C to 400 °C. Then, the total ammonia storage capacity of H-ZSM-5 is 3.13 mmol g^{-1}.

Table S8. A comparison of residual ammonia molecules per unit cell at RT, 100 °C, 200 °C and 300 °C deduced from TG-DTG and Rietveld Refinement.

Temperature	TG-DTG		Rietveld Refinement
(°C)	Amount (mg)	Numbers (/unit cell)	Numbers (/unit cell) = SOF × symmetry = (N1+N2+N3) × 4 + N4 × 8
RT	0.265	18.01	18.00
100	0.148	9.98	9.36
200	0.077	5.23	5.44
300	0.029	1.97	2.00
400	0	0	0

The ZSM-5 sample has the space group of Pnma. N1, N2 and N3 are very close to the special position of the sinusoidal channel, so the symmetry multiplicity of N1, N2 and N3 is 4. N4 is not at the special position so

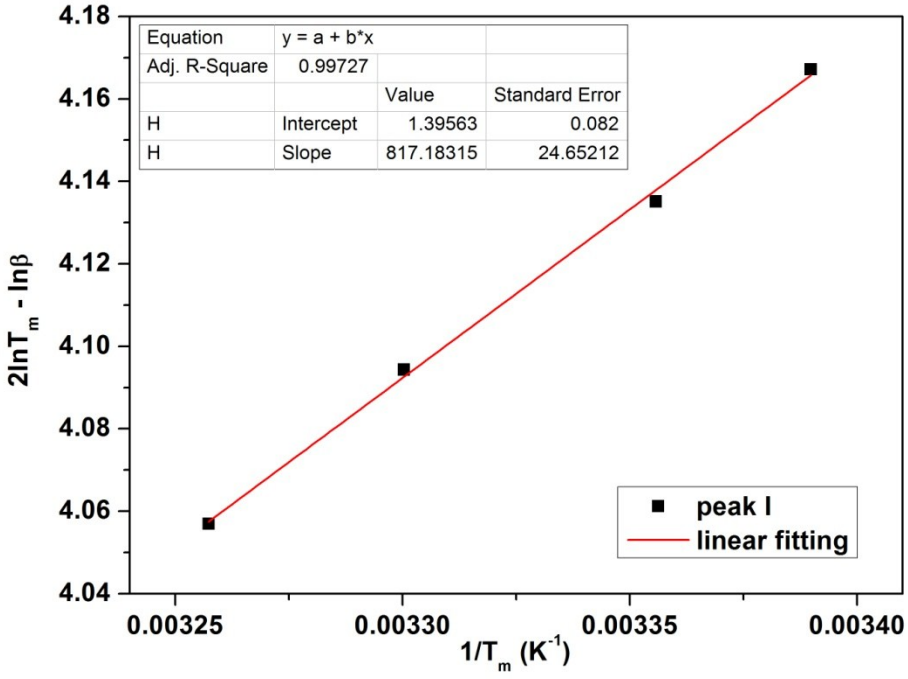
the symmetry multiplicity is 8.

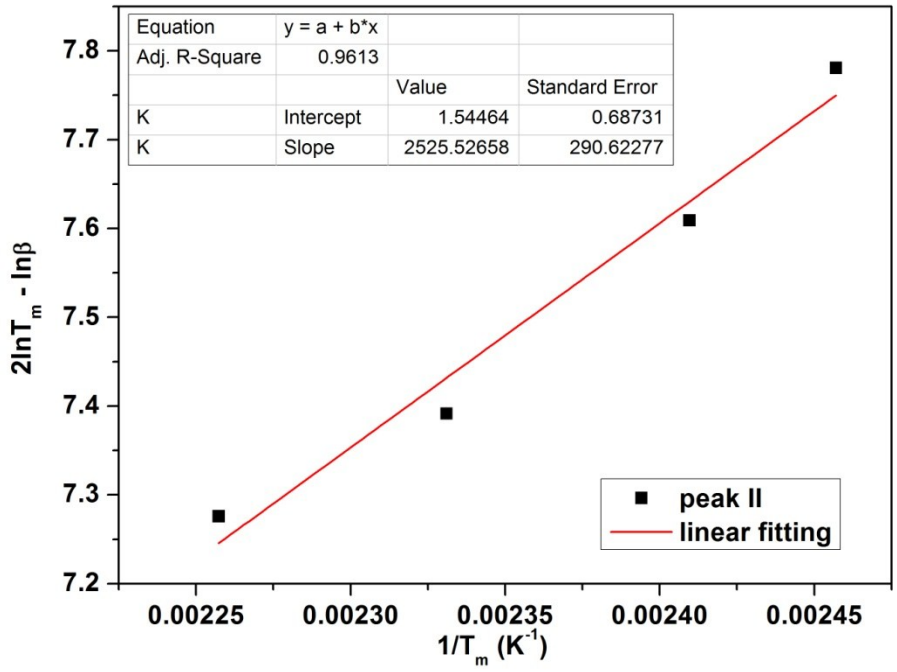
Table S9. The temperatures of the maximum weight change of three types at different temperature ramp rate.

β (°C min^{-1})	7.5	10	15	20	E_{des} = slope×8.314×10^{-3} (kJ mol^{-1})
T_I (°C)	22	25	30	34	6.8(2)
T_{II} (°C)	134	142	156	170	21(2)
T_{III} (°C)	338	347	354	363	113(11)

Table S10. The guiding values of "strong", "moderate" and "weak" hydrogen bonds[8].

	Strong	Moderate	Weak
Interaction type	Strongly covalent	Mostly electrostatic	Electrostat./dispers.
Bond lengths B-H (Å)	1.2 – 1.5	ca. 1.0	ca. 1.0
Bond lengths H···A (Å)	1.2 – 1.5	1.5 – 2.2	> 2.2
Bond lengths B·····A (Å)	2.2 – 2.5	2.5 – 3.2	3.2 – 4.0
Bond energy (kJ mol^{-1})	63 – 167	16 – 63	< 16
Bond angles (°)	170 – 180	> 130	> 90





