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Supplemental information for:

Titanium Hydrazide Gels for Kubas Type Hydrogen Storage

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The difference between system target and materials target

A hydrogen storage system normally exhibits a lower volumetric and gravimetric performance than that of the adsorbing materials in isolation. Therefore, only materials with volumetric and gravimetric adsorption values higher than the DOE standards are promising. Nevertheless, the use of DOE gravimetric and volumetric system targets is still necessary in evaluating the adsorption performance of a material as a benchmark with the idea in mind that the results in a laboratory on small sample quantities may not be representative of the final net performance of a hydrogen storage system employing this material.

Experimental Section

All chemicals were purchased from Sigma-Aldrich and used without further purification. Diethyl ether and toluene were distilled over sodium/benzophenone to remove oxygen and moisture. Distilled solvents were transferred to a Schlenk flask using a canula. Dry Ar gas was bubbled through the flask for 30 min before transferring into a dry-box. Triethylamine was distilled over CaH_2 and bis(trimethylsilyl)methyl chloride was distilled over P_2O_5 before use. H_2 grade 6.0, N_2, Ar, and He were obtained from Praxair Canada. Manipulations were performed in an Ar glove box and on an Ar Schlenk line as low valence Ti species are extremely sensitive to air and moisture. Anhydrous hydrazine was distilled from hydrazine hydrate using a procedure described elsewhere.[1] Hydrazine is toxic, flammable, explosive and must be handled with extreme care. $TiCl_3.0.67\{N(C_2H_5)_3\}$ was synthesized from the reaction of $TiCl_3$ and triethylamine.[2] $LiCH(SiMe_3)_2$ was prepared from $(Me_3Si)_2CHCl$ and Li. $Ti\{CH(SiMe_3)_2\}_3$ was prepared from $TiCl_3.0.67\{N(C_2H_5)_3\}$ and $LiCH(SiMe_3)_2$ by a modified procedure obtained from Baker et al.[3] $Ti\{CH(SiMe_3)_2\}_3$ obtained from the previous reaction as a green viscous oil was quantified by weighing by difference and then dissolving in fresh distilled toluene before further use. The optimized reactions with hydrazine ratios of 1:1 and 1:1.5 relative to Ti are described below. Heating under vacuum after the initial synthesis step is required to drive off and evaporate any further alkane produced. Higher and lower ratios than these were not explored because in previous works by our group were shown in every case to negatively impact hydrogen storage results.[4]

Preparation of 1:1 titanium hydrazide gels. 50 ml of toluene was added to 3.00g (5.7 mmol) of $Ti\{CH(SiMe_3)_2\}_3$ with stirring. 0.18 mL (5.7 mmol) of hydrazine was then added dropwise into the solution. The resulting solution turned dark within minutes and was then stirred at room temperature for 24 h at 25 °C, and 100 °C for 72 h. The solution was then filtered and a solid product was obtained, which was then heated in vacuum for 8 h at room temperature followed by a further 8 h at 100 °C. This sample was named A100. Heating the freshly filtered material at 150 °C under vacuum for 8 h gives A150.

Preparation of 1:1.5 titanium hydrazide gels. The same procedure as above was applied, using 0.27 mL hydrazine. The sample heated at 100 °C for 8 h was labelled B100 and the sample heated at 150 °C for 8 h was named B150.

Hydrogenation of titanium hydrazide gels. 0.3000 g of A100 (or B100) was added to the Advanced Materials PCI sample chamber, which was connected to the Gas Reaction Controller. The sample was soaked with H_2 at 5 bar after which the temperature was raised to 150 °C before H_2 pressure was adjusted to 80 bar. After 2 h the hydrogen was evacuated, and heating was continued for another 2 hours. The hydrogenated product was given the annotation A100-H_2 (or B100-H_2).

Characterization. Powder X-ray diffraction (PXRD) was performed on Siemens D-500 diffractometer with a Cu Kα radiation (40 kV, 40 mA) source. The step size was 0.02° and the counting time was 0.3s for each step. Diffraction patterns were recorded in the 2θ range 1.5 - 52°. Samples for PXRD analysis were put in sealed glass capillary tube to protect sample from air and moisture during the experiment. Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010. All X-ray Photoelectron Spectroscopy (XPS) emissions were referenced to the carbon C-(C, H) emission at 284.8 eV, and the data were obtained using a Physical Electronics PHI-5500 spectrometer. Samples were loaded in an Ar glove box to maintain sample integrity. Elemental analysis (EA) was conducted using a Perkin – Elmer Series II CHNO/S 2400 Analyzer, calibrated with acetanilide standard. Samples for EA were loaded in an Ar glove box, using tin capsules. Infrared spectroscopy was conducted on a Brucker Vector 22 instrument using Nujol or KBr discs. Thermo-gravimetric analysis was conducted on a Mettler Toledo TGA SDTA 851e, using Helium (99.99%) as purging gas with a rate of 30 mL/min. Samples were held at 25 ^{o}C for 30 min before heating to 550 ^{o}C at a rate of 5 ^{o}C/min.

Electron Paramagnetic Resonance (EPR) Measurements. In a typical experiment, an EPR quartz tube fitted with J-Young valves was loaded with 50 mg of the titanium hydrazide powder. For the first measurement the tube was held under Ar. Then, Ar gas was replaced by H_2 and further EPR measurements were carried out. Measurements were conducted from 200 to 6200 Gauss, with 100 scans, at 298 K on a Brucker X-band ESP 300E EPR Spectrometer (9.4 GHz). The signal of sample and sample in H_2 were corrected by subtraction of empty tube signals (including signal of empty cavity) from observed spectra.

Hydrogen adsorption measurements: Hydrogen adsorption isotherms were obtained by using a computer controlled commercial Gas Reaction Controller manufactured by Advanced Materials Corporation, Pittsburgh, PA, except in the case of the isotherm recorded at 298 K and 143 bar, which was obtained on a Hy-Energy PCT Pro. High purity hydrogen (99.9995% purity) was used. All measurements were performed exactly as reported previously by our group to ensure reproducibility.[5] Skeletal densities were collected using a Quantachrome Ultrapycnometer housed in an Ar glove box. This instrument was calibrated bi-monthly as per user manual, using a small sphere with a known volume of 0.0898 cm^3 to monitor the instrument's performance. The volume of an empty cell is collected over several running cycles using He until the values are within ± 2% difference. A pre-weighed portion of sample is loaded into the cell under inert conditions and the volume of the system (sample + cell) is then determined. The skeletal volume of the sample is the difference between volume of sample + cell and the volume of empty cell. Skeletal density is obtained by using the sample mass divided by the sample volume. Excess hydrogen storage measurements on a 100 mg standard AX-21 sample (4.2 wt. % at 30 bar and 77 K, 0.55 wt. % at 80 bar and 298 K) were performed to ensure proper calibration (Figure S1, Supporting Information). Leak testing was also performed during each measurement by checking for soap bubbles at potential leak points. These measurements are all necessary to ensure the veracity of the isotherms. In the H_2 adsorption-desorption experiments a high level of reversibility was observed for all samples across the whole range of pressures. Samples were run at liquid nitrogen temperature (77 K), liquid argon temperature (87 K), and room temperature (298 K) to 85 bar on the Advanced Materials instrument and up to 143 bar on the PCT Pro. Isotherms were always measured first at room temperature and then at 77 K or 87 K and the temperature was kept constant by keeping the sample chamber in liquid N_2, liquid Ar, or water. In the Advanced Materials instrument the sample weight and skeletal density are used to determine the volume of the sample in the sample chamber, which is then subtracted from the sample chamber volume to provide an accurate void space volume. When the skeletal density is used for the gravimetric hydrogen uptake measurement, the compressed hydrogen within the pores is treated as part of the sample chamber volume and hence subtracted. Therefore only the hydrogen contained on or beneath the walls of the structure will be recorded by the PCI instrument. This gravimetric value is termed the adsorption or excess storage. When the bulk density is used the hydrogen in the pores of the sample is automatically included in the calculation without any further correction factors and the final value is termed the total storage or absolute storage,[5] which represents all hydrogen contained in the sample including the compressed gas in the voids and the hydrogen adsorbed on or beneath the walls of the structure. Gravimetric densities are recorded as read from the isotherms while volumetric densities are calculated from the adsorption data and the skeletal or bulk density, depending on the desired value. The excess volumetric storage is typically calculated from the excess storage and the bulk density and gives a measure of the gas adsorbed on or in the solid phase of the material scaled across the entire volume occupied by the sample including the void space. In materials such as MOFs that posses a well-defined and constant ratio between mass and void space this value is often quoted. For compressible materials that may have variable ratios of solid mass and void space it can often help to scale the volumetric density to the solid phase alone as the void space will vary on sample preparation. For this purpose, we have defined the true volumetric adsorption as the amount of hydrogen adsorbed on or in a given volume of the solid portion of the sample. This is calculated from the excess storage data and the skeletal density. This value neglects the void space and is useful in comparing volumetric densities of ball-milled powders and gels (materials with textural porosity only and no intrinsic pore structure) to pure solid phase materials such as metal hydrides. Since the materials in this study stand between hydrides and physisorption materials in their mechanism of storage, this value is important. It also allows us to compare volumetric adsorption values of the solid phase alone from one sample to another without having to correct for the different textural void space in each material. The absolute volumetric adsorption has also been defined[5] and is a representation of the sum of the excess volumetric storage plus the compressed gas in the void space. This can be calculated from the volumetric storage as measured from the instrument and the bulk density, or by taking the volumetric adsorption and adding the amount in the void space calculated from the pore volume and the ideal gas law. The first method is only possible when using the Advanced Materials instrument. In this paper we have chosen not to calculate this value (or the total gravimetric storage) because the differences between the skeletal densities and bulk densities are much smaller than in MOFs and hence the void space compressed gas contribution is negligible and will also vary due to sample preparation.

Enthalpies of adsorption were calculated using a variant of the Clapeyron – Clausius I equation taking both 77 K and 87 K hydrogen excess storage data.[5] Pressure as a function of the amount adsorbed was determined by using exponential fit for each isotherm; the first 10 – 11 points of the isotherms were picked up and fit to the exponential equation. This exponential equation provides an accurate fit over the pressure up to 1 MPa with the goodness of fit (R^2) above 0.95. The corresponding P_1 and P_2 values at a certain amount of H_2 adsorbed at both temperatures can be obtained by the simulated exponential equation. Inputting these numbers into equation 1, we then calculate the adsorption enthalpies. This technique is commonly used to measure enthalpies of amorphous carbons and MOFs.[5,6] The enthalpy for carbon AX-21 calculated using this method using hydrogen adsorption data measured on The Advanced Materials PCI as described above is shown in Figure S2. Since the enthalpy of a reaction does not vary with temperature, unlike Gibbs free energy, this method provides information on hydrogen binding that is meaningful over a wide temperature range.

$$\ln\left(\frac{P_2}{P_1}\right) = -\Delta H_{\text{adsorption}} \frac{T_2 - T_1}{R.T_2.T_1} \qquad (1)$$

Where Pn = pressure for isotherm n, Tn = temperature for isotherm n, R: gas constant.

H_2/Ti Calculations. Calculations on titanium hydrazide samples were based on %Ti values obtained from the thermo-gravimetric analysis data from Table S1. As an example calculation, A100-H_2 absorbs 1.55 wt % of hydrogen at 85 bar and 298 K. This corresponds to 0.0155 g or 0.00775 mol of H_2 for 1 g of sample. Based on the 55.28 wt% Ti in the sample from Table S1, this translates into an average of 0.67 molecules of H_2 per metal center.

