Supporting information to:

Ammonia decomposition on $LaV(O,N)_{3-\delta}$ surfaces: toward a mechanistic understanding

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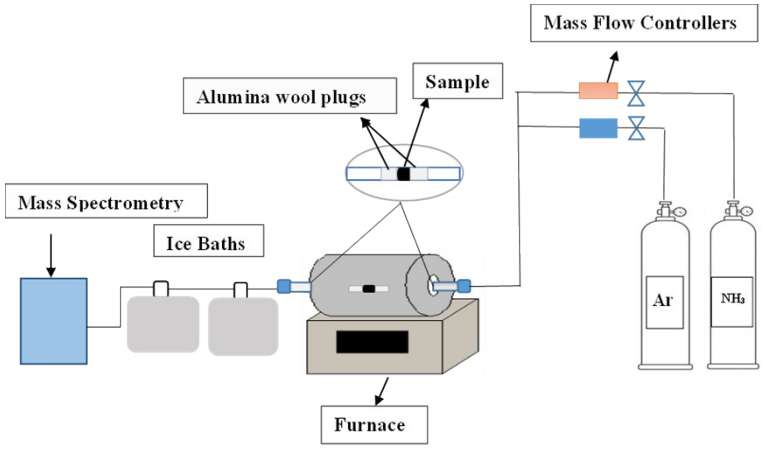

Figure S1 Experimental setup for ammonia decomposition reaction.

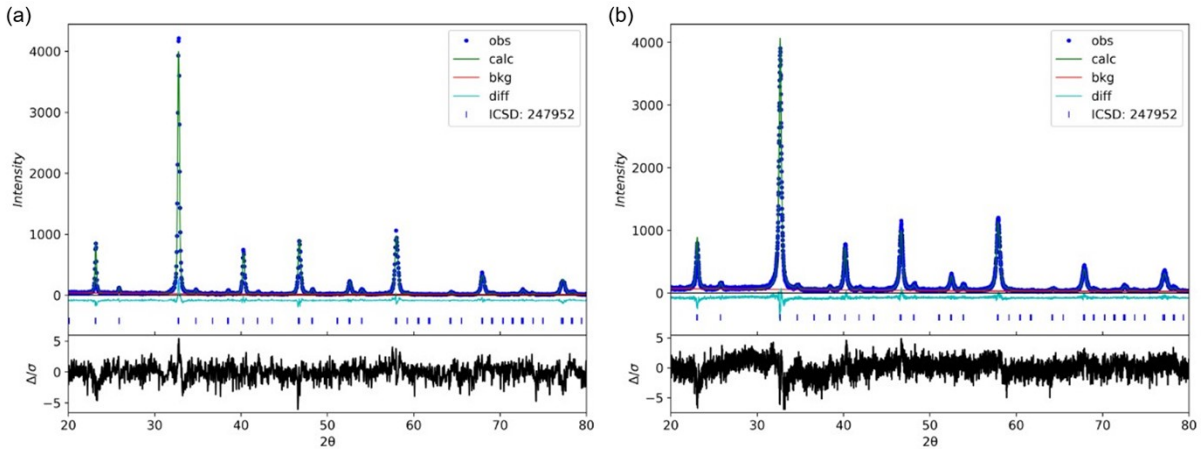

Figure S2 Rietveld refinement plot of (a) LaVON-S and (b) LaVON-P, respectively.

