Supplementary Information for:

Ammonia decomposition catalysis using non-stoichiometric lithium imide

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Section A – Mass spectrometry data analysis description

An in-house computer program was used to analyse the data from the mass spectrometer. For all data, the mass spectrometry output was converted into gas fractions and then percentage conversions were obtained from an average of typically 1000 seconds of data for each temperature after equilibration had been reached.

The raw data obtained from the mass spectrometer during the neutron diffraction experiment was adjusted to take account of the differing electron impact ionization cross-sections for the species detected. These cross-sections were calculated relative to that for the Ar⁺ peak at m/z = 40 for standardised mixtures of H₂/Ar, D₂/Ar, NH₃/Ar, ND₃/Ar, N₂/Ar for the peaks at m/z = 2, 4, 17, 20 and 28 respectively. The cross-sections for the partially deuterated species were estimated as being in a linear relationship with those of the fully deuterated and the fully hydrogenated species.

During the course of the experiment, the mass spectrometer experienced a step when moving from one order of magnitude to the next (e.g. 10^{-6} mbar to 10^{-7} mbar). These steps were removed by simply subtracting the step value from the data remaining. If two steps were present of slightly differing magnitudes, then a linear relationship was assumed for subtracting the data in between.

Section B – Fitting Procedures

A separate program was used to fit the data via a least-squares algorithm. Data from the constant flow, variable temperature experiments (Figure 3 in the manuscript) were fitted using one of two sigmoidal functions. For single process curves (sodium amide), the function was of the form:

 $C = 1 - \exp [-\exp (A / R - E_a / RT)]$

Where C is the ammonia conversion, R is the universal gas constant, T is the temperature in Kelvin, and A and E_a are refined values for a pre-exponential factor and an activation energy, respectively.

For dual process curves (blank reactor, silica/alumina-supported nickel and alumina-supported ruthenium), the function was of the form:

 $C = 1 - \alpha \exp \left[-\exp \left(A_1 / R - E_{a1} / RT \right) \right] - \left(1 - \alpha \right) \exp \left[-\exp \left(A_2 / R - E_{a2} / RT \right) \right]$

Where C is the ammonia conversion, R is the universal gas constant, T is the temperature in Kelvin, and A and E_a are refined values for a pre-exponential factor and an activation energy, respectively, for each process (1 and 2).

The values for each parameter extracted from the fitting procedure are tabulated below.

Table S1 - Single process sigmoid fitting results for sodium amic

Parameter	Value (error)
А	0.163(11)
Ea	121(8)

Table S2 - Dual	process	sigmoid	fitting	results

Sample	A ₁	E _{a1}	A ₂	E _{a2}
Blank reactor	0.245(20)	175(15)	0.195(16)	163(13)
Silica/alumina-supported nickel	0.152(20)	124(12)	0.151(22)	111(20)
Alumina-supported ruthenium	0.096(9)	67(10)	0.190(16)	145(11)
Lithium amide	0.188(3)	133(4)	0.67(2)	480(17)

Section C – X-ray Diffraction Pattern of Li₂ND Sample



Figure S1- Powder X-ray diffraction pattern of the sample of deuterated lithium imide used for the neutron powder diffraction experiment.

Section D – Crystallographic Reduction of Tetragonal Lithium Amide Cell

The structural data listed in Table S3 for $LiNH_2$ was obtained from David et al. (2007) – ref 18.

Table S3 - Structural data for LiNH₂ after David et al. (2007): space group I-4 a=5.04309(7)Å c=10.2262(3)Å.

Atom	Wyck	Х	у	Z	occ
Li1	2a	0.00	0.00	0.00	1.0
Li2	2d	0.00	0.50	0.25	1.0
Li3	4f	0.50	0.00	0.003(4)	1.0
N1	8g	0.234(2)	0.246(5)	0.1130(6)	1.0
H1	8g	0.23(2)	0.18(2)	0.194(9)	1.0
H2	8g	0.37(2)	0.35(2)	0.12(2)	1.0

Table S4 - Transformation and unit cell reduction of LiNH₂ structural data from Table S3 to conform to the average Li₂NH face-centred cubic lattice, combining a shift in coordinates such that nitrogen is located near the origin, followed by halving of the *c*-axis. The net transformation and unit cell reduction corresponds to x_{new} = x-0.25; y_{new} = y-0.25; z_{new} = 2×(z-0.125).

Atom	х	у	Z
Li1	-0.25	-0.25	-0.25
Li2	-0.25	0.25	0.00
Li3	0.25	-0.25	-0.244(8)
N1	-0.016(2)	0.004(5)	-0.024(12)
H1	-0.02(2)	-0.07(2)	0.14(2)
H2	0.12(2)	0.10(2)	-0.01(4)

Table S5 - Symmetrisation of the translated and reduced LiNH₂ structure to conform with Fm3m space group symmetry.

Atom	Wyck	Х	у	Z	occ
Li1	8c	0.25	0.25	0.25	0.5
N1	4a	0.00	0.00	0.00	1.0
H1	96j	0.00	-0.07(2)	0.16(2)	1/24
H2	96j	0.14(2)	0.10(2)	0.00	1/24

Table S6 - Fixed hydrogen positions corresponding to N-D bond length 1.05Å and a reference lattice parameter of 5.18Å.

Atom	Wyck	Х	у	Z	occ
Li1	8c	0.25	0.25	0.25	0.5
N1	4a	0.00	0.00	0.00	1.0
H1	96j	0.00	-0.081	0.186	1/24
H2	96j	0.165	0.118	0.00	1/24



Section E – POLARIS Blank Cell Ammonia Decomposition Experiment

Figure S2 – POLARIS empty sample cell ammonia decomposition experiment, showing a) pressure and deuterated ammonia flow rate, b) the temperature and ammonia decomposition efficiency and c) the mass spectrometry data for the various m/z traces examined in this experiment.





Figure S3 - Neutron powder diffraction patterns of the lithium imide sample taken at the ISIS Facility, showing data from detector bank four of the POLARIS instrument. Data shown are regions a) i and b) ii from Figure 6 in the main text. Tick marks indicate the peak positions of phases refined in the Rietveld analysis. The observed pattern is shown in black, the calculated pattern in red, and the difference between the two patterns is shown in grey. The Rwp value for the fits to the data were 3.835 and 3.124, respectively.



Figure S4 - Neutron powder diffraction patterns of the lithium imide sample taken at the ISIS Facility, showing data from detector bank four of the POLARIS instrument. Data shown are regions a) iii and b) iv from Figure 6 in the main text. Tick marks indicate the peak positions of phases refined in the Rietveld analysis. The observed pattern is shown in black, the calculated pattern in red, and the difference between the two patterns is shown in grey. The Rwp value for the fits to the data were 3.482 and 3.237, respectively.



Section G – Exponential Fits to Mass Spectrometry Data

Figure S5 – Exponential fits to (a) H_2 and (b) HD signals after the switch to NH₃ in the POLARIS experiment. The refined parameters *a* and *b* were 0.2379(6) and 1.273(7) for H₂, and 0.234(1) and 3.71(6) for HD, based on a least-squares fitting procedure.

Section H – Long duration experiment data



Figure S6 – Plots of a) gas fractions and reaction temperature, and b) ammonia conversion produced by a 60 sccm ammonia gas flow over a 0.5 g sample of lithium imide. The sample was heated under argon gas flow to 550 °C prior to exposure to ammonia.