Table S1: Elemental analysis results of synthetic titanium hydrazide samples.

Material	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Titanium (%)[(a)]
A100	20.18	4.28	12.97	54.42
A150	6.18	1.34	10.41	N/A
B100	13.93	3.27	15.01	43.56
B150	5.54	0.87	7.45	N/A
A100-H_2	9.83	2.47	12.69	55.28
B100-H_2	12.92	3.20	14.85	47.48

(a): From thermo-gravimetric analysis.

Table S2: Proposed unit formula of synthetic materials assuming complete loss of hydrocarbon.

Material	Proposed chemical formula	Titanium (%)	Hydrogen (%)	Nitrogen (%)
A100	TiN_2H_2	61.45	2.59	35.96
B100	TiN_3H_4	50.97	4.29	44.74
A100-H_2	TiN_2H_2	61.45	2.59	35.96
B100-H2	TiN_3H_4	50.97	4.29	44.74

Table S3. Summary of excess storage results on vanadium hydrazide materials and carbon AX-21. Data recorded at 85 bar.

Material	BET Surface Area (m^2/g)	Skeletal Density (g/cm3)	Gravimetric Adsorption (wt. %)	True Volumetric Adsorption (kg/m3)	Retention (%)
A100	117	1.3228	1.99 (at 77K) 1.28 (at 298K)	26.3 (at 77K) 16.9 (at 298K)	64
A150	95	1.4045	2.22 (at 77K) 1.24 (at 298K)	31.2 (at 77K) 17.4 (at 298K)	56
B100	176	1.4856	2.02 (at 77K) 0.99 (at 298K)	30.0 (at 77K) 14.7 (at 298K)	49
B150	129	1.6827	1.79 (at 77K) 1.11 (at 298K)	30.1 (at 77K) 18.73 (at 298K)	62
A100-H2	301	1.3944	3.49 (at 77K) 1.55 (at 298K)	48.7 (at 77K) 21.6 (at 298K)	44
B100-H2	190	1.7914	2.68 (at 77K) 1.15 (at 298K)	48.0 (at 77K) 20.6 (at 298K)	43

AX-21	3225	2.1030	4.2 (at 77K, 65bar) 0.55 (at 298K)	14 (at 77K, 65bar) -	13
MOF-5	3534		5.10 (at 77K) 0.28 (at 298K)		5.5

Table S4. Average number H_2 adsorbed per Ti site at 85 bar using TGA data.

Sample	Number of H_2/Ti at 77 K	Number of H_2/Ti at 298 K
A100	0.87	0.56
B100	1.11	0.54
A100-H_2	1.51	0.67
B100-H_2	1.35	0.58

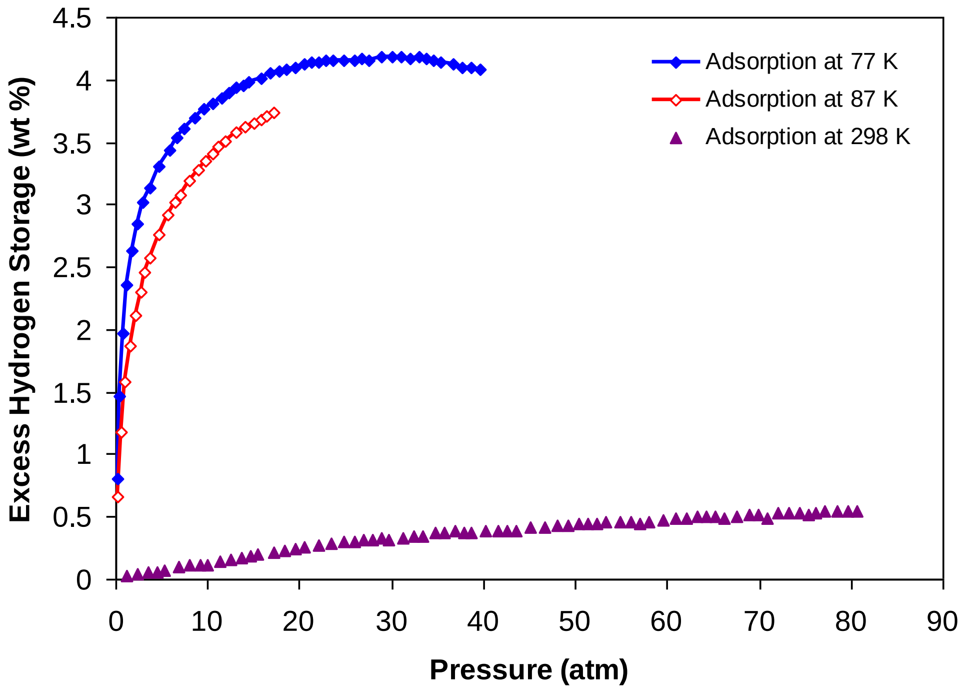

Figure S1: Hydrogen excess storage at 77 K, 87 K, and 298 K of carbon AX-21 up to 80 bar recorded on Advanced Materials PCI.

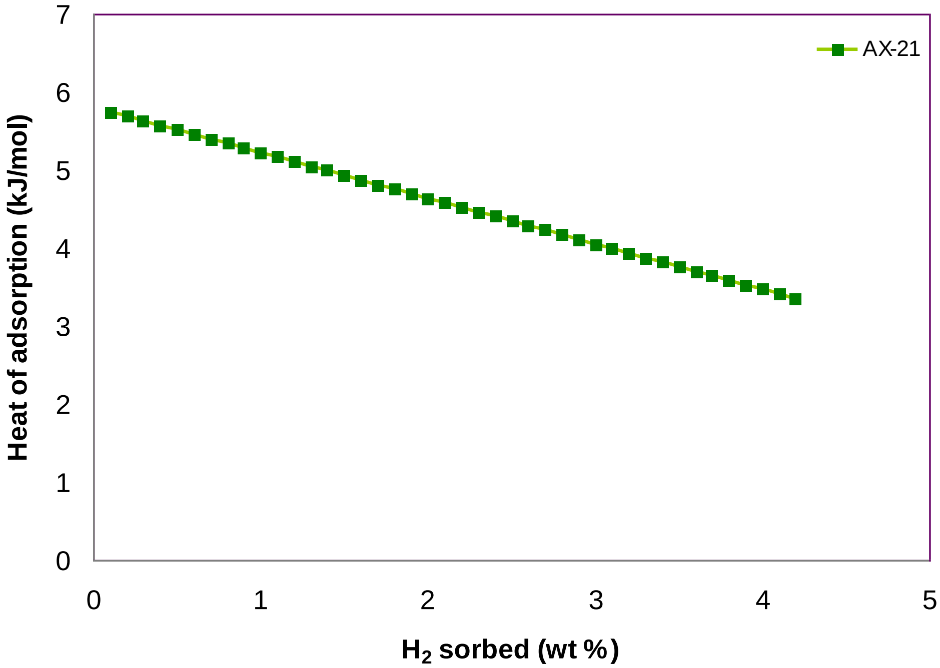

Figure S2: Heat of hydrogen adsorption of carbon AX-21 calculated from data in S1.

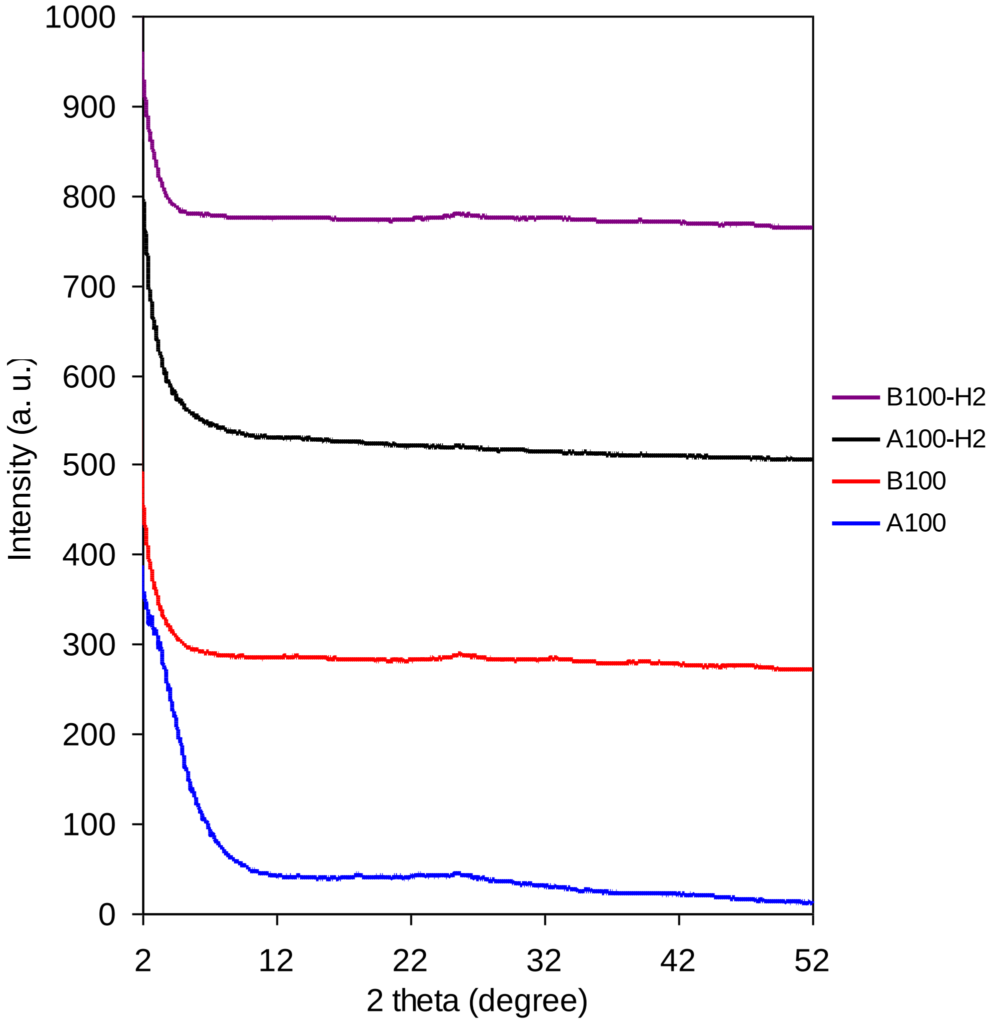

Figure S3: Powder X-ray diffraction of titanium hydrazide materials. From top to bottom: B100-H_2, A100-H_2, B100, and A100 samples.