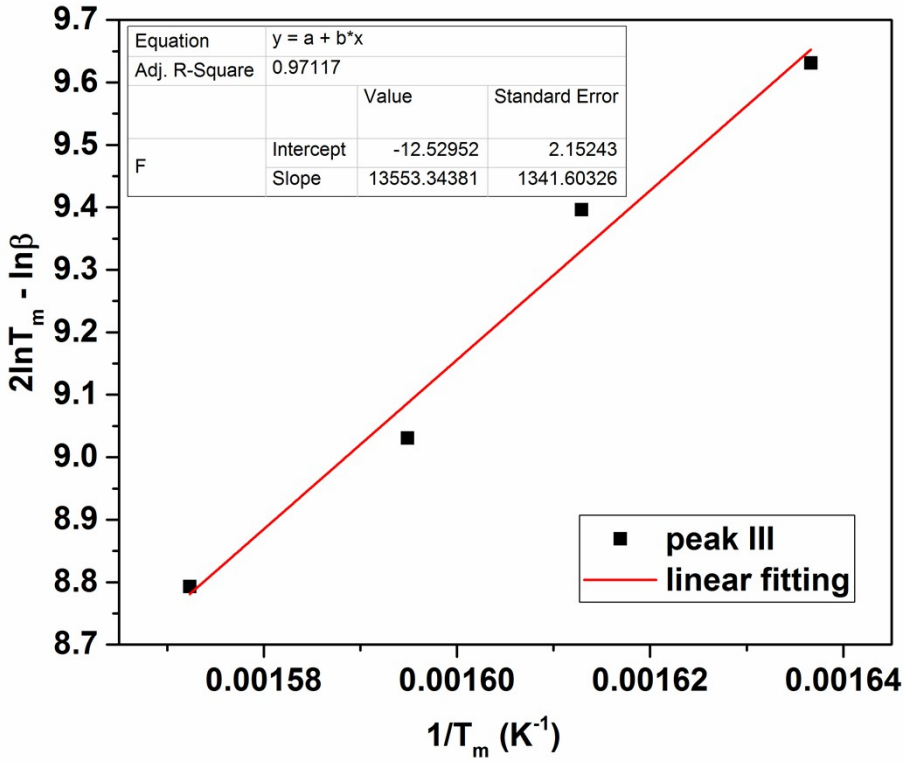


Figure S8. Linear fitting of the maximum temperature of three types of desorption at different temperature ramp rates. The R^2 0.997 (peak I), 0.961 (peak II) and 0.971 (peak III) shows the good fitting. The slope multiply by mole gas constant R is the desorption energy of ammonia (E_{des}).

As the E_{des} of peak III is 113 kJ mol^{-1}, which is on the range of "Strong" hydrogen bonding. Therefore, the angle of O··H···N is mostly linear. So the closest distance between O-N could be used to estimate the Brønsted acid sites-ammonia interaction.

8 *In situ* Synchrotron PXRD and Rietveld Refinement of ammonia adsorbed H-ZSM-5 at various temperatures.

Table S11. Crystallographic data and details of ammonia adsorbed H-ZSM-5 at various temperatures.

	100 °C	200 °C	300 °C	400 °C
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pnma*	*Pnma*	*Pnma*	*Pnma*
NH_3 per unit cell	10.1	5.3	2.1	0
2θ range refinement (°)	3 - 55	3 - 55	3 - 55	3 - 55
Detector	Multi-analyser crystals			
Number of parameters	149	149	143	135
Number of hkls	4174	4174	4172	4172
Refinement methods	Rietveld	Rietveld	Rietveld	Rietveld
a (Å)	20.11851(4)	20.12129(4)	20.11047(3)	20.11098(4)
b (Å)	19.94929(3)	19.95194(3)	19.94394(3)	19.94619(4)
c (Å)	13.43452(3)	13.43445(3)	13.42542(3)	13.42460(3)
V (Å^3)	5391.944(19)	5393.378(19)	5384.694(19)	5385.110(21)
R_{wp} / $R_{p.}$ / $R_{exp.}$ (%)	9.048/6.971/3.411	9.047/6.955/3.389	9.413/7.237/3.593	9.623/7.510/4.072
Wavelength (Å)	0.826617(4)	0.826617(4)	0.826209(3)	0.826209(3)
2θ Zero point (°)	0.000254(3)	0.000254(3)	-0.000489(2)	-0.000489(2)
Gof $\chi 2$	2.653	2.669	2.619	2.364