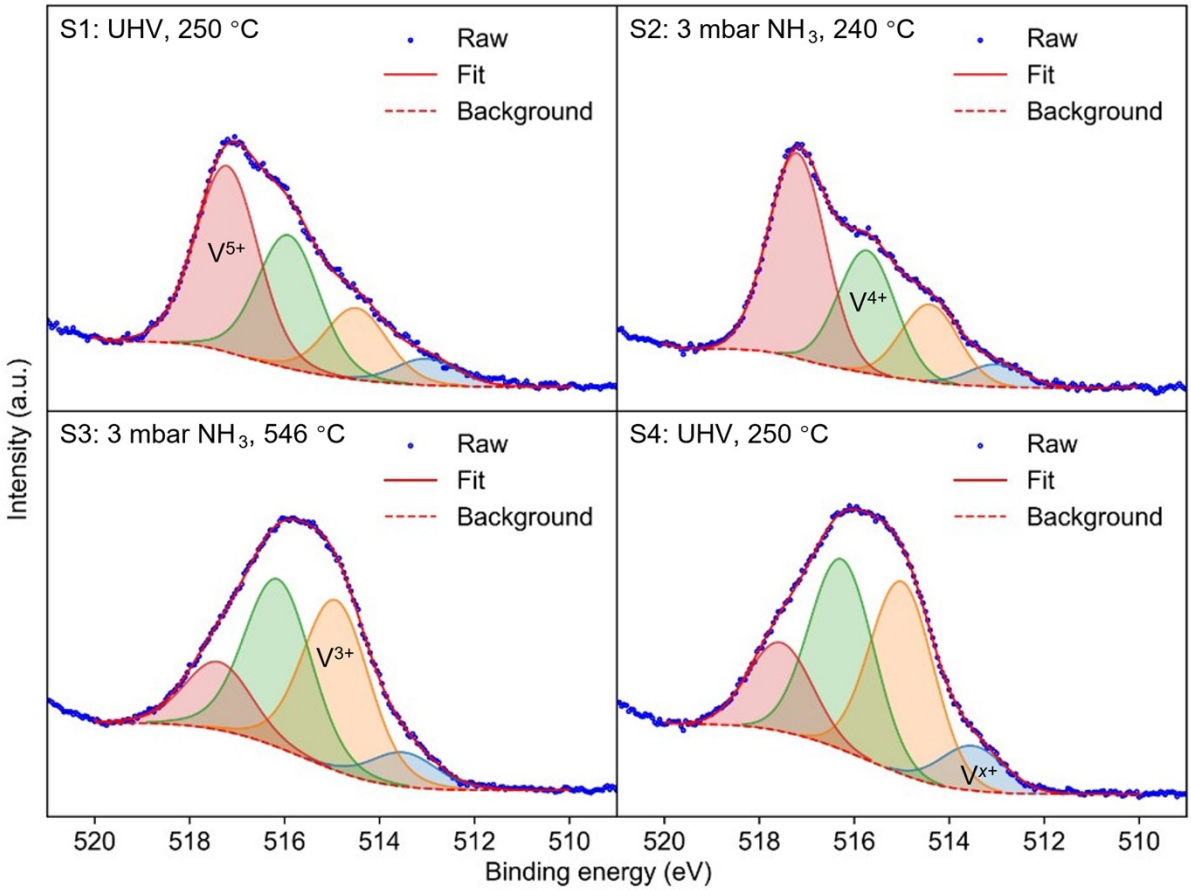

Figure S3 Deconvolution of the NAP-XPS spectra of V $2p_{3/2}$. V^{x+} represented the V cations with lower oxidation states ($0<x<3$).