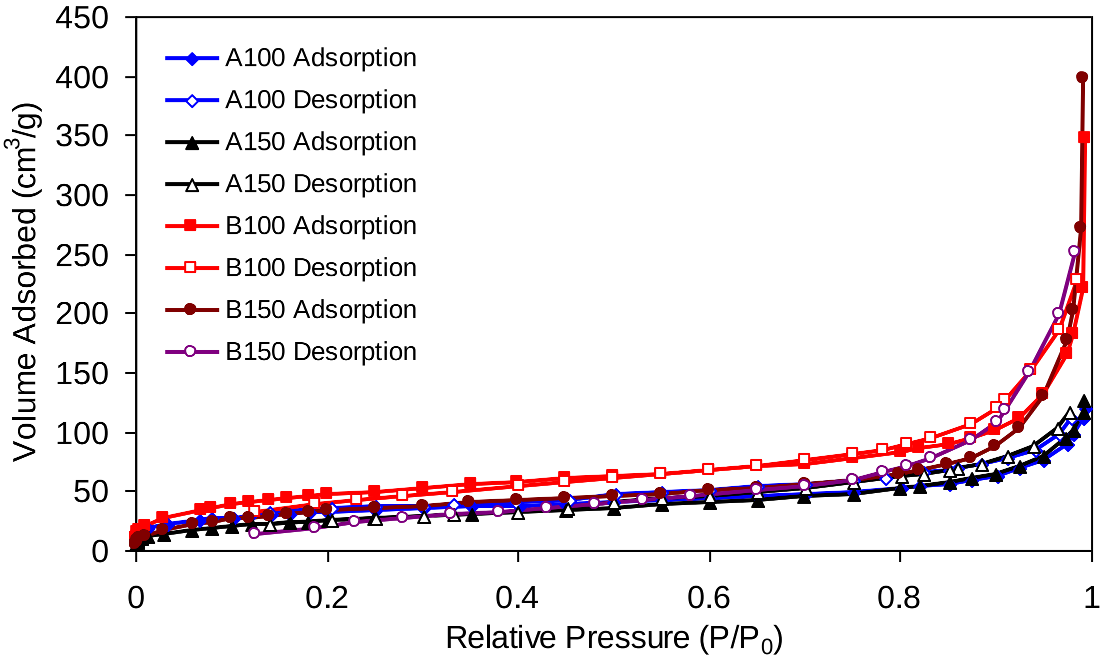

Figure S4a: Nitrogen adsorption – desorption isotherms of titanium hydrazide materials heated at 100 ^{o}C and 150 ^{o}C. Samples were measured on an ASAP-2010 instrument at 77 K.

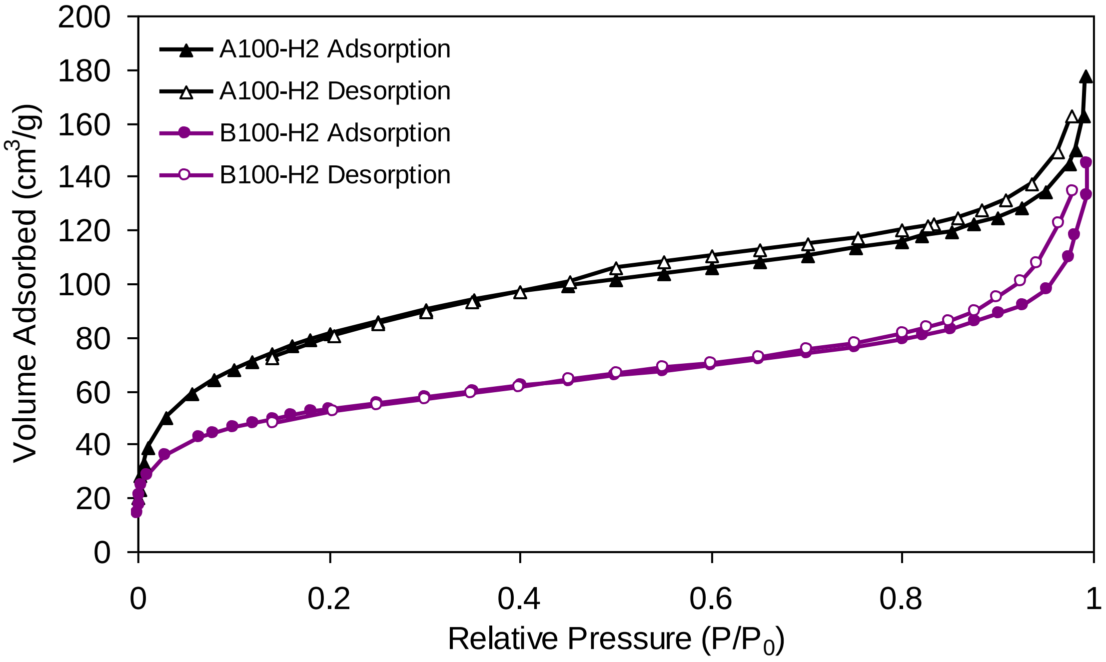

Figure S4b: Nitrogen adsorption – desorption isotherms of titanium hydrazide materials hydrogenated at 80 bar H_2, 150 ^{o}C, 2h. Samples were measured on an ASAP-2010 instrument at 77 K.

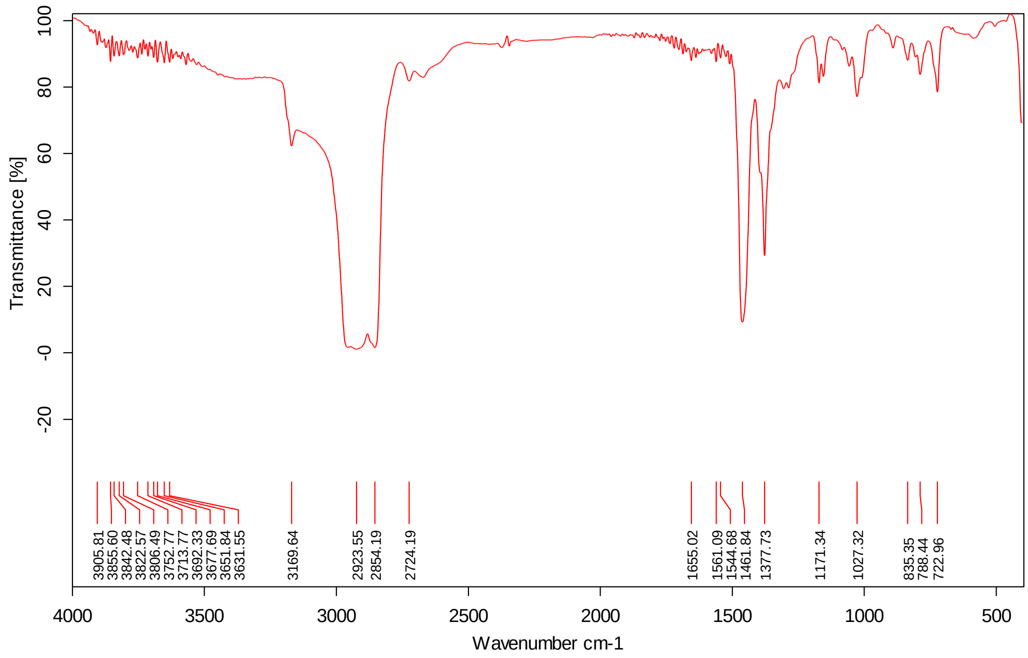

Figure S5a: Infrared spectrum of $TiCl_3.0.67\{N(C_2H_5)_3\}$

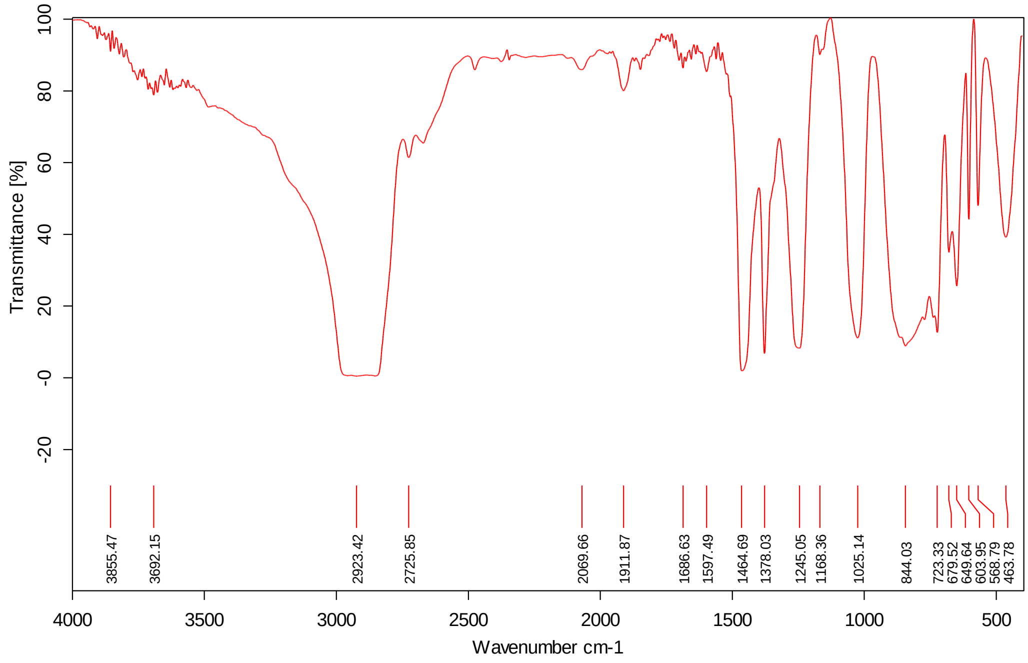

Figure S5b: Infrared spectrum of $LiCH(SiMe_3)_2$ in Nujol.

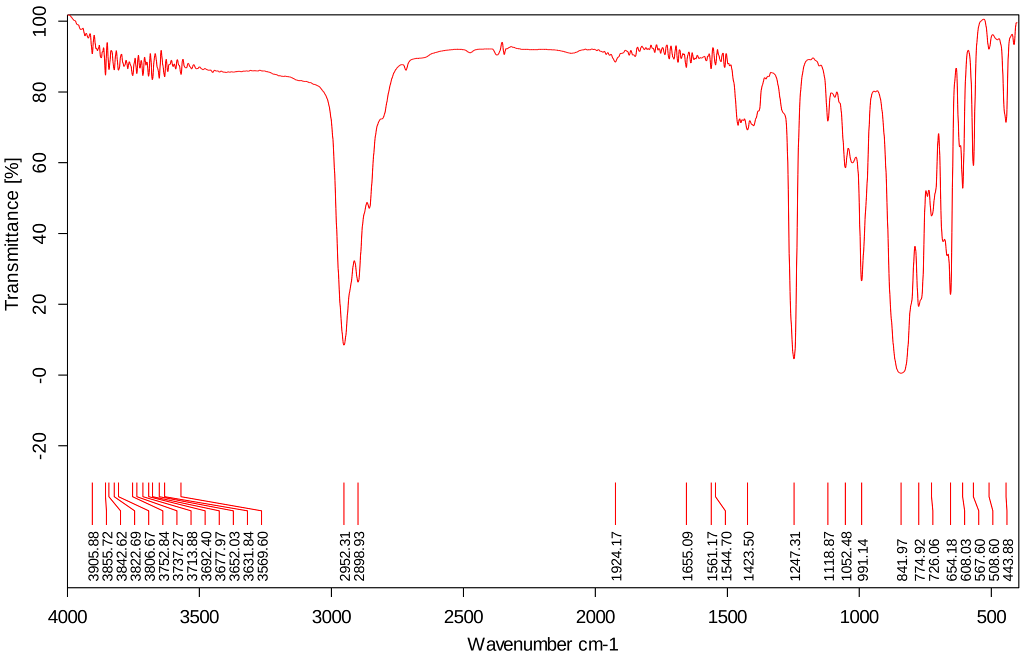

Figure S5c: Infrared spectrum of Ti{(CH(SiMe$_3$)$_2$}$_3$ in Nujol.

