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An *in-situ* study on solid state decomposition of Ammonia Borane: unmitigated by-product suppression by naturally abundant layered clay mineral

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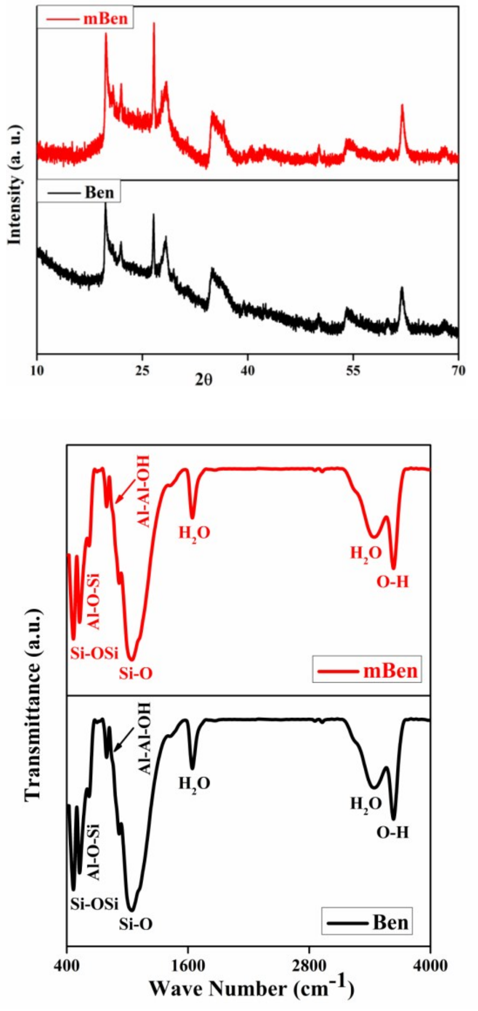

Figure S1. **(a)** XRD pattern **(b)** FTIR spectra of Pure(Ben) and modified Bentonite(mBen)

1. mBen characterization: XRD study: phases: 1) Halloysite 10A 19.73°[100], 26.66° [003], 35.09° [110], 54.28° [006], 62.02° [300], 73.5° [220]; 2) Pyrophyllite 20.88° [020], 22.06° ° [110], 28.37°

[006], 42.37° [043], 50.08° [224], 67.99° [158], 76.64° [336]. FTIR spectroscopy: structural O-H stretching frequency 3632 cm^{-1}, absorbed moisture 3400cm^{-1}, AL-AL-OH bending vibration 918 cm^{-1}, Si-O stretching freq 1048cm^{-1}, Al-O-Si bending frequency 525cm^{-1}, Si-O-Si bending frequency 468cm^{-1}.

2. Size Strain analysis methods

Scherrer method

$$Cos\theta = \frac{1k\lambda}{\beta\ \delta}$$

where,

δ is the size of the ordered domain

k is the shape factor, conventionally and here considered as 0.9

λ is thewavelength of Cu $K_{\alpha 1}$beam used for data acquisition

β is peak broadening, expressed through the FWHM of peaks

θ is the Bragg angle of reflections

The most widely used method for crystallite size determination is using Scherrer formula20. The simplified assumption made in Scherrer formula is that the peak broadening is solely contributed by the change in the crystallite size. Thus, a linear fit of the peak position vs the peak broadening can directly provide the crystallite size as shown in (Fig. S2) in ESI. However, the total peak broadening is attributed to both changes in crystallite size as well as the lattice strain components. The effect of the lattice strain on the peak broadening is not included in Scherrer formula while appears in the well-known Williamson Hall expression.