8.1 The Rietveld refinement and details of ammonia adsorbed H-ZSM-5 at 100 °C.

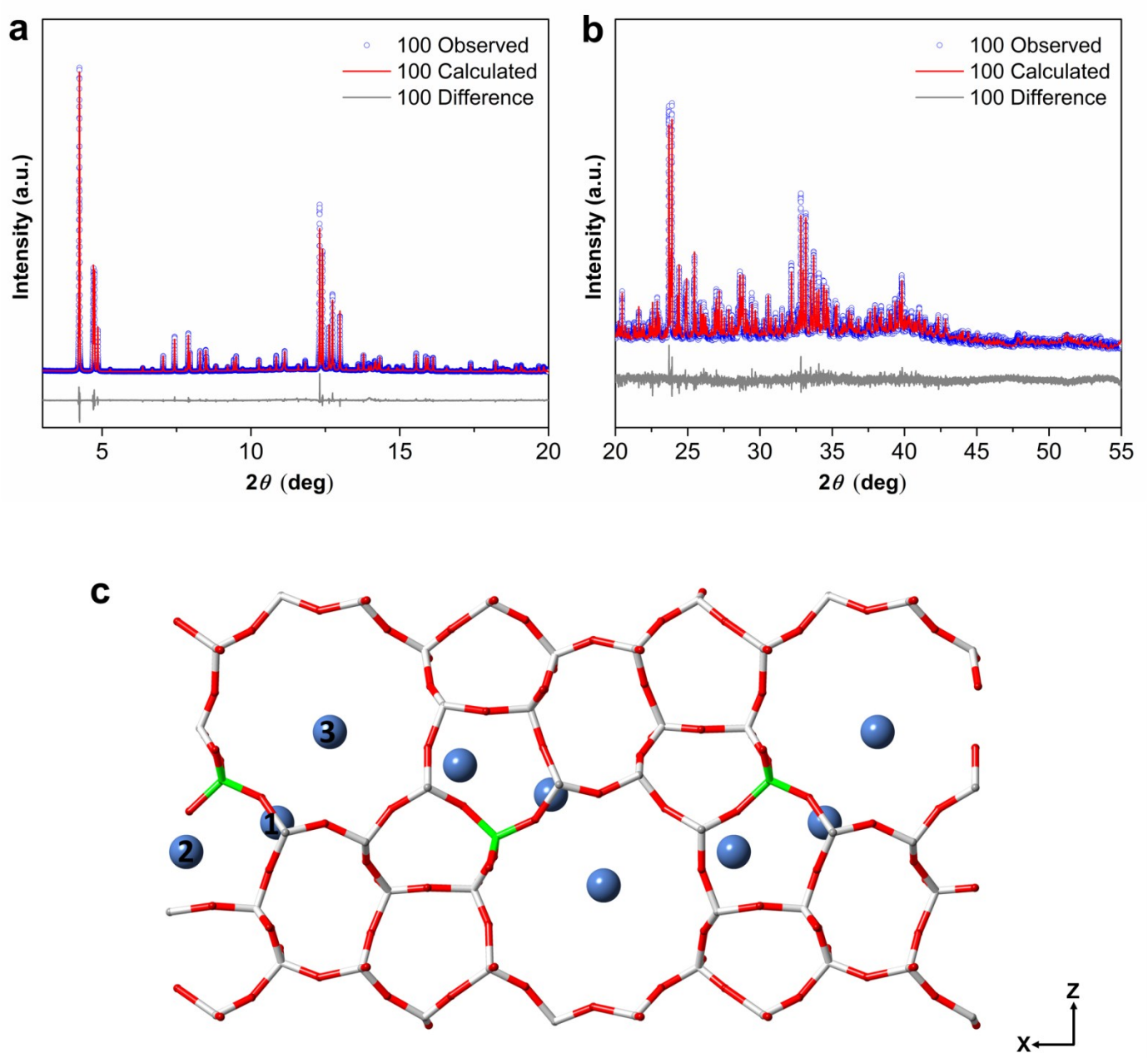


Figure S9. Synchrotron PXRD refinement and the crystal structure of ammonia adsorbed H-ZSM-5 at 100 °C. Comparison of the experiment data (blue circle) and Rietveld refinement (red line) and the difference between them (grey line), (a) range from 3-20° and (b) range from 20-55°. (c) The refined structure of ammonia adsorbed H-ZSM-5 at 100 °C (viewed from *y*-axis). The framework of H-ZSM-5 is using the stick mode, red stick is O and grey stick is Si. The Al sites are highlighted in green and the N of NH_3 is blue ball, without showing the symmetrical ammonia and Al sites between the mirror plane. The sinusoidal channels are along *x*-axis and straight channels along *y*-axis. The ammonia N4 is desorbed at 100 °C, while N1, N2 and N3 are in the channel.

Table S12. Crystallographic information files from the Rietveld refinement of ammonia adsorbed H-ZSM-5 at 100 °C.

Species	Atom	*x*	*Y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37560(47)	0.06238(55)	0.74925(60)	1	2.549(35)	8d
	O2	0.30868(46)	0.05882(47)	0.91545(56)	1	2.549(35)	8d
	O3	0.20212(43)	0.05357(51)	0.01532(44)	1	2.549(35)	8d
	O4	0.09788(38)	0.06018(51)	0.91611(64)	1	2.549(35)	8d
	O5	0.11217(44)	0.05436(59)	0.72055(57)	1	2.549(35)	8d

	O6	0.24402(42)	0.05735(67)	0.75728(58)	1	2.549(35)	8d
	O7	0.36958(47)	0.84858(46)	0.76486(61)	1	2.549(35)	8d
	O8	0.30234(52)	0.84204(39)	0.93343(58)	1	2.549(35)	8d
	O9	0.19066(51)	0.84021(36)	0.03428(52)	1	2.549(35)	8d
	O10	0.08708(45)	0.84558(45)	0.90962(70)	1	2.549(35)	8d
	O11	0.11710(49)	0.84402(47)	0.73923(67)	1	2.549(35)	8d
	O12	0.23423(44)	0.84860(50)	0.73986(66)	1	2.549(35)	8d
	O13	0.31310(42)	0.94718(45)	0.81818(46)	1	2.549(35)	8d
	O14	0.07991(37)	0.96168(46)	0.81788(59)	1	2.549(35)	8d
	O15	0.42091(45)	0.12862(49)	0.60634(72)	1	2.549(35)	8d
	O16	0.40159(45)	0.99834(46)	0.57392(78)	1	2.549(35)	8d
	O17	0.40433(49)	0.86100(44)	0.57521(79)	1	2.549(35)	8d
	O18	0.18818(56)	0.12801(43)	0.61915(57)	1	2.549(35)	8d
	O19	0.19668(58)	0.00615(43)	0.58903(63)	1	2.549(35)	8d
	O20	0.19613(56)	0.87802(42)	0.58337(58)	1	2.549(35)	8d
	O21	0.99669(46)	0.04988(66)	0.79030(60)	1	2.549(35)	8d
	O22	0.99387(47)	0.85243(55)	0.79026(63)	1	2.549(35)	8d
	O23	0.42080(64)	0.7500	0.63040(92)	1	2.549(35)	4c
	O24	0.19305(79)	0.7500	0.65964(77)	1	2.549(35)	4c
	O25	0.28418(62)	0.7500	0.05096(87)	1	2.549(35)	4c
	O26	0.10062(67)	0.7500	0.05720(02)	1	2.549(35)	4c
	Si1	0.42288(25)	0.06151(28)	0.65849(36)	1	0.886(18)	8d
	Si2	0.30876(31)	0.02938(22)	0.80744(36)	1	0.886(18)	8d
	Si3	0.27953(22)	0.06112(27)	0.03164(35)	1	0.886(18)	8d
	Si4	0.12180(23)	0.06450(28)	0.02350(37)	1	0.886(18)	8d
	Si5	0.06876(24)	0.03148(24)	0.81544(38)	1	0.886(18)	8d
	Si6	0.18413(24)	0.05587(27)	0.67206(33)	1	0.886(18)	8d
	Si7	0.42375(26)	0.82995(25)	0.66933(40)	1	0.886(18)	8d
	Si8	0.30482(28)	0.86846(24)	0.81327(34)	1	0.886(18)	8d
	Si9	0.27512(25)	0.82829(23)	0.03073(38)	1	0.886(18)	8d
	Si10	0.11984(25)	0.82585(25)	0.02576(40)	1	0.886(18)	8d
	Si11	0.07077(25)	0.87360(27)	0.81519(40)	1	0.886(18)	8d
	Si12	0.18580(28)	0.82649(22)	0.68117(38)	1	0.886(18)	8d
Ammonia 1	Translate	0.9163(20)	0.7600(45)	0.2118(30)			
	N1	0.9160	0.7600	0.2120	0.87(1)	2.48(31)	4c
	H12	0.8800	0.7400	0.1700	0.87(1)	2.98(37)	4c
	H13	0.9100	0.7390	0.2780	0.87(1)	2.98(37)	4c
	H14	0.9600	0.7500	0.1800	0.87(1)	2.98(37)	4c
Ammonia 2	Translate	0.7497(37)	0.2429(12)	-0.3679(44)			
	N2	0.7500	0.2430	0.6320	0.67(1)	3.23(40)	4c
	H22	0.7500	0.2800	0.6800	0.67(1)	3.87(48)	4c
	H23	0.7090	0.2500	0.5900	0.67(1)	3.87(48)	4c
	H24	0.7910	0.2500	0.5900	0.67(1)	3.87(48)	4c
Ammonia 3	Translate	0.9873(31)	0.3039(26)	0.5407(42)			
	N3	0.9870	0.3040	0.5410	0.80(1)	3.23(40)	4c
	H32	0.0280	0.3300	0.5500	0.80(1)	3.87(48)	4c