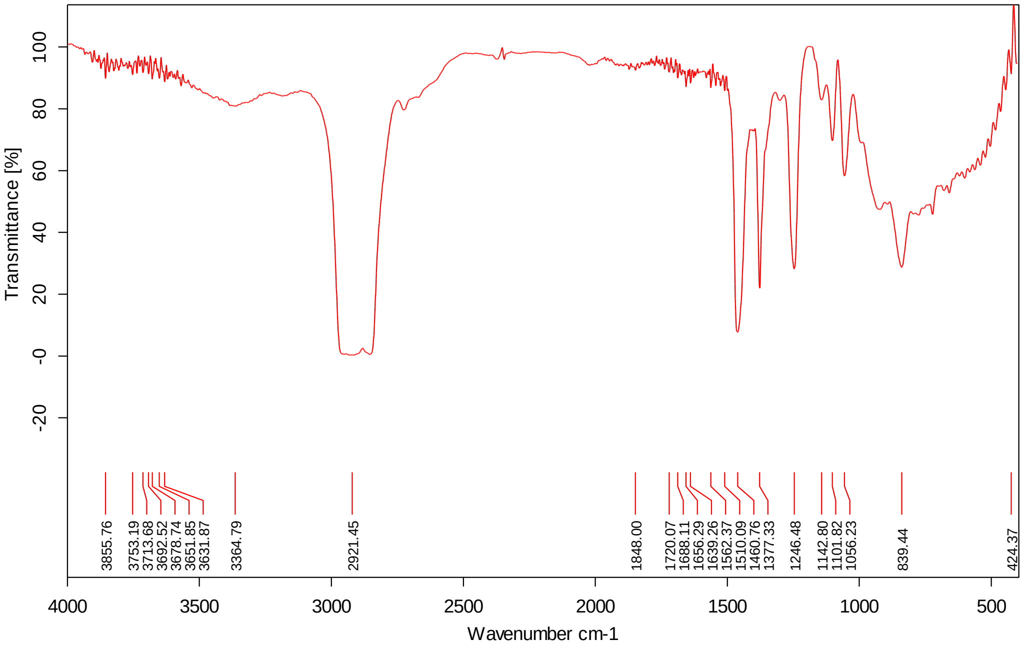

Figure S5d: Infrared spectrum of A100 in Nujol.

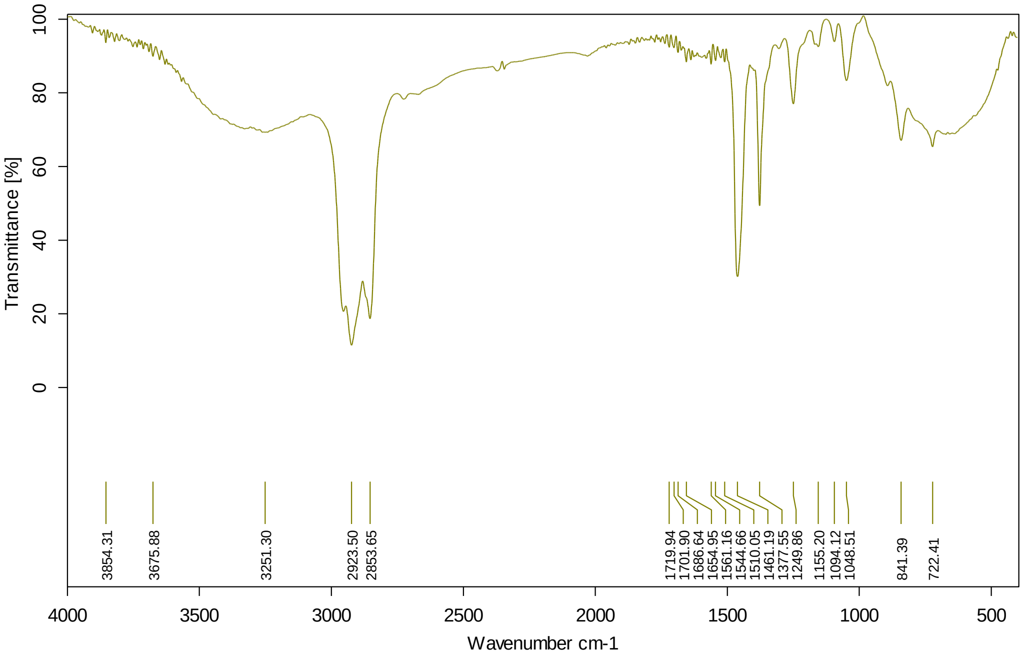

Figure S5e: Infrared spectrum of A150 in Nujol.

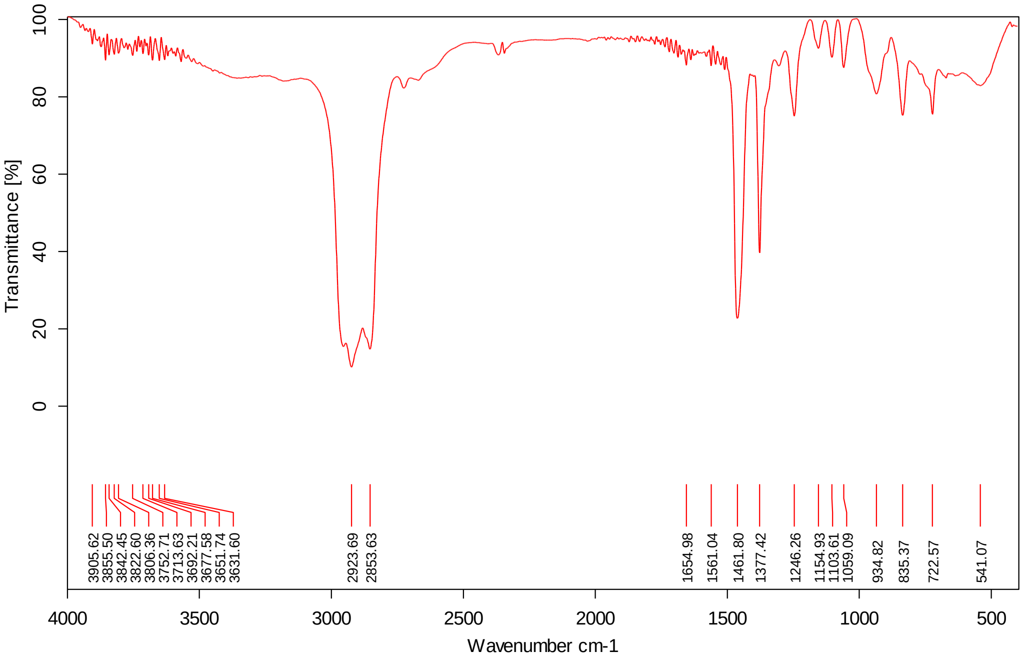

Figure S5f: Infrared spectrum of B100 in Nujol.

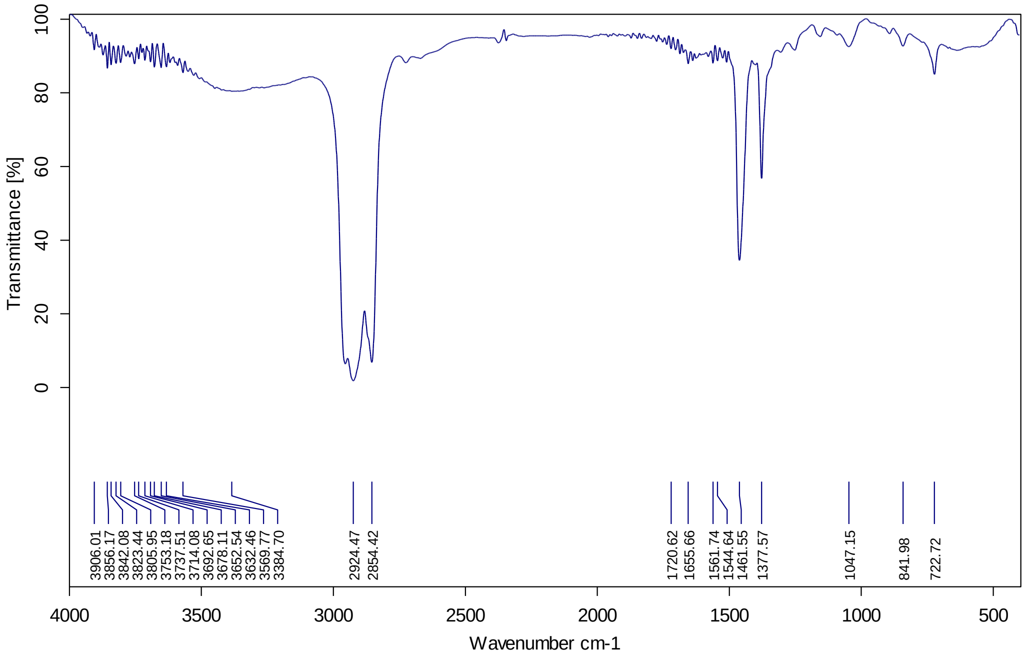

Figure S5g: Infrared spectrum of B150 in Nujol

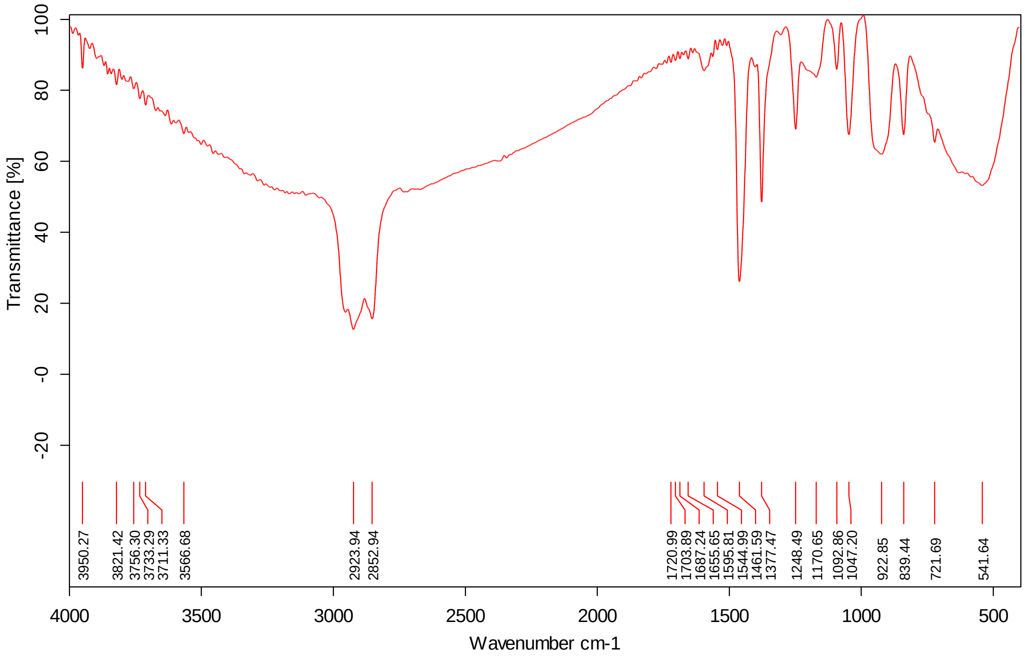

Figure S5h: Infrared spectrum of A100-H_2 in Nujol.