The assumption made in the Williamson Hall approach is that the total peak broadening is a linear combination of the strain and size components and uniformly isotropic crystal growth. The Williamson Hall expression is as follows:

$$\beta_{hkl}cos\theta = 4\varepsilon sin\theta + k\lambda/\delta$$

The lattice strain (ε) was derived from differentiation of the Bragg's law and expressed as the error in the interplanar spacing. For both the Scherrer and Williamson Hall method, the background of the XRD line profile was subtracted and Kα2 stripped using Rachinger method. The profiles were fitted in to pseudovoight lineshape and the obtained FWHM and 2θ values were used to evaluate the crystallite size and lattice strain [Fig. S3]. Although WH is more accurate for consideration of the strain component, but for crystallite size determination, both WH and Scherrer methods assume the uniform growth of crystallite size. However, Warren Averbach method operates through representation of the line profile in reciprocal space, thus have an advantage in terms of better accuracy. In this work, the peak profiles were fitted to the XRD line profiles using a Fourier cosine deconvolution program in the commercial software package Xpowder 12. The most significant advantage of the Warren Averbach method over other methods is its process of elimination of instrumental broadening and operational inconsistencies.

The warren Averbach equation suggests that the real values of Fourier cosine coefficients are sum of the size and the strain coefficients (S2 in ESI) and finally expressed as

$$ln(A_{L,q}) = ln(A_L^s) - 2\pi^2 L^2 q^2 \langle \varepsilon_L^2 \rangle$$

Notably, L is here stated as correlation length, sometimes also as ‘Fourier length’, and denoted as the perpendicular length between the two consecutive lattices or as the distance at which atom locations can be predicted. The nomenclatures of the parameters in Warren Averbach equation is provided in S2.

The plot of pure size dependent Fourier-Cosine coefficients (A_L^s) versus correlation length L, leads to determination of the crystallite size (Fig. S4), or more appropriately termed as “coherently ordered domain size”. The plot also provides RMS strain, averaged over a distance in real space.[1] The notable observation in the Warren Averbach is the hyperbolic distribution for the size strain plot (Fig. 2d), suitably explaining the relation of size induced strain. The elimination of any hook effect indicates introduction of insignificant operational error. [2]–[4]

Warren Averbach derivation

The instrumental profile was calculated by using Caglioti approximation and selected distribution function (pseudo Voigt) of a standard sample. polycrystalline Silicon was used for calibration of instrumental broadening.

WA method states that the absolute values of Fourier cosine coefficients are sum of the size and the strain coefficients and expressed as

$$A_{L,q} = A_L^s + A_{L,q}^\varepsilon$$

Where,

$A_{L,q}$ is the absolute cosine Fourier coefficient of the true profile

A_L^s is the size dependent absolute cosine Fourier coefficient

$A_{L,q}^{\varepsilon}$ is the strain (ε), L and q dependent absolute cosine Fourier coefficient

q is the diffraction vector expressed as $\frac{2\sin\theta}{\lambda}$

The mathematical expression of the strain dependent Fourier coefficient, as given by Turunen et al., can be stated as

$$A_{L,q}^{\varepsilon} = \left\langle cos\frac{2\pi L\varepsilon(L)}{d} \right\rangle$$

Replacing d from Bragg's law, and by rearranging the equation, obtained the following expression [5]

$$A_{L,q}^{\varepsilon} = e^{-2\pi^2 L^2 q^2 \left\langle \varepsilon_L^2 \right\rangle}$$

Substituting (9) in (7) and then taking logarithm of eqn (7) provides the final Warren averbach equation

$$ln\left(A_{L,q}\right) = ln\left(A_L^S\right) - 2\pi^2 L^2 q^2 \left\langle \varepsilon_L^2 \right\rangle$$

Therefore from the linear plot of $ln\left(A_{L,q}\right)$ vs. q^2 for a fixed L value, the A_L^Svalue can be evaluated from the intercept of the straight line and the $A_{L,q}^{\varepsilon}$ from the slope of the fitted straight line.

For the computation purpose, 2θ step size, q step size and Δq for the analysis were maintained to be $0.26056 * 10^{-3}$, 0.00003 and 0.018. Thereafter the deconvolution of the observed XRD profile provides with the structural profile of the sample pattern. The absolute cosine Fourier coefficients obtained from the individual structural profiles *(hkl)* is then normalized and plotted vs L.