H33	0.0000	0.2570	0.5300	0.80(1)	3.87(48)	4c
H34	0.9600	0.3100	0.6000	0.80(1)	3.87(48)	4c

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

All the SOFs of the N-sites of ammonia are constrained in 1.

The values for the H-sites of ammonia are share the same SOF and 1.2 times of the B_{eq} for the coordinated N-sites.

The B_{eq} of N2 and N3 is 1.3 times of N1.

8.2 The Rietveld refinement and details of ammonia adsorbed H-ZSM-5 at 200 °C.

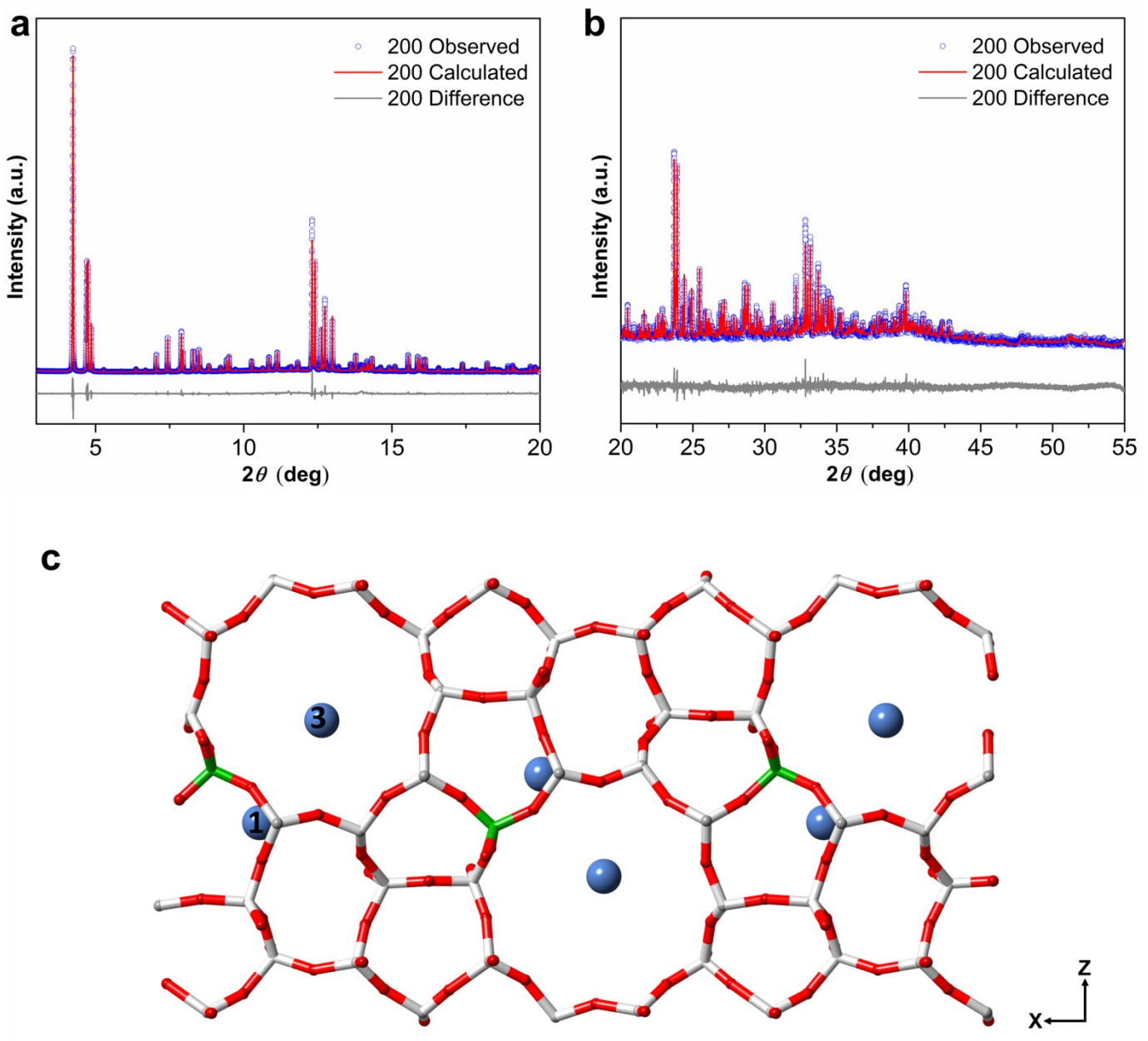


Figure S10. Synchrotron PXRD refinement and the structure detail of ammonia adsorbed H-ZSM-5 at 200 °C. Comparison of the experiment data (blue circle) and Rietveld refinement (red line) and the difference between them (grey line), (a) range from 3-20° and (b) range from 20-55°. (c) The refined structure of ammonia adsorbed H-ZSM-5 at 200 °C. The framework of H-ZSM-5 is using the stick mode, red stick is O and grey stick is Si. The Al6 sites are highlighted in green and the N of NH_3 is blue ball, without showing the symmetrical ammonia and Al6 sites between the mirror plane. The sinusoidal channels are along *x*-axis, and straight channels (along *y*-axis). The ammonia N4 and N2 are totally desorbed at 200 °C.

Table S13. Crystallographic information files from the Rietveld refinement of ammonia adsorbed H-ZSM-5 at 200 °C.