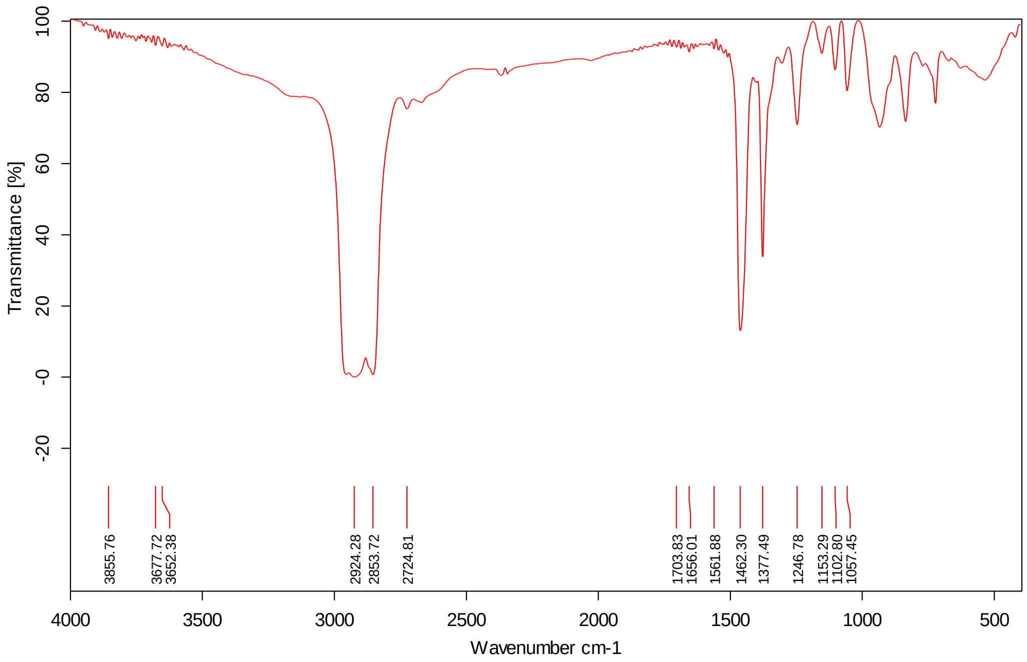

Figure S5i: Infrared spectrum of B100-H_2 in Nujol.

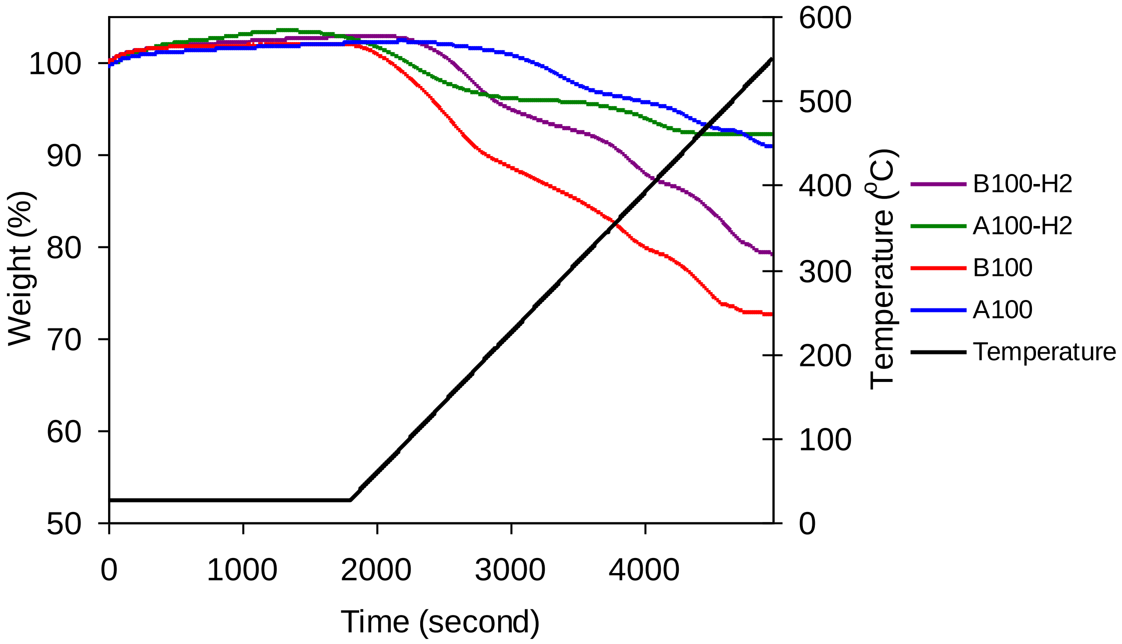

Figure S6: Thermo-gravimetric analysis results of titanium hydrazide materials.

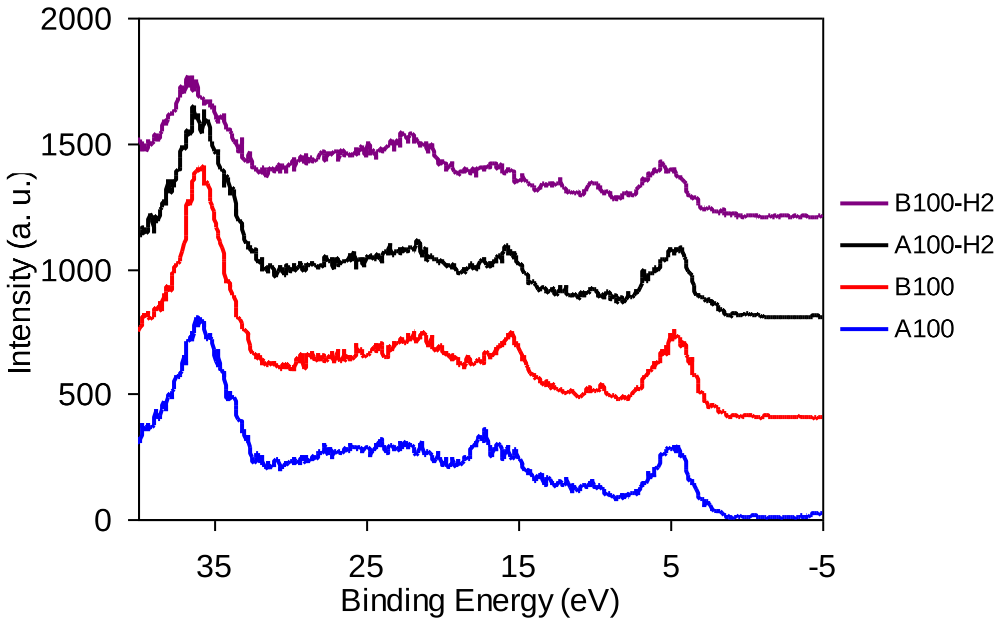

Figure S7: Valence region of XPS spectrum of titanium hydrazide materials heated to 100 °C. From top to bottom: B100-H_2, A100-H_2, B100, and then A100.

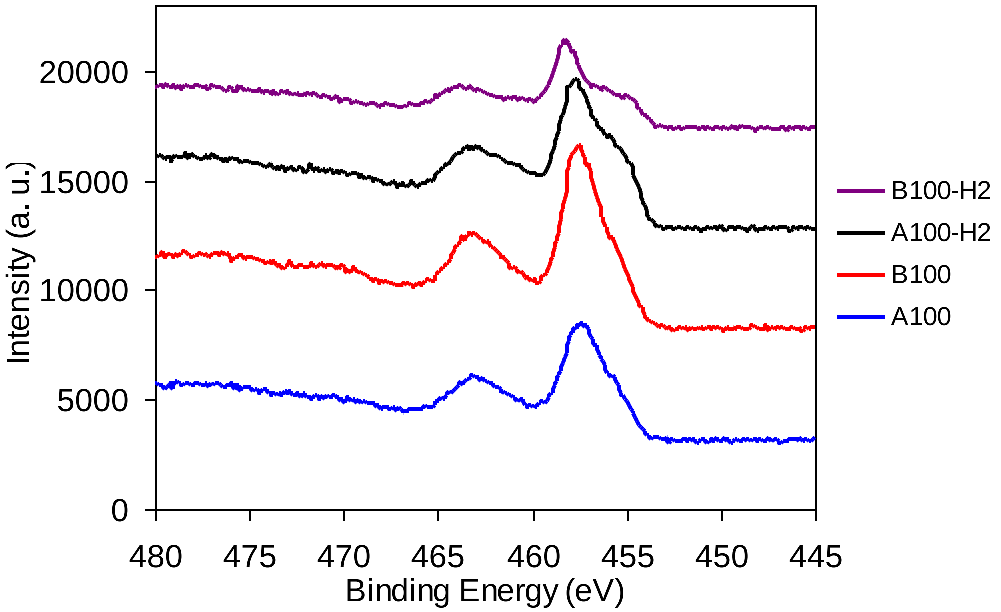

Figure S8a: Titanium 2p1/2 and 2p3/2 region of XPS spectrum of titanium hydrazide materials heated to 100 °C and hydrogenated at 150 °C, 80 bar, 2h. From top to bottom: B100-H_2, A100-H_2, B100, and then A100.

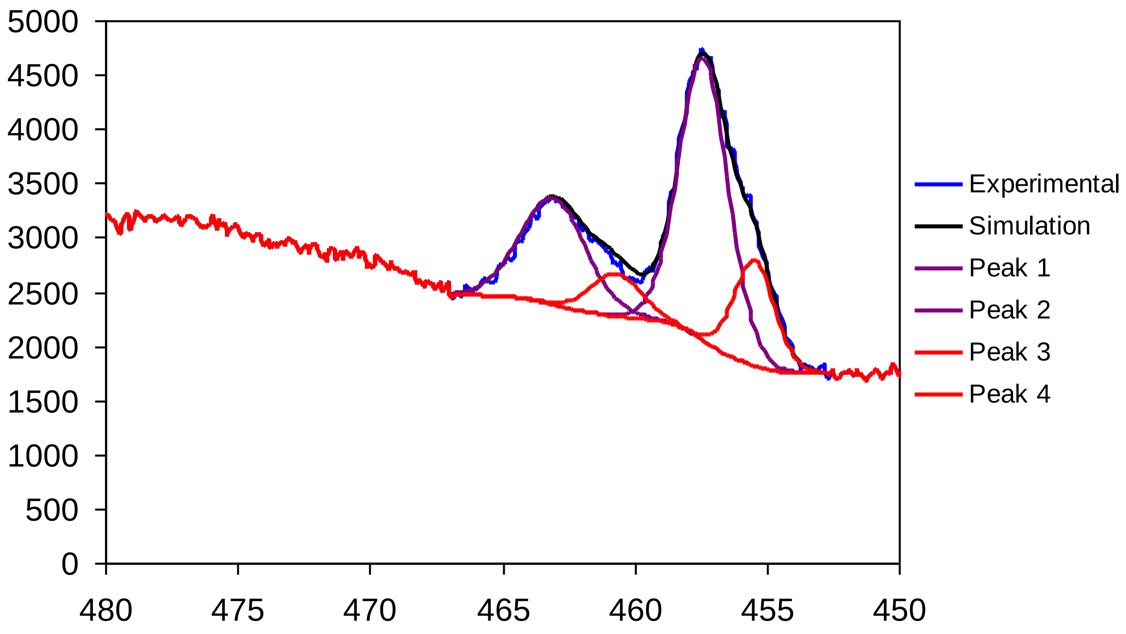

Figure S8b: Peak fitting of titanium 2p1/2 and 2p3/2 emissions in the XPS spectrum of A100 sample.