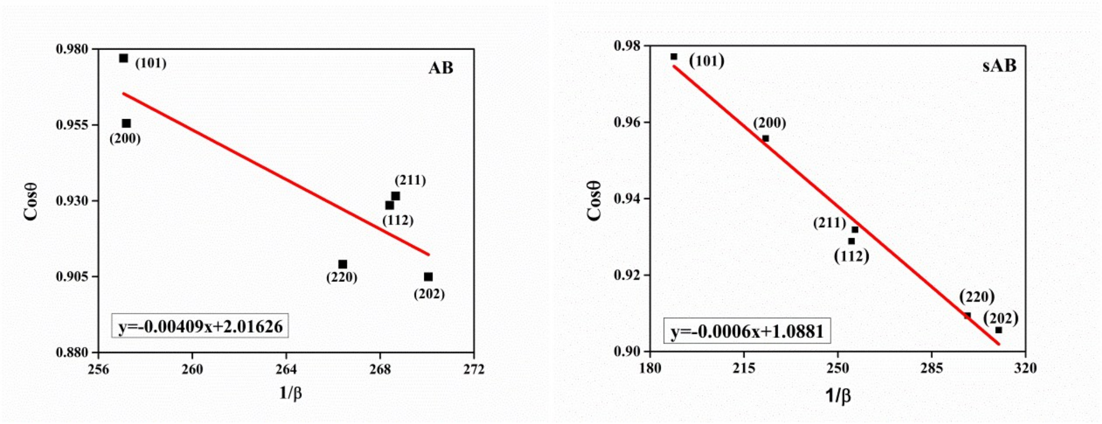

Figure S2.Scherrer plot for pure ammonia borane (AB) and supported AB (sAB)

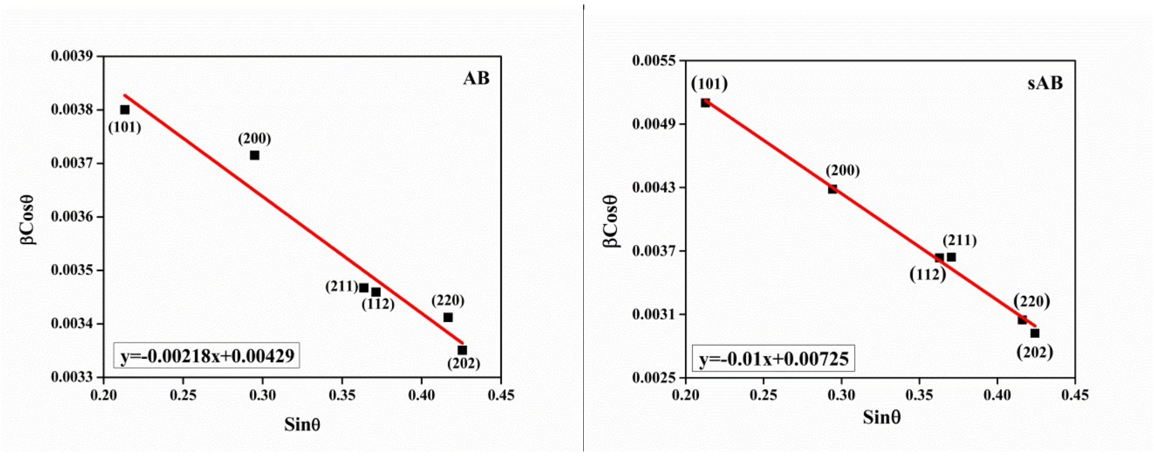

Figure S3.Williamson Hall plot for pure ammonia borane (AB) and supported AB (sAB)