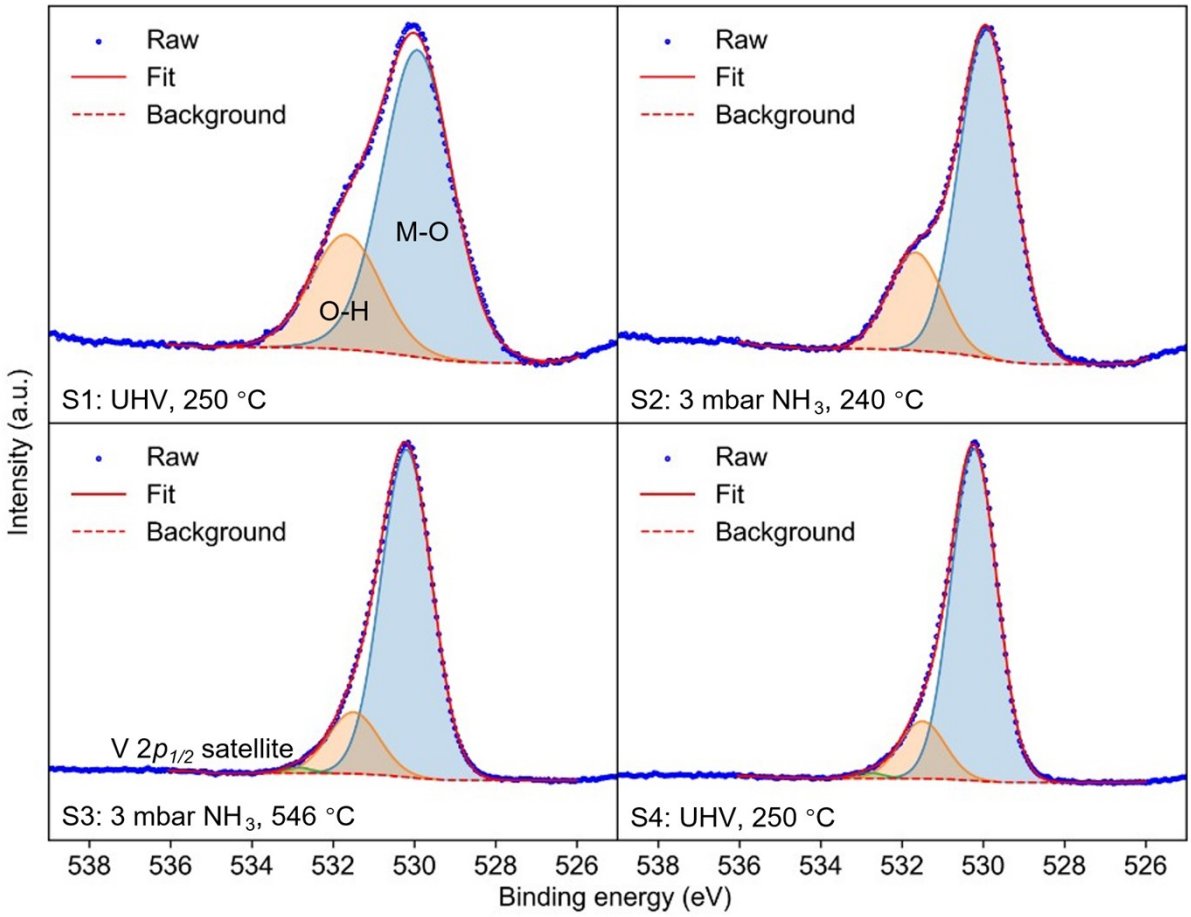

Figure S4 Deconvolution of the NAP-XPS spectra of O 1s.

