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Supplementary materials to manuscript "Local probes show that framework modification in zeolites occurs on ammonium loading without calcination"

1. Synthesis of zeolite Y and exchange with NH_4

Method used was modified from Ginter et al. (D. M. Ginter, A. T. Bell and C. J. Radke, in *Molecular sieves*, eds. M. L. Occelli and H. Robson, Van Nostrand Reinhold, New York, 1992, pp. 6-31.)

	Sample 1	Sample 2
Seed gel (1)	9.97g Deionised Water 2.03g Sodium Hydroxide 1.05g Sodium Aliminate 11.36g Sodium Silicate Solution	33.84g Deionised Water 6.79g Sodium Hydroxide 3.50g Sodium Aluminate 37.92g Sodium Silicate Solution
Aging	1 day	30 days
Feedstock (2)	65.49g Deionised Water 0.07g Sodium Hydroxide 6.55g Sodium Aluminate 71.21g Sodium Silicate Solution	209.4g Deionised Water 0.242g Sodium Hydroxide 20.94g Sodium Aluminate 227.9g Sodium Silicate Solution
Overall gel	Added (2) to 8.25g of (1) Stirred for 30 minutes 150ml HDPE bottle	Added (2) to 26.47g of (1) Stirred for 20 minutes 500ml HDPE bottle
Preparation	Prepared at 100degC for 5 hours Washed with deionised water Yielded about 15g of white, zeolite powder	Prepared at 100degC for 5 hours Washed with deionised water Yielded about 57g of white zeolite powder

Table S1: Synthesis conditions and chemicals used for preparation of two samples. Sodium Silicate Solution (Riedel-de Haen) ($Na_2Si_3O_7$); Sodium Hydroxide (Sigma-Aldrich) ≥98%; Sodium Aluminate (Riedel-de Haen).

Sample 3 was made by hydrothermal exchange (2 periods of 8 hours) of sample 1 with NH_4NO_3 (Sigma-Aldrich 95+%) at 60degC. For the exchange, an excess of ammonium nitrate (40g per 10g of zeolite) was used (40g:10g:1000ml = NH_4NO_3:zeolite:H_2O). The sample was consequently washed with deionised water and dried at 230degC.
Sample 4 was made by a similar exchange but with ND_4Cl in the ratio (10g:3g:200ml =ND_4Cl: zeolite:D_2O approximately), this sample was only used for PDF analysis using neutron diffraction data collected on GEM in ISIS. The sample was consequently washed with D2O and dried at 230degC.

2. TEM data on zeolite Y and NH_4-Y

	wt%(1^{st} measurement)	Wt%(2^{nd} measurement)	%	%
Si	42.95(0.06)	47.71(0.07)	1.529	1.698
Al	20.31(0.05)	22.02(0.06)	0.753	0.816
Na	2.88(0.02)	7.32(0.04)	0.125	0.318
O	33.86(0.06)	22.95(0.07)	2.116	1.434

Table S2: EDX data for sample 1, these were collected twice. Both measurements are shown in columns 2 and 3.

Calculation of Si/Al from EDX data gives us 2.03 and 2.08 for first and second measurements, with averaged number equal to 2.06. This is in good agreement with elemental analysis data presented in table 1 and 2.

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	wt%(1st measurement)	Wt%(2nd measurement)	%	%
Si	44.96(0.07)	45.50(0.10)	1.600	1.619
Al	21.19(0.06)	21.19(0.08)	0.785	0.785
Na	0.0	0.0	0.0	0.0
O	34.18(0.07)	33.37(0.10)	2.136	2.111

Table S3: EDX data for sample 3, these were collected twice. Both measurements are shown in columns 2 and 3.

Calculation of Si/Al from EDX data gives us 2.03 and 2.06 for first and second measurements, with averaged number equal to 2.05.
This calculation assumes an interrupted framework, so this number is naturally in good agreement with Si/Al ratio for sample 3 in table 1 and 2.