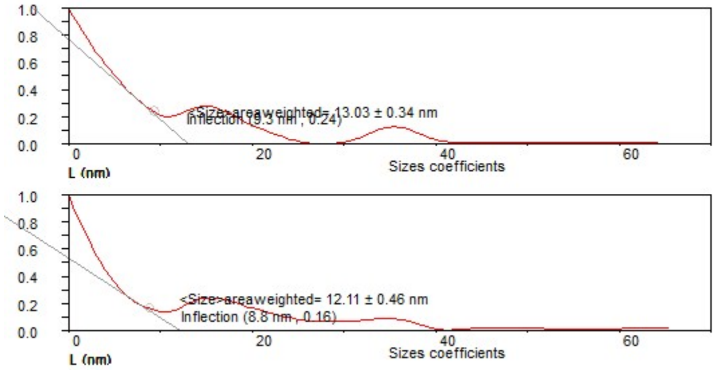

Figure S4. Size coefficient vs. L plot (Warren Averbach) for pure and supported AB (AB and sAB respectively)

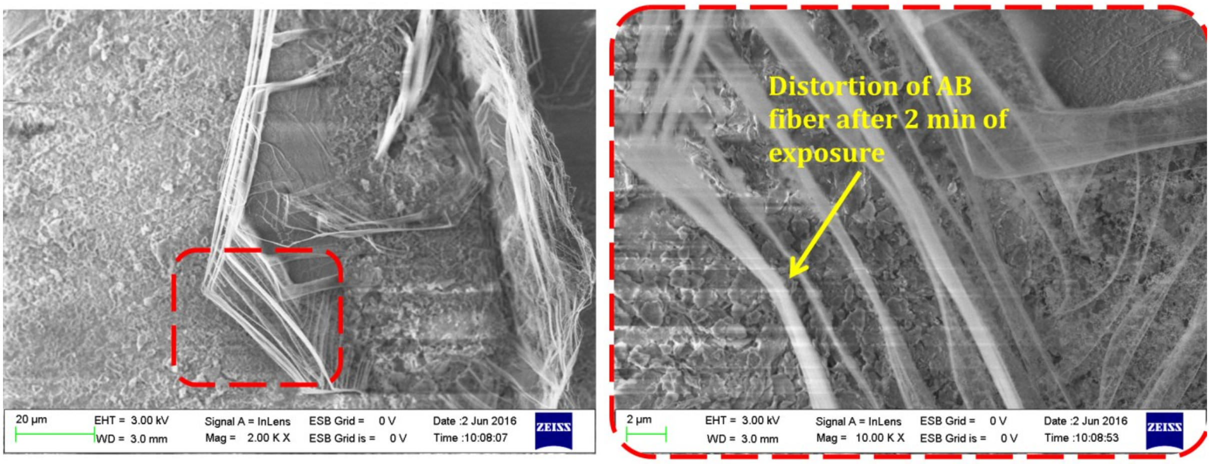

Figure S5. Electron beam induced damage of sAB under scanning electron microscope (SEM).