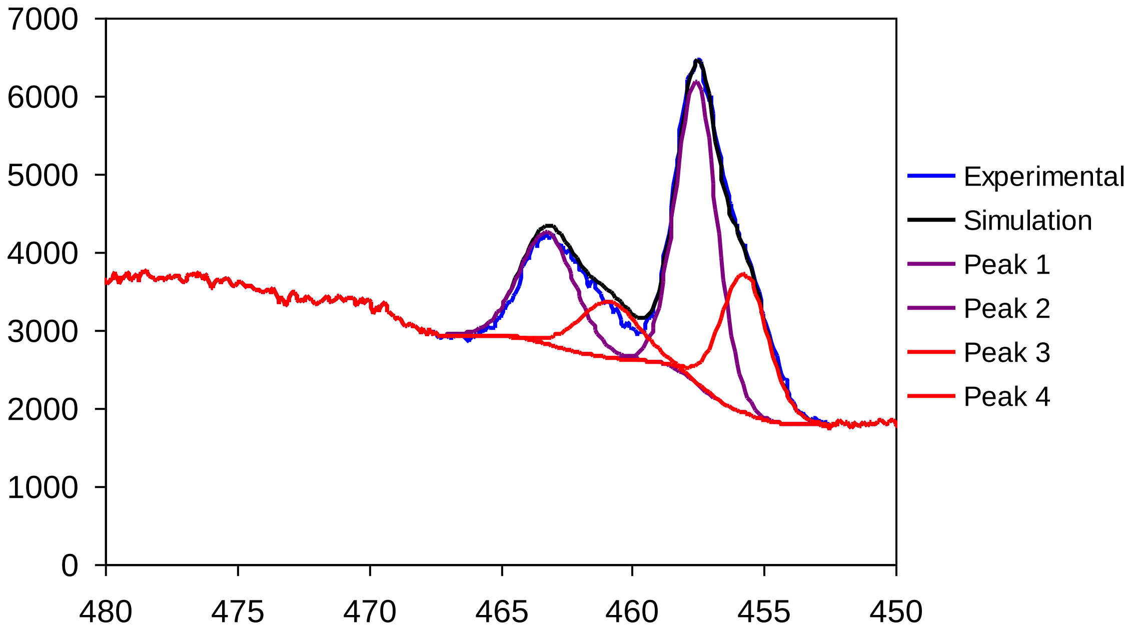

Figure S8c: Peak fitting of titanium 2p1/2 and 2p3/2 emissions in the XPS spectrum of B100 sample.

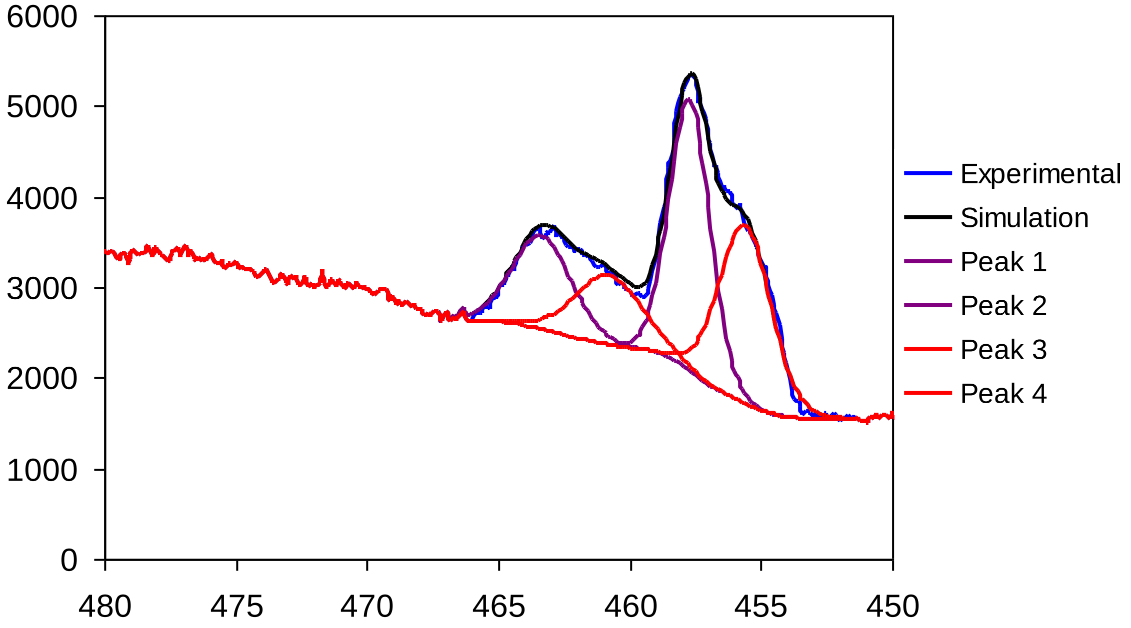

Figure S8d: Peak fitting of titanium 2p1/2 and 2p3/2 emissions in the XPS spectrum of A100-H_2 sample.

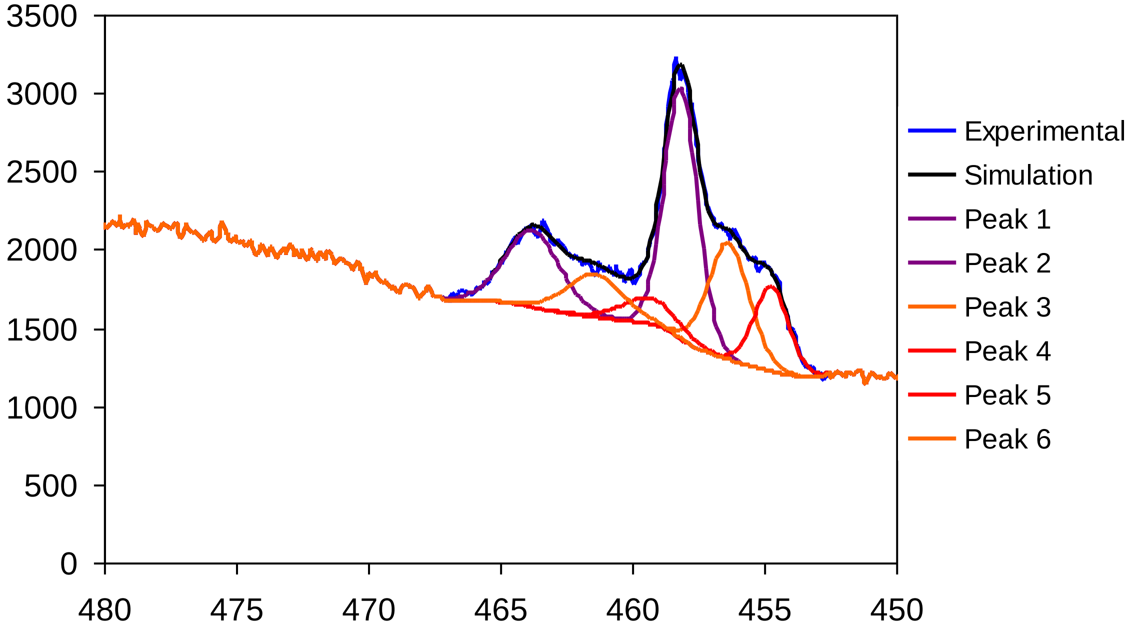

Figure S8e: Peak fitting of titanium 2p1/2 and 2p3/2 emissions in the XPS spectrum of B100-H_2 sample.

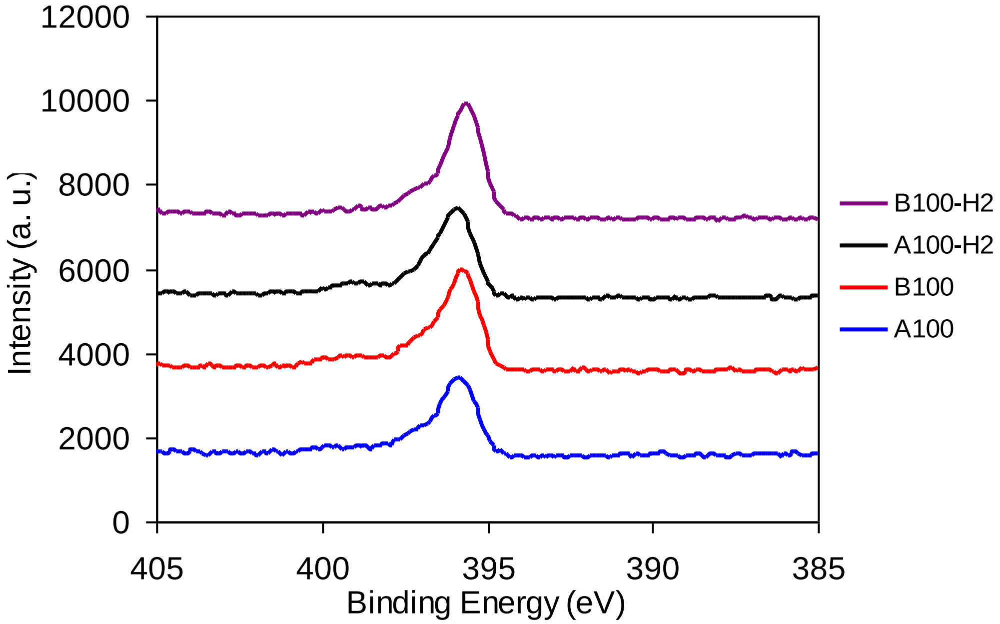

Figure S9a: Nitrogen 1s region of XPS spectrum of titanium hydrazide materials heated to 100 °C and hydrogenated at 150 °C, 80 bar, 2h. From top to bottom: B100-H_2, A100-H_2, B100, and then A100.

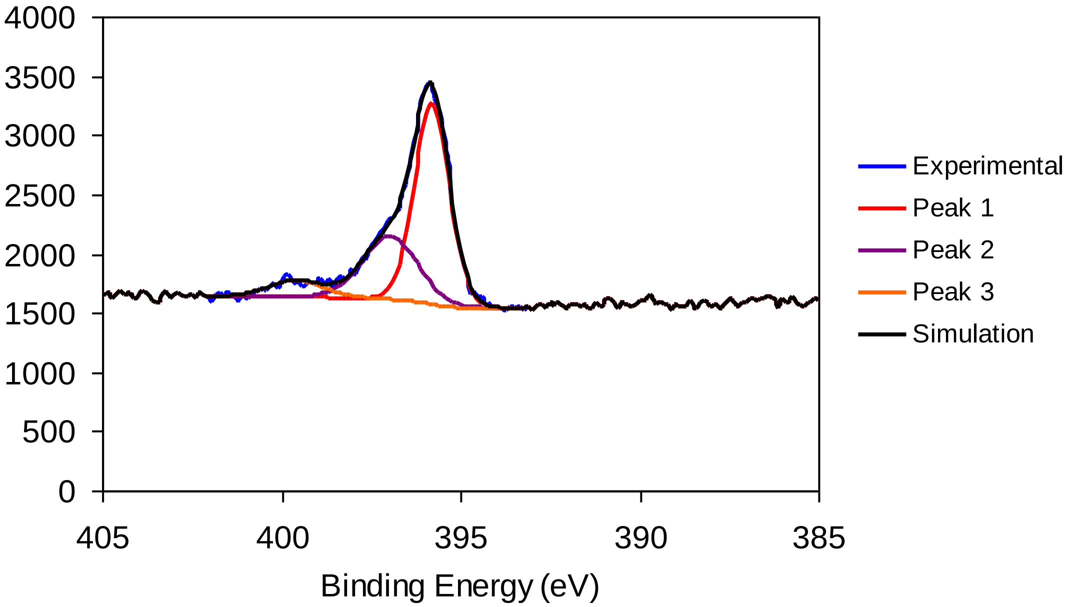

Figure S9b: Peak fitting of N 1S region of XPS Spectrum of A100 sample.