3. Synthesis of Na-A zeolite and exchange

For zeolite A we:

1. mixed 46.3g of water with 15.67g of Sodium Aluminate. Stirred and dissolved completely;
2. mixed (1) with 110.6g of tetramethyleammoium hydroxide, stirred;
3. mixed (2) with 45.8g of Ludox HS-40 Silica, stirred for 30 minutes.
4. Incubated the resulting gel for 40 hours.
5. Crystallised in the oven at 90degC for 24 hours.

After crystallization, the mixture was washed until pH neutral, and dried in the oven at 100degC. The resulting power yield was about 35g. This sample is called 1a.

For exchange we used about 500ml of deionised water, 30g of ammonium nitrate for 30g of zeolite. All of the above were mixed together and stirred at 60degC for 6 hours - three times. Between each exchange, we washed the powder with water and dried in the oven at 100degC for about 6 hours. This sample is called 2a.

4. X-ray diffraction of zeolite A (sample 1a) and exchanged NH4-A (sample 2a)

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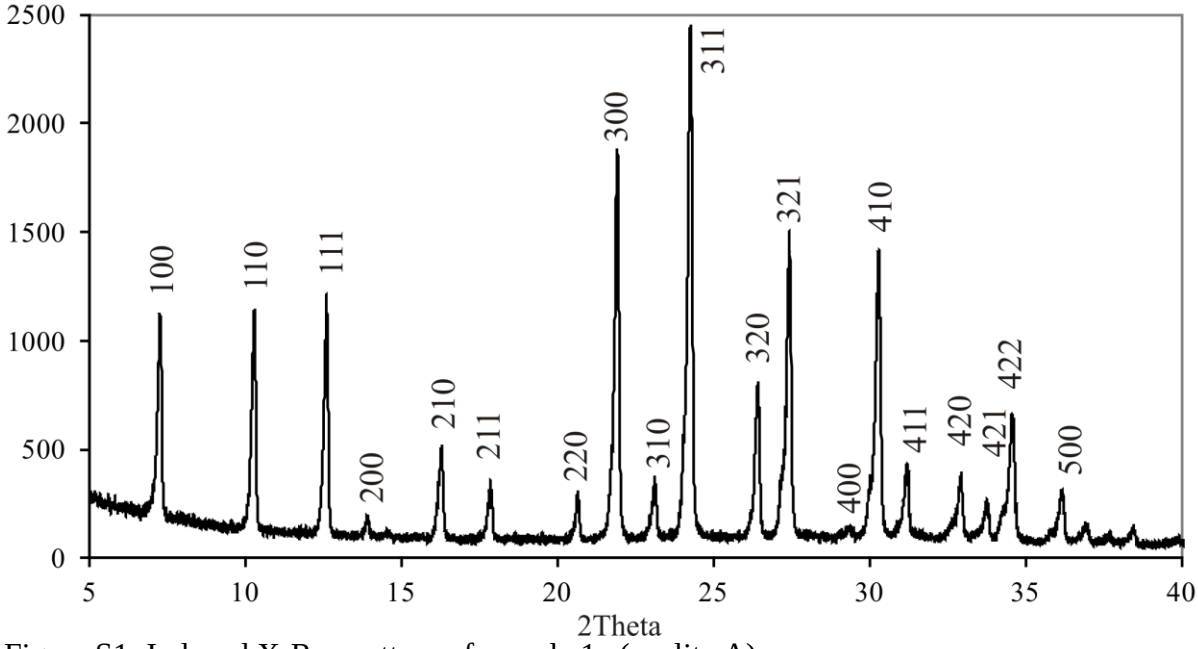

Figure S1: Indexed X-Ray pattern of sample 1a (zeolite A).