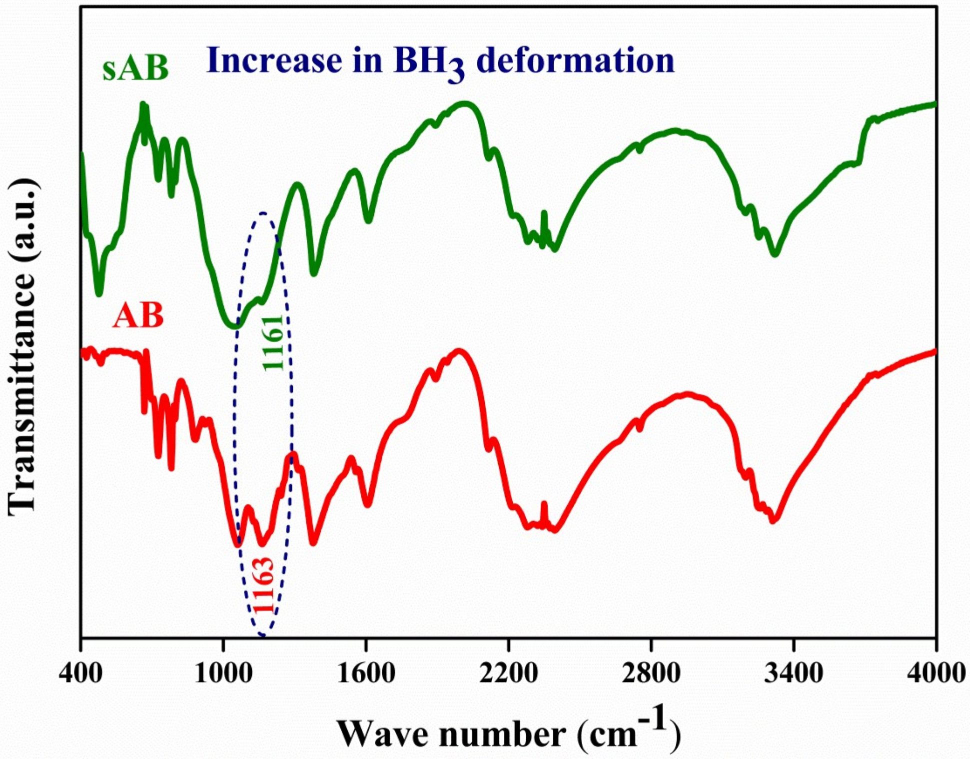

Figure S6: FTIR spectra of AB and sAB

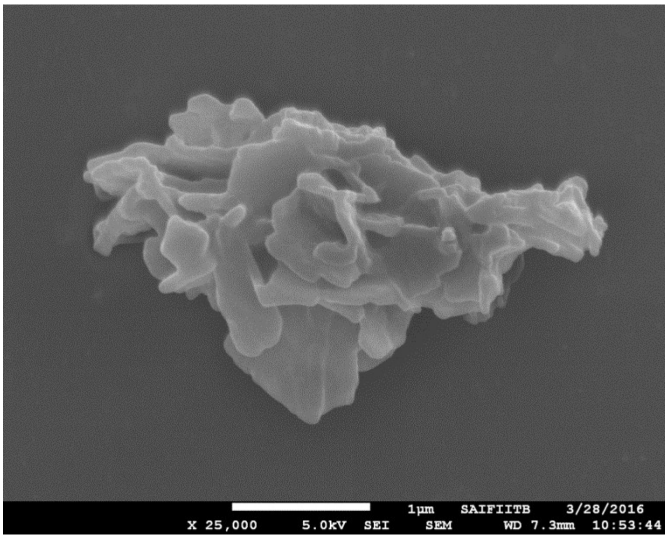

Figure S7: SEM image of pure ammonia borane

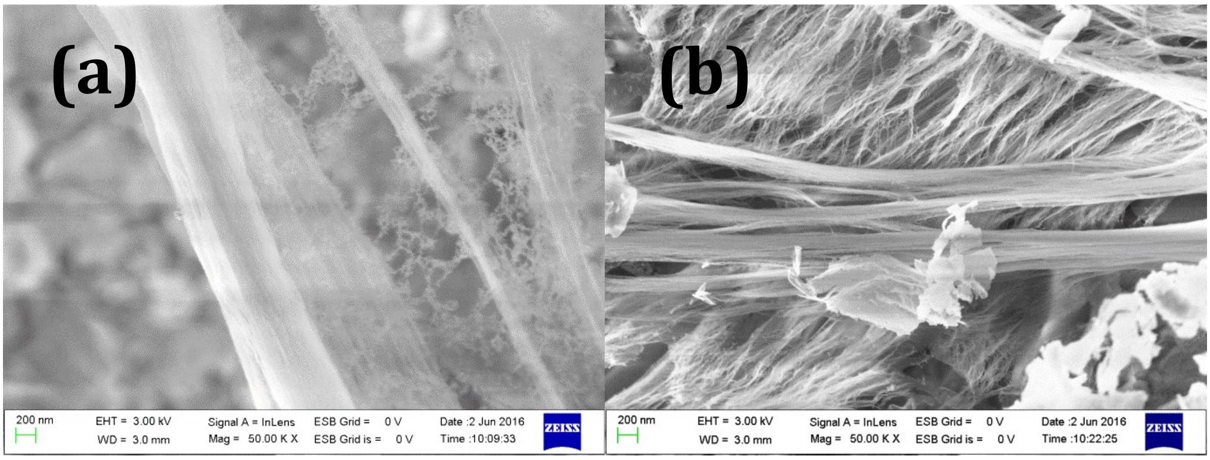

Figure S8: SEM image of (a) preheated and (b) post heated sAB

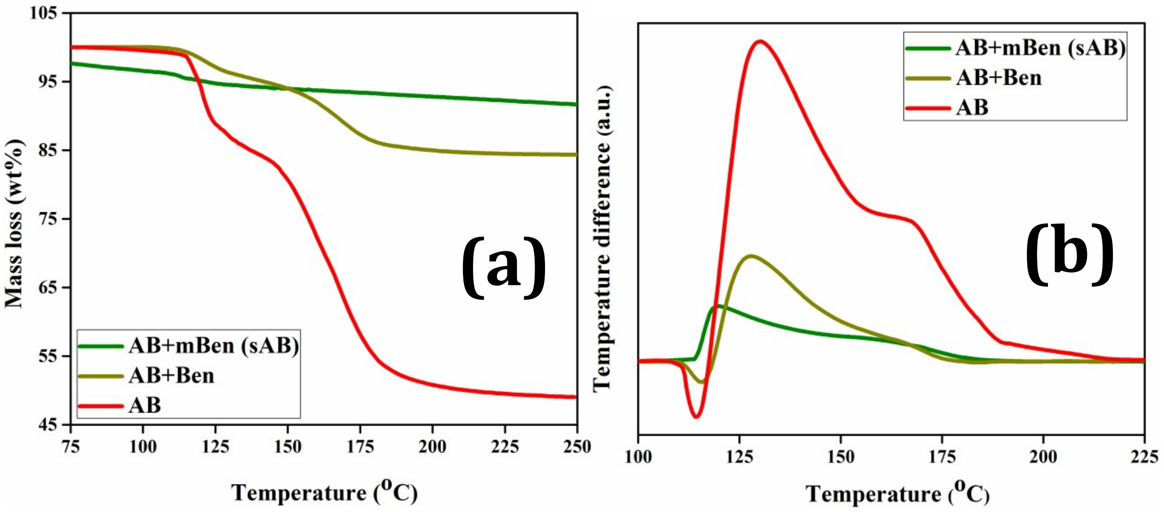

Figure S9. (a) TGA and (b) DTA of pure AB (red), AB+Ben (dark yellow) and AB+mBen (green)

References

[1] R. Delhez, T. H. de Keijser, and E. J. Mittemeijer, "Determination of Crystallite Size and Lattice Distortions through X-Ray Diffraction Line Profile Analysis," *Anal. Chemie*, vol. 312, pp. 1–16, 1982.

[2] V. D. Mote, Y. Purushotham, and B. N. Dole, "Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles," *J. Theor. Appl. Phys.*, vol. 6:6, pp. 2–9, 2012.

[3] D. Balzar, N. Audebrand, M. R. Daymond, A. Fitch, A. Hewat, J. I. Langford, A. Le Bail, D. Louer, O. Masson, C. N. McCowan, N. C. Popa, P. W. Stephens, and B. H. Toby, "Size – strain line-broadening analysis of the ceria round-robin sample," *J. Appl. Crystallogr.*, vol. 37, pp. 911–924, 2004.

[4] B. Marinkovic, R. R. de Avillez, A. Saavedra, and F. C. R. Assuncao, "A Comparison between the Warren-Averbach Method and Alternate Methods for X-Ray Diffraction microstructure analysis of polycrystalline specimens. *Mater Res*. 2001;4(2):71-76. doi:10.1590/S1516-14392001000200005