Species	Atom	*x*	*Y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37642(49)	0.05700(62)	0.75602(64)	1	2.909(35)	8d
	O2	0.31000(48)	0.06301(45)	0.91929(62)	1	2.909(35)	8d
	O3	0.20398(45)	0.06229(42)	0.01724(46)	1	2.909(35)	8d
	O4	0.09666(38)	0.06112(52)	0.91176(68)	1	2.909(35)	8d
	O5	0.11553(46)	0.04679(59)	0.72142(65)	1	2.909(35)	8d
	O6	0.24334(45)	0.05349(68)	0.75356(63)	1	2.909(35)	8d
	O7	0.36961(49)	0.84413(48)	0.76818(64)	1	2.909(35)	8d
	O8	0.30031(52)	0.84737(39)	0.93415(63)	1	2.909(35)	8d
	O9	0.19904(51)	0.84318(33)	0.03084(52)	1	2.909(35)	8d
	O10	0.08606(46)	0.84732(48)	0.91522(74)	1	2.909(35)	8d
	O11	0.11932(50)	0.83941(48)	0.74398(70)	1	2.909(35)	8d
	O12	0.23465(45)	0.84566(51)	0.74176(71)	1	2.909(35)	8d
	O13	0.31350(45)	0.94990(48)	0.82010(47)	1	2.909(35)	8d
	O14	0.08154(38)	0.95987(50)	0.81544(60)	1	2.909(35)	8d
	O15	0.42065(46)	0.12766(51)	0.60059(73)	1	2.909(35)	8d
	O16	0.40184(46)	0.99763(50)	0.58615(81)	1	2.909(35)	8d
	O17	0.40349(49)	0.86710(51)	0.56900(79)	1	2.909(35)	8d
	O18	0.19168(63)	0.12953(45)	0.61812(60)	1	2.909(35)	8d
	O19	0.20038(59)	0.00339(46)	0.59695(67)	1	2.909(35)	8d
	O20	0.19864(57)	0.87113(45)	0.57710(61)	1	2.909(35)	8d
	O21	0.99730(49)	0.05083(67)	0.79317(62)	1	2.909(35)	8d
	O22	0.99490(50)	0.85274(53)	0.79499(66)	1	2.909(35)	8d
	O23	0.41795(66)	0.7500	0.64329(90)	1	2.909(35)	4c
	O24	0.19096(87)	0.7500	0.66020(77)	1	2.909(35)	4c
	O25	0.27431(56)	0.7500	0.06211(90)	1	2.909(35)	4c
	O26	0.09338(62)	0.7500	0.05532(106)	1	2.909(35)	4c
	Si1	0.42292(26)	0.06190(31)	0.66311(40)	1	1.177(17)	8d
	Si2	0.30908(32)	0.03024(23)	0.80952(37)	1	1.177(17)	8d
	Si3	0.27905(23)	0.06354(27)	0.03466(38)	1	1.177(17)	8d
	Si4	0.12102(24)	0.06130(31)	0.02531(40)	1	1.177(17)	8d
	Si5	0.06993(26)	0.02949(25)	0.81652(42)	1	1.177(17)	8d
	Si6	0.18563(26)	0.05675(29)	0.67322(37)	1	1.177(17)	8d
	Si7	0.42370(27)	0.83179(26)	0.66995(45)	1	1.177(17)	8d
	Si8	0.30653(31)	0.86852(26)	0.81783(35)	1	1.177(17)	8d
	Si9	0.27685(25)	0.82796(23)	0.03013(41)	1	1.177(17)	8d
	Si10	0.12199(26)	0.82667(25)	0.02388(42)	1	1.177(17)	8d
	Si11	0.07132(27)	0.87284(30)	0.81453(41)	1	1.177(17)	8d
	Si12	0.18770(31)	0.82481(22)	0.68206(41)	1	1.177(17)	8d
Ammonia 1	Translate	0.8989(22)	0.7403(70)	0.1859(36)			
	N1	0.8990	0.7400	0.1860	0.93(1)	2.94(46)	4c
	H12	0.8540	0.7500	0.1600	0.93(1)	3.52(55)	4c
	H13	0.9330	0.7600	0.1400	0.93(1)	3.52(55)	4c
	H14	0.9000	0.7600	0.2550	0.93(1)	3.52(55)	4c
Ammonia 3	Translate	0.9910(69)	0.3103(62)	0.5460(88)			

N3	0.9950	0.3100	0.5430	0.43(1)	3.82(60)	4c
H32	0.0000	0.3600	0.5400	0.43(1)	4.58(72)	4c
H33	0.0400	0.2900	0.5800	0.43(1)	4.58(72)	4c
H34	0.9500	0.3000	0.5800	0.43(1)	4.58(72)	4c

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

All the SOFs of the N-sites of ammonia are constrained in 1.

The values for the H-sites of ammonia are share the same SOF and 1.2 times of the B_{eq} for the coordinated N-sites.

The B_{eq} of N2 and N3 is 1.3 times of N1.