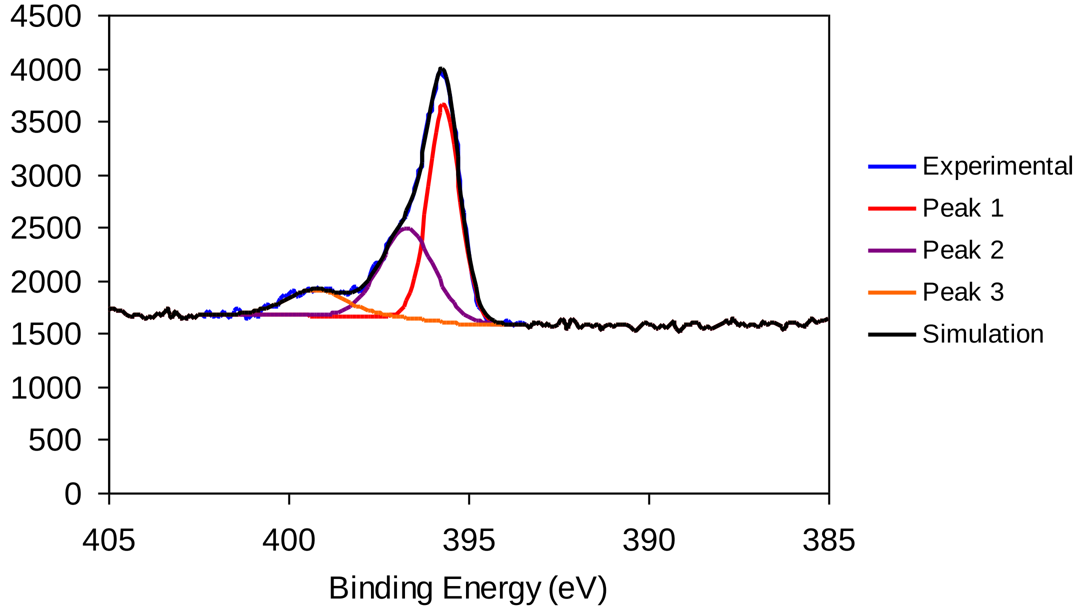

Figure S9c: Peak fitting of N 1S region of XPS Spectrum of B100 sample.

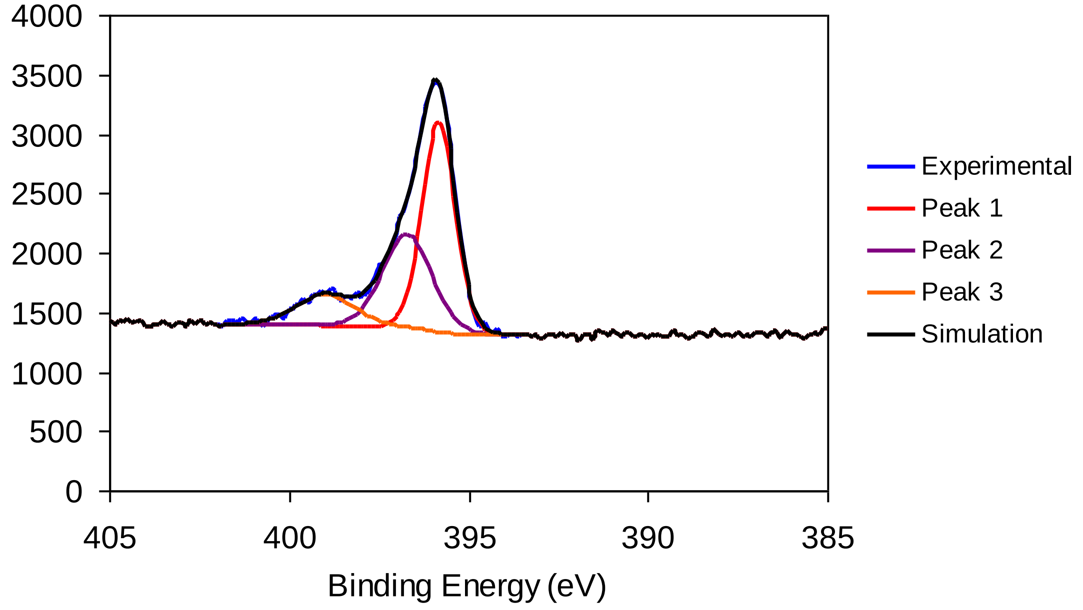

Figure S9d: Peak fitting of N 1S region of XPS Spectrum of A100-H_2 sample.

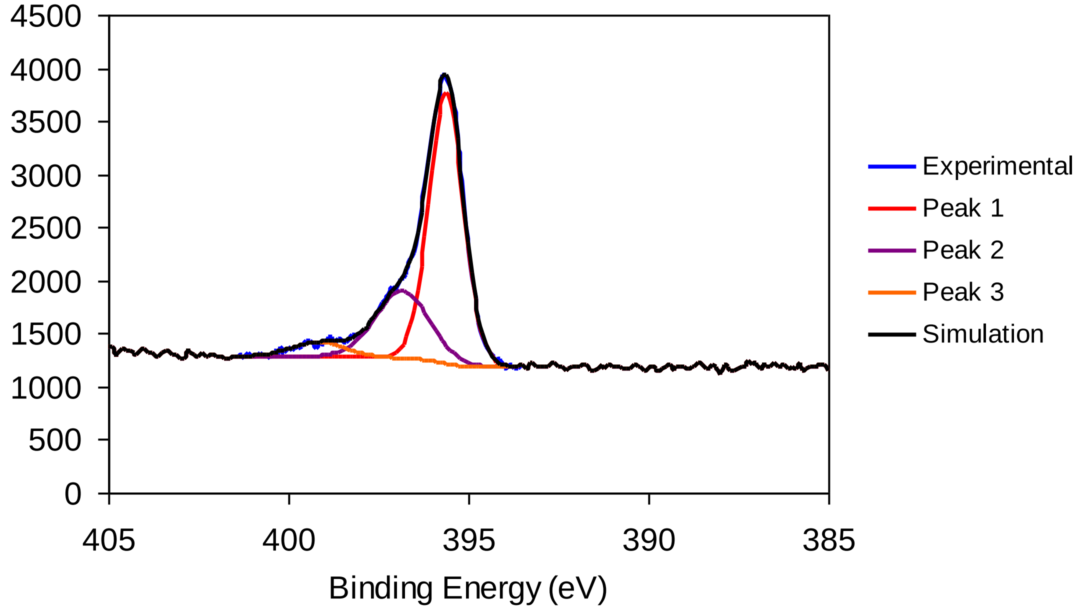

Figure S9e: Peak fitting of N 1S region of XPS Spectrum of B100-H_2 sample.

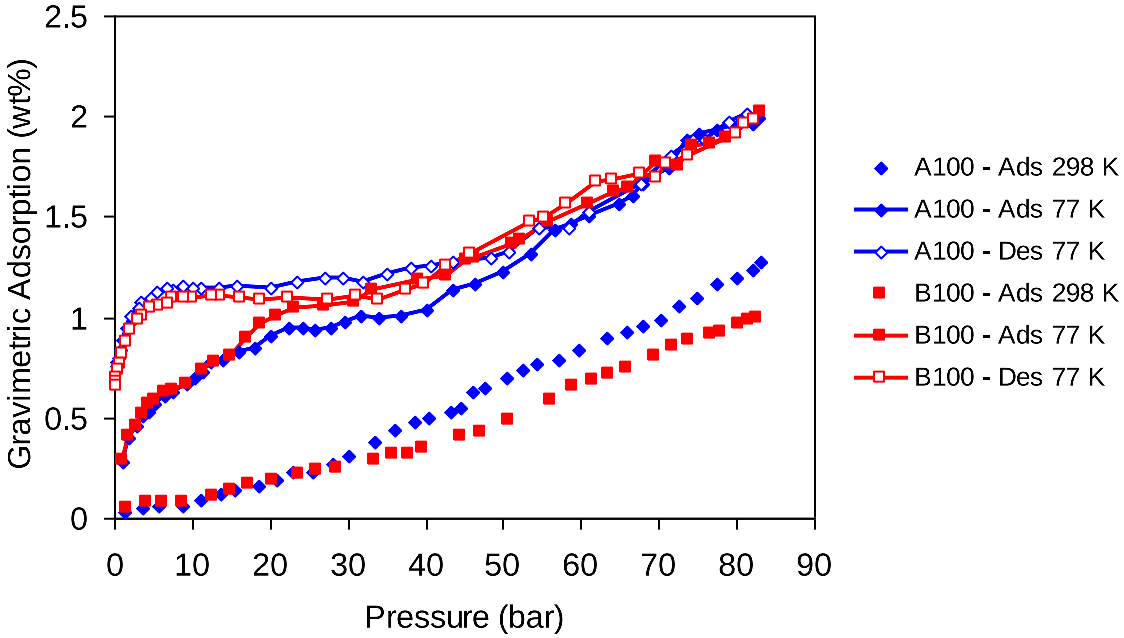

Figure S10: Excess storage isotherms of A100 and B100 materials. Desorption of 298 K isotherms omitted for clarity.

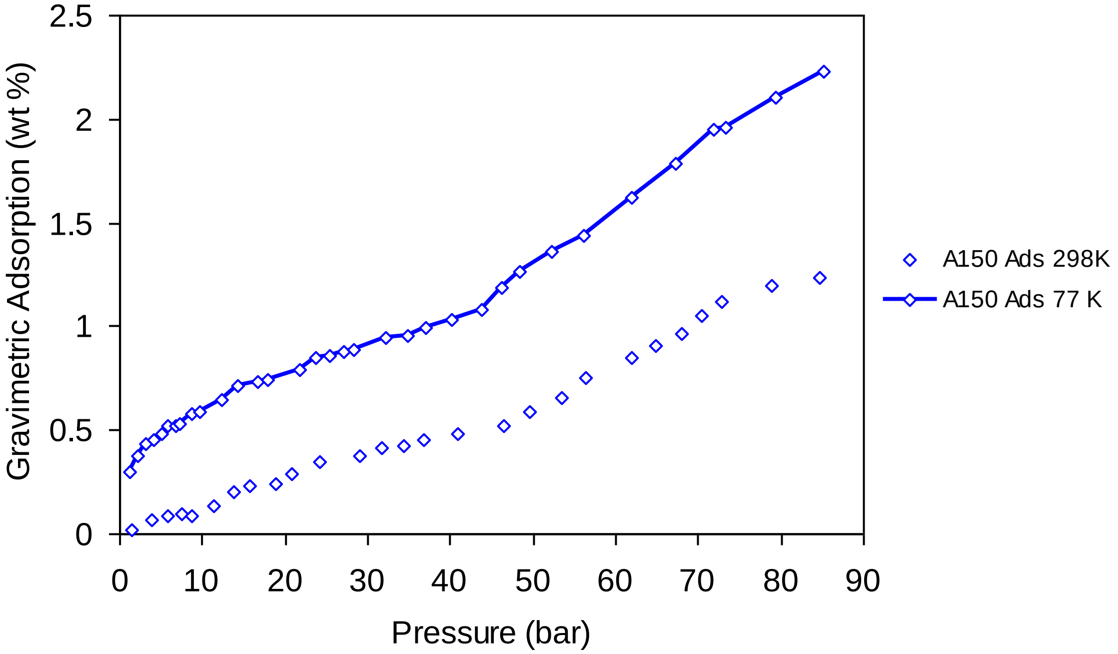

Figure S11: Excess storage isotherms of A150 materials.