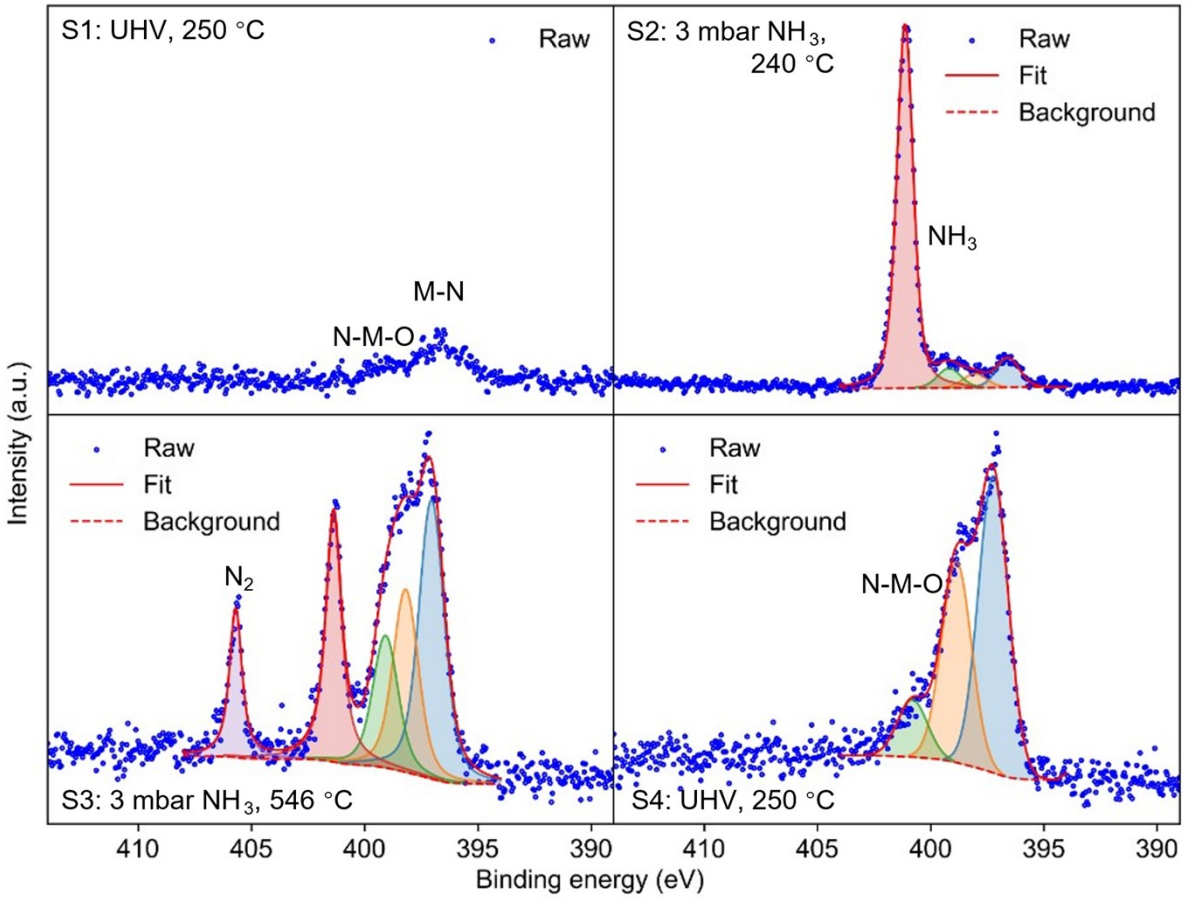

Figure S5 Deconvolution of the NAP-XPS spectra of N 1*s*. The fitting of S1: UHV, 250 °C is absent due to the low signal intensity and composition ambiguity.