8.3 The Rietveld refinement and details of ammonia adsorbed H-ZSM-5 at 300 °C.

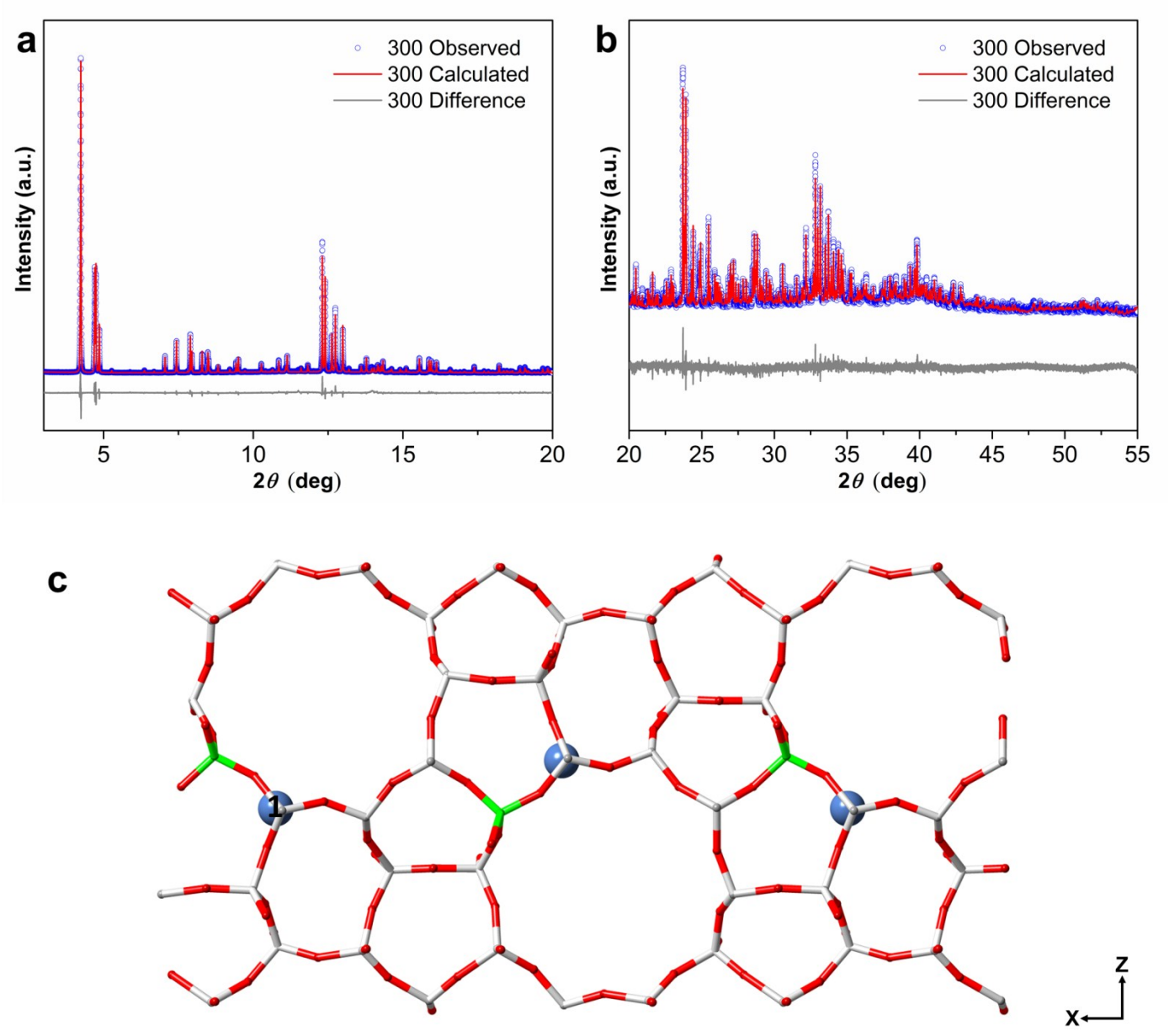


Figure S11. Synchrotron PXRD refinement and the structure detail of ammonia adsorbed H-ZSM-5 at 300 °C. a, Comparison of the experiment data (blue circle) and Rietveld refinement (red line) and the difference between them (grey line), (a) range from 3-20° and (b) range from 20-55°. (c) The refined structure of ammonia adsorbed H-ZSM-5 at 300 °C (viewed from *y*-axis). The framework of H-ZSM-5 is using the stick mode, red stick is O and grey stick is Si. The Al6 sites are highlighted in green and the N of NH_3 is blue ball, without showing the symmetrical ammonia and Al6 sites between the mirror plane. The sinusoidal channels are along *x*-axis and straight channels along *y-axis*. The ammonia N4, N2 and N3 are desorbed and little N1 remained at 300 °C.

Table S14. Crystallographic information files from the Rietveld refinement of ammonia adsorbed H-ZSM-5 at 300 °C.

Species	Atom	*x*	*Y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37520(52)	0.05196(70)	0.75575(67)	1	3.481(36)	8d
	O2	0.30867(55)	0.06262(49)	0.92244(66)	1	3.481(36)	8d
	O3	0.20145(49)	0.05850(49)	0.02160(47)	1	3.481(36)	8d
	O4	0.09524(42)	0.06376(54)	0.91395(71)	1	3.481(36)	8d
	O5	0.11755(49)	0.05735(69)	0.72764(64)	1	3.481(36)	8d
	O6	0.24527(48)	0.05737(70)	0.75535(67)	1	3.481(36)	8d
	O7	0.37101(51)	0.83914(51)	0.76617(70)	1	3.481(36)	8d
	O8	0.30354(60)	0.84506(41)	0.93106(69)	1	3.481(36)	8d
	O9	0.19533(56)	0.84028(35)	0.03070(52)	1	3.481(36)	8d
	O10	0.08822(49)	0.84767(49)	0.92292(79)	1	3.481(36)	8d
	O11	0.11573(54)	0.84648(52)	0.74597(72)	1	3.481(36)	8d
	O12	0.23838(50)	0.84675(54)	0.74786(73)	1	3.481(36)	8d
	O13	0.31376(49)	0.95051(54)	0.81810(49)	1	3.481(36)	8d
	O14	0.07864(39)	0.95596(58)	0.81991(60)	1	3.481(36)	8d
	O15	0.41978(50)	0.12525(52)	0.60703(77)	1	3.481(36)	8d
	O16	0.40299(52)	0.99730(53)	0.59248(79)	1	3.481(36)	8d
	O17	0.40087(52)	0.86477(51)	0.56193(77)	1	3.481(36)	8d
	O18	0.19136(66)	0.13166(47)	0.61882(64)	1	3.481(36)	8d
	O19	0.20282(64)	0.00256(48)	0.59519(70)	1	3.481(36)	8d
	O20	0.19709(64)	0.86900(47)	0.58171(64)	1	3.481(36)	8d
	O21	0.99575(53)	0.04976(69)	0.79451(61)	1	3.481(36)	8d
	O22	0.99404(55)	0.85123(55)	0.79742(65)	1	3.481(36)	8d
	O23	0.41658(72)	0.7500	0.63753(95)	1	3.481(36)	4c
	O24	0.19328(91)	0.7500	0.65918(80)	1	3.481(36)	4c
	O25	0.27832(61)	0.7500	0.05764(96)	1	3.481(36)	4c
	O26	0.09411(69)	0.7500	0.06854(108)	1	3.481(36)	4c
	Si1	0.42278(27)	0.06021(32)	0.66457(41)	1	1.374(16)	8d
	Si2	0.30891(36)	0.02995(22)	0.81037(38)	1	1.374(16)	8d
	Si3	0.27983(24)	0.06382(27)	0.03698(38)	1	1.374(16)	8d
	Si4	0.12083(24)	0.05982(32)	0.02670(40)	1	1.374(16)	8d
	Si5	0.06902(28)	0.02947(27)	0.81822(43)	1	1.374(16)	8d
	Si6	0.18732(29)	0.05534(29)	0.67503(37)	1	1.374(16)	8d
	Si7	0.42392(28)	0.82857(27)	0.67284(47)	1	1.374(16)	8d
	Si8	0.30778(34)	0.87109(26)	0.81977(37)	1	1.374(16)	8d
	Si9	0.27496(26)	0.82978(24)	0.03025(42)	1	1.374(16)	8d
	Si10	0.12126(28)	0.82356(25)	0.02677(43)	1	1.374(16)	8d
	Si11	0.07219(28)	0.87106(32)	0.81548(43)	1	1.374(16)	8d
	Si12	0.18781(33)	0.82624(23)	0.68478(42)	1	1.374(16)	8d
Ammonia 1	Translate	0.9202(34)	0.7626(30)	0.1866(30)			
	N1	0.9202	0.7630	0.1870	0.50(1)	3.19(87)	4c
	H12	0.9600	0.7400	0.1800	0.50(1)	3.82(105)	4c
	H13	0.8900	0.7500	0.1300	0.50(1)	3.82(105)	4c
	H14	0.9000	0.7500	0.2510	0.50(1)	3.82(105)	4c