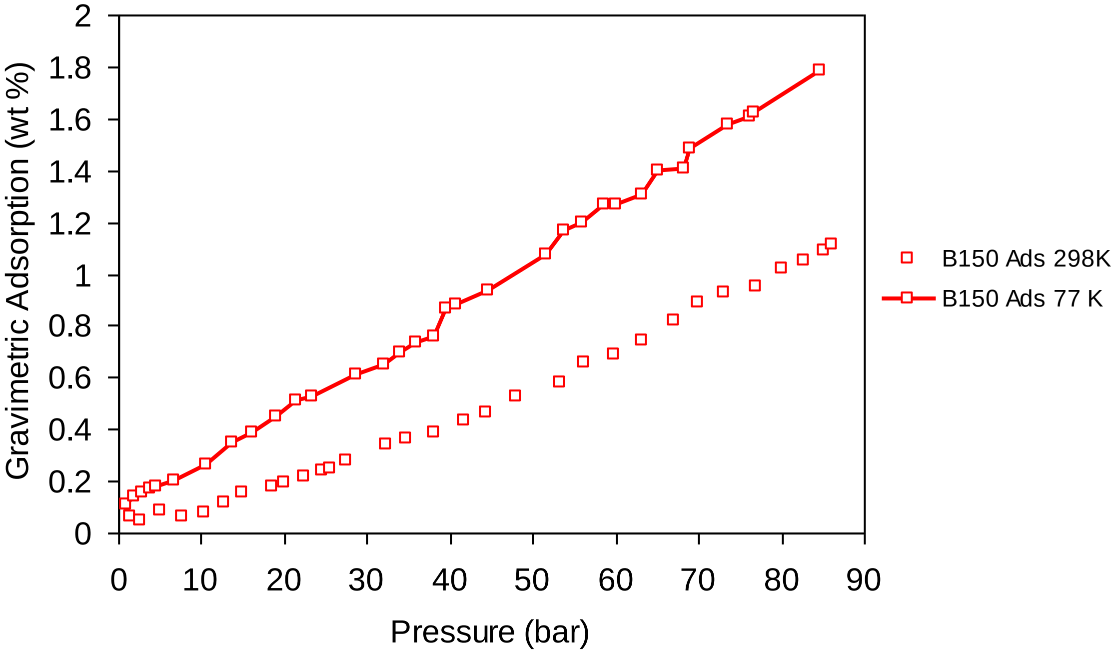

Figure S12: Excess storage isotherms of B150 materials.

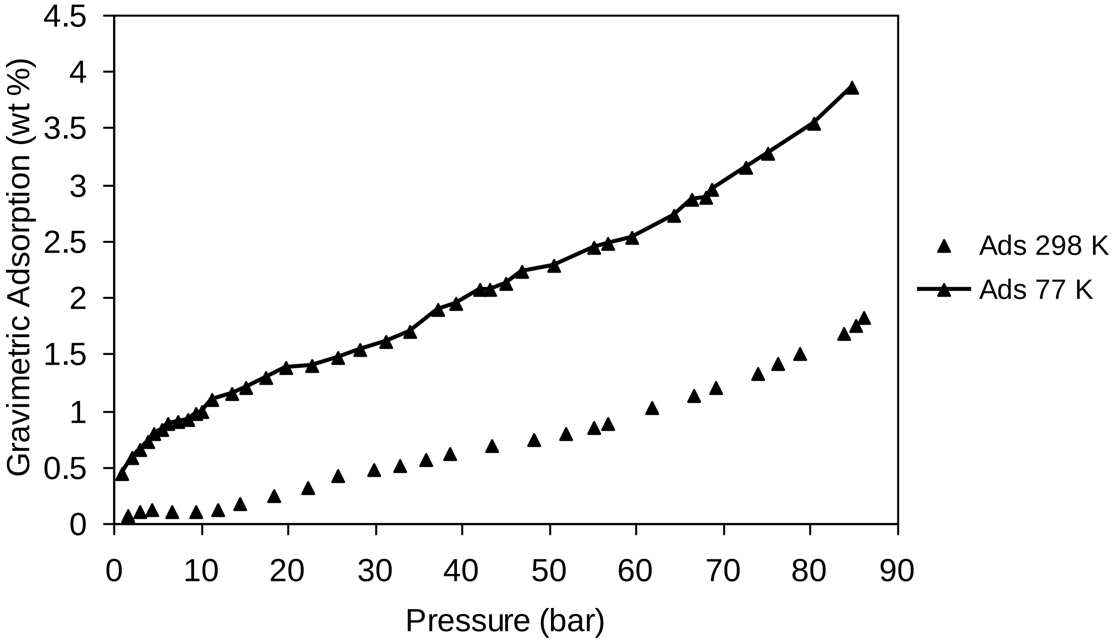

Figure S13: Excess storage isotherms at 298 K and 77 K of a pellet of the A100-H_2 material compressed at 500 Psi.

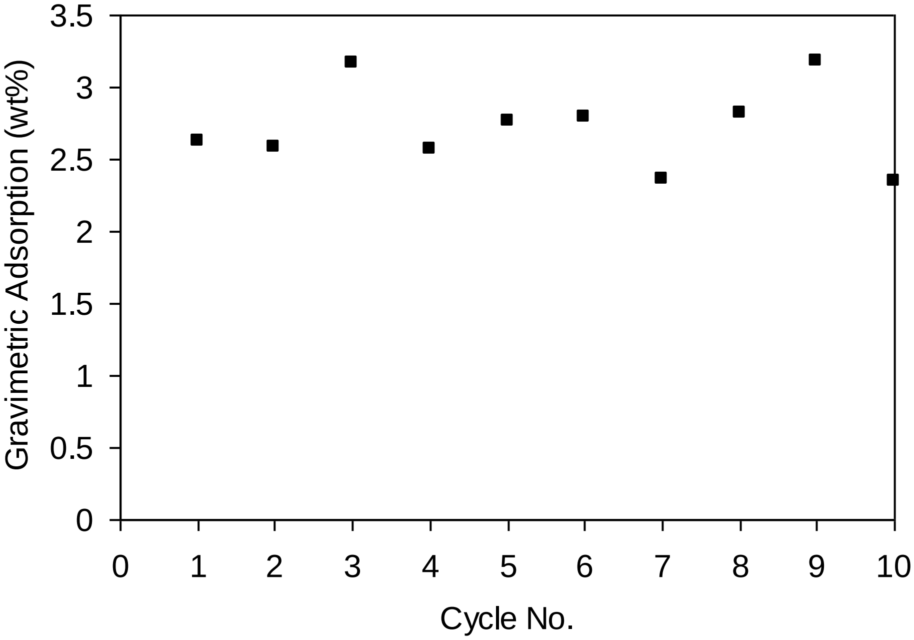

Figure S14: Hydrogen adsorption capacity at 298 K in a 20 cycle test to 143 bar of the A100-H2 sample.

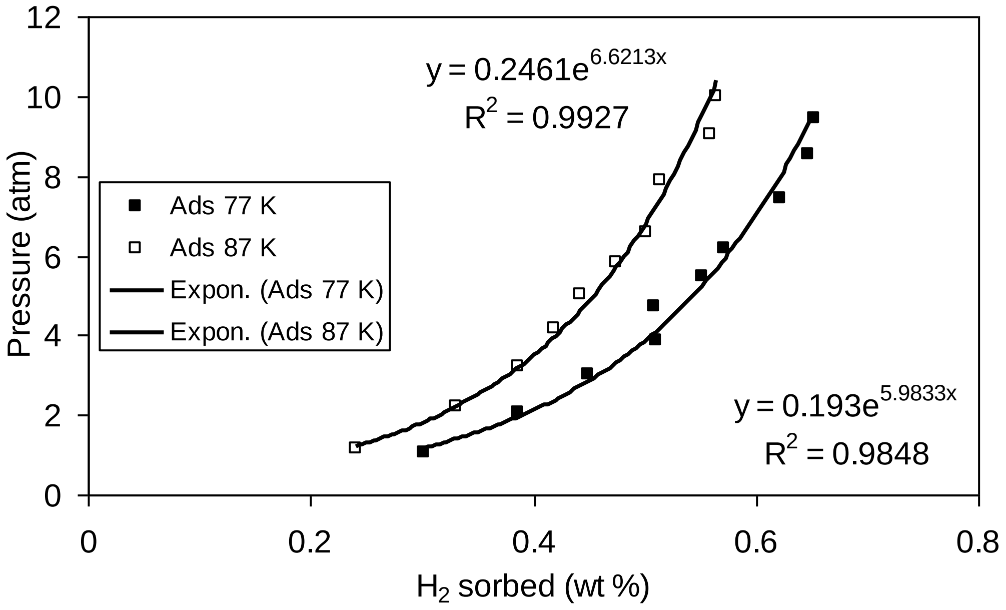

Figure S15: Exponential fitting of adsorption data at 77 K and 87 K on A100-H_2 materials for enthalpy calculation.

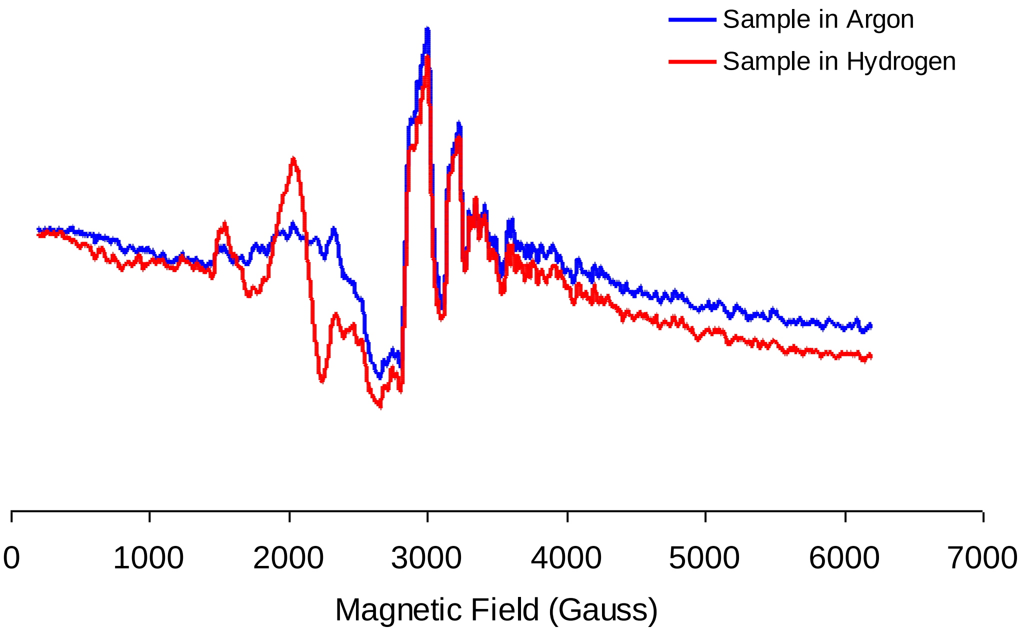

Figure S16: X-band EPR of A100-H_2 materials in Ar and in H_2.

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