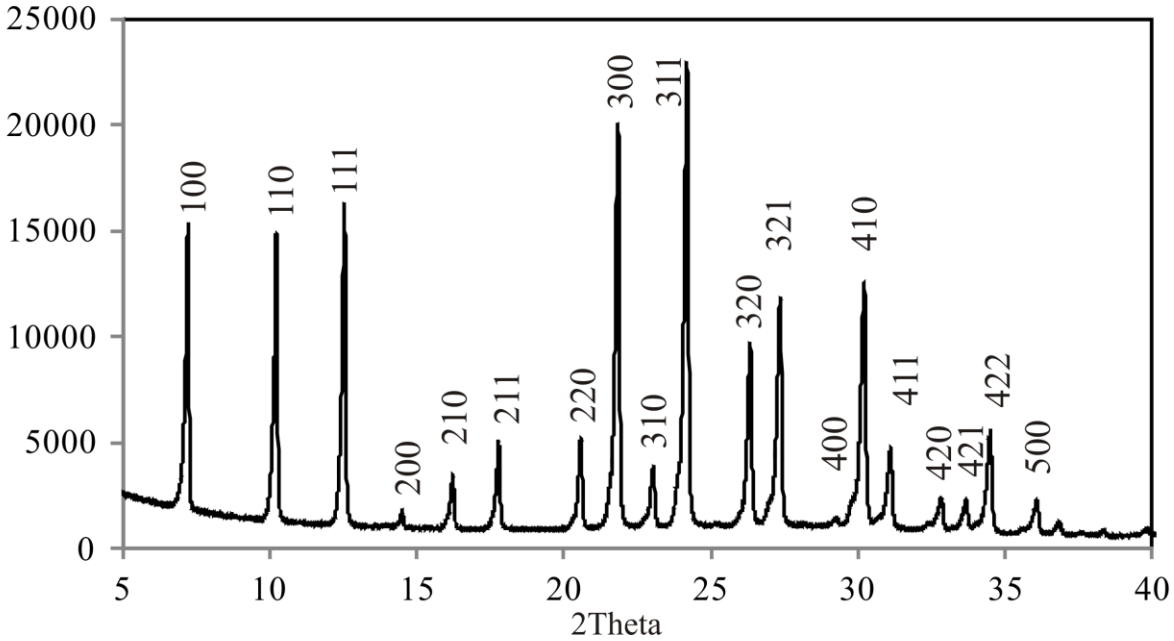

Figure S2: Indexed X-Ray pattern of exchanged sample 2a (zeolite NH_4-A).

5. MAS SS NMR data on zeolite A

	Si/Al	δ(ppm)				
		Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)
1a (Na-A)	1.57	-88.57	-93.77	-99.65	-105.44	-110.40
2a(NH_4-A)	1.60* 1.91**	-91.32	-95.24	-100.24	-105.94	-110.21

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Table S4: NMR data for Na-A and NH_4-A zeolites from ^{29}Si spectra. *Value of Si/Al ratio calculated from ^{29}Si spectra. **Value recalculated from 27Al spectra, which takes into account the appearance of octahedral aluminiums.

Table 3 shows chemical shifts for Si local environments in Na-A and NH_4-A zeolites. As we replace Na to ammonium, we see a shift of two peaks Si(4Al) and Si(3Al), other three peaks hardly move. The values for Si/Al ratio listed in table were calculated using equation (4). The deconvolution of the ^{29}Si spectrum of Na-A leads to ratio of intensities of five peaks of 3.61:4.46:3.49:2.40:0.72, leading Si/Al=1.57. The deconvolution of the ^{29}Si spectrum of NH_4-A leads to ratio of intensities of five peaks of 3.15:4.80:3.71:2.40:0.73, leading Si/Al=1.60.

Using the ^{27}Al NMR data, if we assume that all aluminiums in a tetrahedral peak have coordination number 4 and all aluminiums in octahedral peak have coordination number 6, than average coordination number for NH_4-A zeolite is 4.1.