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

All the SOFs of the N-sites of ammonia are constrained in 1.

The values for the H-sites of ammonia are share the same SOF and 1.2 times of the B_{eq} for the coordinated N-sites.

The B_{eq} of N3 is 1.3 times of N1.

8.4 The Rietveld refinement and details of ammonia adsorbed H-ZSM-5 at 400 °C.

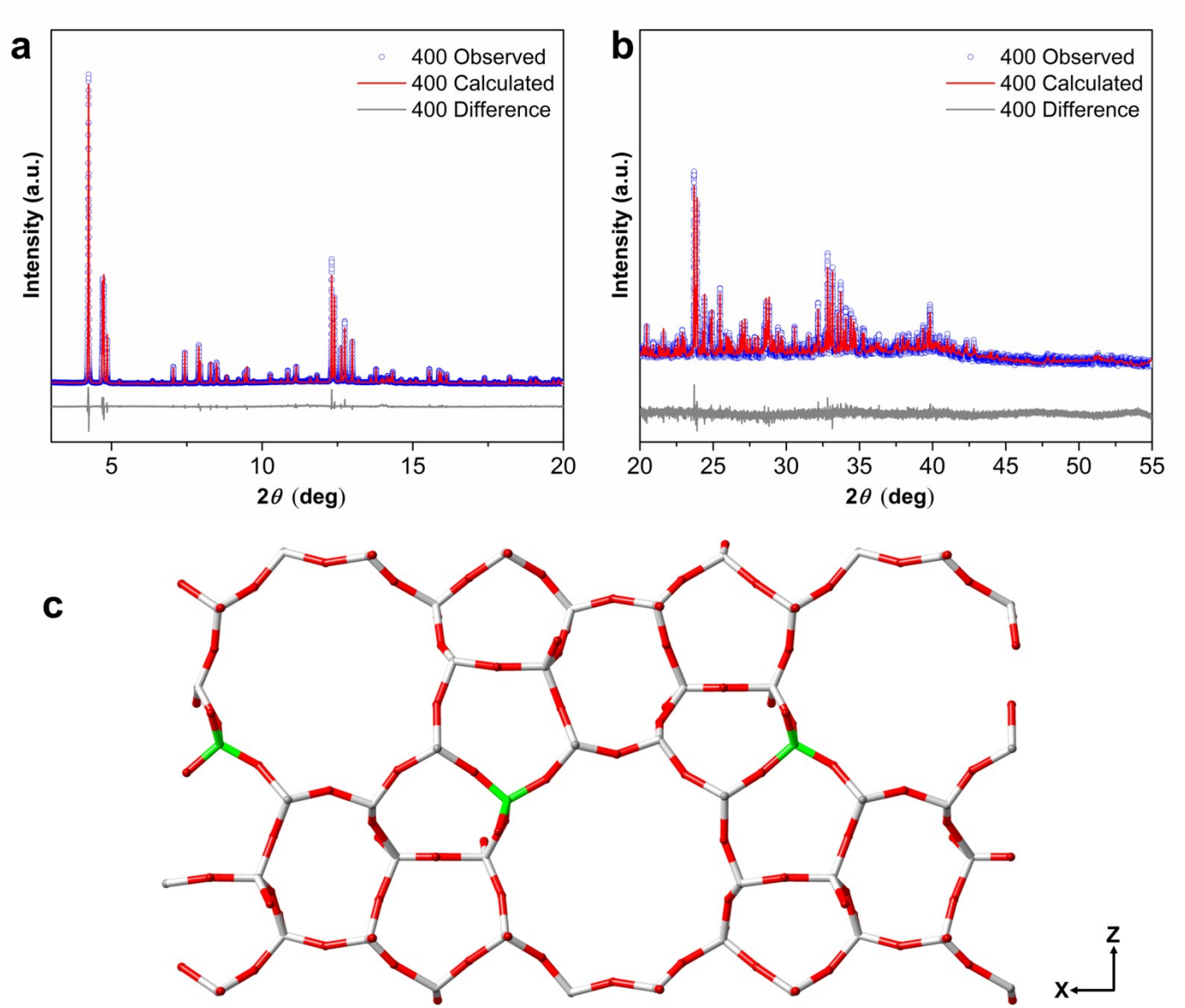


Figure S12. Synchrotron PXRD refinement and the structure detail of ammonia adsorbed H-ZSM-5 at 400 °C. a, Comparison of the experiment data (blue circle) and Rietveld refinement (red line) and the difference between them (grey line), (a) range from 3-20° and (b) range from 20-55°. (c) The refined structure of ammonia adsorbed H-ZSM-5 at 400 °C (viewed from *y-axis*). The framework of H-ZSM-5 is using the stick mode, red stick is O and grey stick is Si. The Al6 sites sites are highlighted in green and the N of NH_3 is blue ball. See from *y-axis* (sinusoidal channels along *x*-axis, straight channels along *y-axis*). The ammonia N4, N2, N3 and N1 are completely desorbed 400 °C.

Table S15. Crystallographic information files from the Rietveld refinement of ammonia adsorbed H-ZSM-5 at 400 °C.