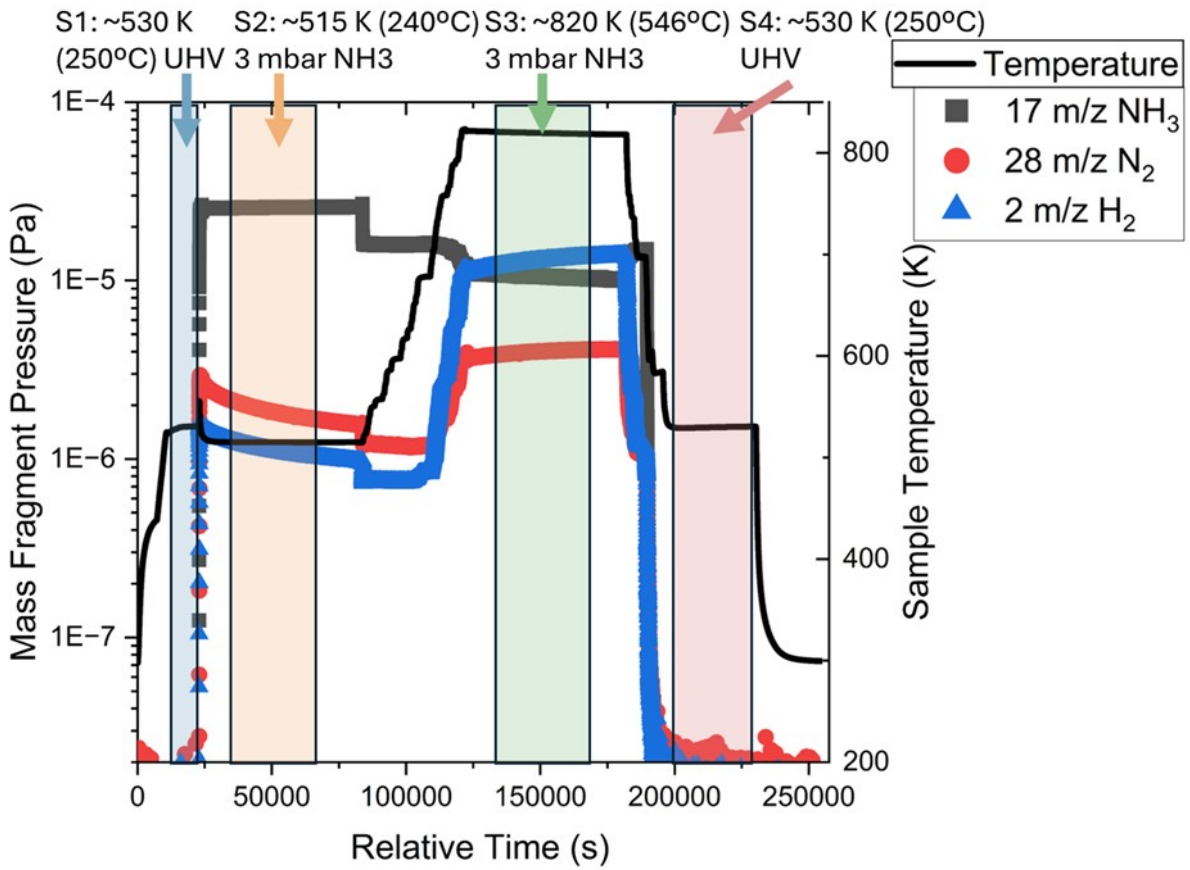

Figure S6 NAP-XPS instrument trace, correlating mass fragments of ammonia to products, with temperature recorded on the sample plate. Transparent boxes indicating approximate timing of when XPS measurements were taken with their corresponding conditions.

Table S1 The energy along the reaction path for ammonia decomposition on different surfaces. The reference energy (ΔE = 0 eV) refers to an isolated NH_3 molecule and naked surfaces.

ΔE (eV)	*+NH_3 (g)	NH_3*	NH_2*+H*	NH*+2H*	N*+3H*	*+0.5N_2(g)+1.5H_2(g)
$LaVO_3$	0	-0.92	-1.64	0.05	1.77	1.09
$LaV(O,N)_{3-\delta}$	0	-0.86	-2.24	-3.32	-2.62	1.09
$LaVON_2$	0	-0.93	-1.87	-0.91	-0.29	1.09

Table S2 Deconvolution model of the V 2*p* and O 1*s* spectra. FWHM is short for full width half maximum.

	S1: UHV, 250 °C			S2: 3 mbar NH_3, 240 °C		
	Binding energy (eV)	FWHM (eV)	Atomic ratio (%)	Binding energy (eV)	FWHM (eV)	Atomic ratio (%)
V $2p_{3/2}$ V^{5+}	517.2	1.6	44.7	517.2	1.4	48.4
V $2p_{3/2}$ V^{4+}	515.9		31.9	515.7		28.4
V $2p_{3/2}$ V^{3+}	514.5		17.1	514.4		18.0
V $2p_{3/2}$ V^{x+}	513.0		6.3	513.0		5.2
O 1*s* MO	529.9	2.0		529.9	1.6	
O 1*s* -OH	531.7			531.7		
	S3: 3 mbar NH_3, 546 °C			S4: UHV, 250 °C		
	Binding energy (eV)	FWHM (eV)	Atomic ratio (%)	Binding energy (eV)	FWHM (eV)	Atomic ratio (%)
V $2p_{3/2}$ V^{5+}	517.4	1.7	15.5	517.6	1.6	17.2
V $2p_{3/2}$ V^{4+}	516.1		38.1	516.3		36.9
V $2p_{3/2}$ V^{3+}	514.9		38.6	515.0		37.2
V $2p_{3/2}$ V^{x+}	513.5		7.8	513.5		8.7
O 1*s* MO	530.2	1.5		530.2	1.3	
O 1*s* -OH	531.5			531.5		
V 2*p* Satellite	532.7	0.8		532.8	0.9	

Table S3 Deconvolution model of the N 1*s* spectra. FWHM is short for full width half maximum. The peak fits presented only represent the best possible fits with least components and may not attribute to the actual compositions.

	S1: UHV, 250 °C		S2: 3 mbar NH_3, 240 °C	
	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)
M-N			396.6	
N-M-O (1)			398.0	1.2
N-M-O (2)			399.2	
-NH_3			401.1	0.9
	S3: 3 mbar NH_3, 546 °C		S4: UHV, 250 °C	
	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)
M-N	397.0		397.2	
N-M-O (1)	398.2	1.3	398.9	1.6
N-M-O (2)	399.1		400.8	
-NH_3	401.4	0.9		
-N_2	405.7	0.7		