Species	Atom	*x*	*y*	*z*	SOF	B_{eq} (Å^2)	Wyckoff
Zeolite framework	O1	0.37736(66)	0.05331(72)	0.75523(84)	1	3.865(55)	8d
	O2	0.30947(66)	0.06264(58)	0.92641(80)	1	3.865(55)	8d
	O3	0.20385(57)	0.05641(61)	0.02465(59)	1	3.865(55)	8d
	O4	0.09330(53)	0.06688(60)	0.91660(87)	1	3.865(55)	8d
	O5	0.11922(62)	0.06028(69)	0.73160(80)	1	3.865(55)	8d
	O6	0.24472(61)	0.05458(88)	0.75232(88)	1	3.865(55)	8d
	O7	0.37280(65)	0.83552(57)	0.76765(89)	1	3.865(55)	8d
	O8	0.30362(77)	0.84479(50)	0.92785(85)	1	3.865(55)	8d
	O9	0.18994(64)	0.83699(42)	0.02948(64)	1	3.865(55)	8d
	O10	0.09000(60)	0.85115(58)	0.91709(95)	1	3.865(55)	8d
	O11	0.11578(70)	0.84921(60)	0.74896(90)	1	3.865(55)	8d
	O12	0.24567(68)	0.84861(69)	0.75621(96)	1	3.865(55)	8d
	O13	0.31544(59)	0.94963(64)	0.82147(60)	1	3.865(55)	8d
	O14	0.07905(48)	0.95436(70)	0.81721(73)	1	3.865(55)	8d
	O15	0.42140(61)	0.12475(59)	0.61799(94)	1	3.865(55)	8d
	O16	0.40099(62)	0.99572(62)	0.59388(91)	1	3.865(55)	8d
	O17	0.40166(66)	0.86281(59)	0.56106(90)	1	3.865(55)	8d
	O18	0.19096(78)	0.13676(51)	0.62312(79)	1	3.865(55)	8d
	O19	0.20224(74)	0.00475(55)	0.59570(84)	1	3.865(55)	8d
	O20	0.19859(79)	0.86767(54)	0.58141(83)	1	3.865(55)	8d
	O21	0.99592(66)	0.05110(80)	0.79697(74)	1	3.865(55)	8d
	O22	0.99728(70)	0.85003(66)	0.79661(77)	1	3.865(55)	8d
	O23	0.41574(86)	0.7500	0.62442(124)	1	3.865(55)	4c
	O24	0.19171(09)	0.7500	0.65522(101)	1	3.865(55)	4c
	O25	0.27359(71)	0.7500	0.06908(124)	1	3.865(55)	4c
	O26	0.08904(78)	0.7500	0.08014(123)	1	3.865(55)	4c
	Si1	0.42180(32)	0.05770(39)	0.66422(50)	1	1.455(23)	8d
	Si2	0.30851(42)	0.02973(26)	0.81211(47)	1	1.455(23)	8d
	Si3	0.27992(28)	0.06377(32)	0.04033(44)	1	1.455(23)	8d
	Si4	0.12078(29)	0.05877(38)	0.02634(48)	1	1.455(23)	8d
	Si5	0.06831(33)	0.03048(32)	0.82136(52)	1	1.455(23)	8d
	Si6	0.18719(35)	0.05597(35)	0.67605(46)	1	1.455(23)	8d
	Si7	0.42470(34)	0.82576(32)	0.67469(56)	1	1.455(23)	8d
	Si8	0.31002(40)	0.87134(30)	0.82252(46)	1	1.455(23)	8d
	Si9	0.27526(32)	0.83011(29)	0.02857(50)	1	1.455(23)	8d
	Si10	0.12087(33)	0.82257(30)	0.02942(53)	1	1.455(23)	8d
	Si11	0.07277(36)	0.87088(37)	0.81494(53)	1	1.455(23)	8d
	Si12	0.18886(42)	0.82717(27)	0.68660(50)	1	1.455(23)	8d

All the T-sites (T=Al, Si) of ZSM-5 share the same value of SOF and B_{eq}.

All the O-sites of ZSM-5 share the same value SOF and B_{eq}.

Table S16. Summary the refinement result of ammonia adsorption and desorption *in situ* synchrotron PXRD of H-ZSM-5.

Temperature	RT	100 °C	200 °C	300 °C	400 °C
SOF (ammonia 1)	0.89(1)	0.87(1)	0.93(1)	0.50(1)	–
SOF (ammonia 2)	0.76(1)	0.67(1)	–	–	–
SOF (ammonia 3)	0.97(1)	0.80(1)	0.43(1)	–	–
SOF (ammonia 4)	0.94(1)	–	–	–	–
N1-O5 (Å)	3.358(12)	3.856(15)	4.068(23)	3.838(12)	
N1-O18 (Å)	3.460(12)	3.817(15)	3.891(21)	4.030(12)	–
N2-N1 (Å)	3.430(12)	3.523(16)	–	–	–
N3-N1 (Å)	3.835 (27)	4.055(6)	4.480(5)	–	–
N4-N3 (Å)	4.358(9)	–	–	–	–

The errors of distances are calculated from the percent of translate errors time distances.

9 Further Research

In order to characterize the H positions to further elucidate the structures of adsorbed ammonia molecules within the H-ZSM-5, neutron diffraction will be carried out.

10 References

1 Y. Y. Chu, Z. W. Yu, A. M. Zheng, H. J. Fang, H. L. Zhang, S. J. Huang, S. B. Liu and F. Deng, *J. Phys. Chem. C*, 2011, **115**, 7660-7667.

2 S. P. Thompson, J. E. Parker, J. Potter, T. P. Hill, A. Birt, T. M. Cobb, F. Yuan and C. C. Tang, *Rev. Sci. Instrum.*, 2009, **80**.

3 J. E. Parker, J. Potter, S. P. Thompson, A. R. Lennie and C. C. Tang, *Mater. Sci. Forum*, 2012, **706-709**, 1707-1712.

4 N. H. Heo, C. W. Kim, H. J. Kwon, G. H. Kim, S. H. Kim, S. B. Hong and K. Seff, *J. Phys. Chem. C*, 2009, **113**, 19937-19956.

5 P. Thompson, D. E. Cox and J. B. Hastings, *J. Appl. Crystallogr.*, 1987, **20**, 79-83.

6 A. Kyrlidis, S. J. Cook, A. K. Chakraborty, A. T. Bell and D. N. Theodorou, *J. Phys. Chem.*, 1995, **99**, 1505-1515.

7 Y. Y. Guo, Y. R. Li, J. Wang, T. Y. Zhu and M. Ye, *Chem. Eng. J.*, 2014, **236**, 506-512.

8 T. Steiner, *Angew. Chem. Int. Edit*, 2002, **41**, 48-76.