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Future Recovered Gas Dryer Development

SRTE FY2019 PRDR SR19009

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EXECUTIVE SUMMARY

A manifold was designed and constructed to evaluate the isotopic exchange of deuterium for hydrogen using Pt catalyzed zeolites, deuterated water, and deuterated ammonia. Using varying catalytic loadings on the 5A substrate and real-time RGA monitoring of the effluent stream, isotopic exchange was successfully demonstrated between H_2 and D_2O or ND_3. The catalytic isotopic exchange was further verified when compared against an uncatalyzed sample of zeolite, demonstrating little-to-no activity. Based on the experiments performed here, the removal of tritium from tritiated water and tritiated ammonia is possible for future RGD beds using a Pt catalyzed zeolite.

Work is still ongoing with the planned manifold improvements and scheduled testing of other catalyzed zeolite substrates.

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FC	Mass flow controller
MS	Mass spectrometer
PDRD	Plant Directed Research and Development
RGA	Residual gas analyzer
RGD	Recovered Gas Drier
SRNL	Savannah River National Laboratory
SRTE	Savannah River Tritium Enterprise
SV	Sample volume
TCAP	Thermal Cycling Absorption Process
TPD	Temperature programmed desorption
wt%	Weight percent

1.0 Introduction

The primary purpose of the Recovered Gas Dryers (RGDs) is to remove moisture. This is accomplished using 5A molecular sieve materials that can be regenerated by heating to moderate temperatures. Unfortunately, 5A molecular sieve materials do not selectively remove only water from a gas stream. Other tritiated compounds, such as ammonia, can also be absorbed and are not easily removed during conventional regeneration. Due to tritium decay heat energy, these tritiated impurities cause the bed temperatures to remain greater than 100°C, even after regeneration. Further, high levels of adsorbed tritium complicate disposal of RGDs at their end of life. Previous small-scale testing indicates that full ammonia desorption can be achieved by heating to 600°C, but such a high temperature bake-out is not currently an option for remediation. Alternative to high temperature bake-outs, moisture-ammonia isotope exchange could reduce tritium content in the 5A zeolite, but the SRTE RGD location does not have a moisture source to perform such a task.

Due to these limitations, a catalytic isotope exchange process with hydrogen (H_2) is proposed for next generation RGD materials. This project builds on our successfully developed water detritiation process and extends it to ammonia detritiation.[1,2] In these processes, isotopic exchange between flowing H_2 with adsorbed tritiated species is facilitated by trace amounts of an active catalyst component (e.g. Pt) that is loaded onto 5A zeolite. Since the catalyst loading may alter the 5A pore size, Pt/5A performance for moisture and ammonia adsorption will also need verification in addition to characterization of the remediation process. The performance will be evaluated for catalytic isotope exchange of HDO and NDH_2 (surrogates) with H_2. If developed successfully, tritium in the future RGD bed (Pt/5A) can be removed even at ambient temperature by catalytic isotope exchange with H_2 into HT/H_2 for tritium recovery in HT-TCAP, allowing the RGD to remain in operation or staged for disposal.

The work performed here was broken down into the three FY2019 milestones;

- Bed material development (e.g. Pt/5A)
- Performance evaluation of catalytic isotope exchange
- Performance evaluation of H_2O and NH_3 adsorption on the material

2.0 Experimental Procedure

2.1 RGD Bed Separation Material

A series of Pt catalyst zeolite materials were prepared, varying catalyst loading concentration and method. Zeolite materials were dried at 110 °C for at least 24 hours prior to use. A list of zeolites used can be found summarized in Table 2-1. Chloroplatinic acid (Sigma Alrdich, Lot # MKCB8675, 38 wt% Pt) was used for catalyst preparation.

Table 2-1: Zeolite substrates used in separation material preparation.

Manufacturer	Type	Description	Lot Number
ASGE	4A	1/8” pellets	2007009256
ASGE	5A	1/8” pellets	2008008625
ASGE	13X	1/16” pellets	20070113328
Zeolyst	HY (CBV-400)	1/16” pellets	001-43-1

2.1.1 Material Preparation

Void volumes for each of the zeolite substrates was determined prior to use. Platinum was loaded on each of the substrates using an incipient wetness impregnation technique. Target Pt weight percentages were selected to determine Pt salt loadings then diluted in deionized water. The Pt salt solution was then added to the zeolite and allowed to soak. Excess Pt solution was removed, and the material allowed to air dry. The Pt/zeolite was dried further at 110 °C prior to calcination at 550 °C. Actual Pt loadings were calculated on the dried weight of the calcined material and solution uptake (Equations 1 and 2), where $m_{[Pt]}$ is the mass of the Pt salt, x_{Pt} is the metal content of the salt, v_i is the initial volume of Pt salt solution added to the material, v_f is the volume of excess solution removed, m_{Pt} is the mass of the Pt, and $m_{mat.}$ is the mass of the calcined material. The resulting data is summarized in Table 2-2.

$$\left(m_{[Pt]} \cdot x_{Pt}\right)\left(\frac{v_i - v_f}{v_i}\right) = m_{Pt} \qquad \text{(Eq. 1)}$$

$$\frac{m_{Pt}}{m_{mat.}}(100) = wt\%\ Pt \qquad \text{(Eq. 2)}$$

Table 2-2: Summary of prepared separation materials.

Sample ID	Zeolite	Calculated wt% Pt	Metal Dispersion (%)
PB-00382-10	HY	0.901	107.6
PB-00382-11	HY	1.775	113.6
PB-00382-12	4A	0.765	8.1
PB-00382-13	4A	1.522	14.2
PB-00382-15	13X	0.895	42.4
PB-00382-16	13X	1.730	2.6
PB-00382-20	5A	0.624	23.7
PB-00382-21	5A	1.115	12.4

Platinum dispersion and metallic surface area was determined via a chemisorption technique using the Micromeritics ASAP 2020c, summarized in Table 2-2. Values obtained from the analysis provided information regarding the Pt dispersion efficiency on the surface of the material.

2.2 RGD Manifold

The manifold was designed and constructed to operate at ambient conditions (e.g. atmospheric pressure, room temperature). The manifold (Figure 2-1) allows for simple monitoring of the process using a hygrometer and a Residual Gas Analyzer (RGA). The sample bed was constructed of ½” stainless steel, typically containing 20 g of material. Two mass flow controllers (FC-01 and FC-02) allowed for controlled gas flow (Ar and H_2) through the system and sample bed. FC-01 was used for lower flow rates (0-500 sccm), and FC-02 was used for higher rates (0-2000 sccm). A furnace allowed for the material to undergo bakeouts between experiments without having to remove it from the system. A septum (S-01) allowed for the direct injection of liquid samples just before the sample bed. Effluent gases passed though the chilled mirror moisture hygrometer, and an RGA monitored the effluent composition. The Lecture Bottle Station was used to deliver gaseous ammonia to the system, loading a sample volume (SV-01, 1.5 L). Once full, the flow of gas was redirected in to SV-01, moving it into the system and over the sample bed.

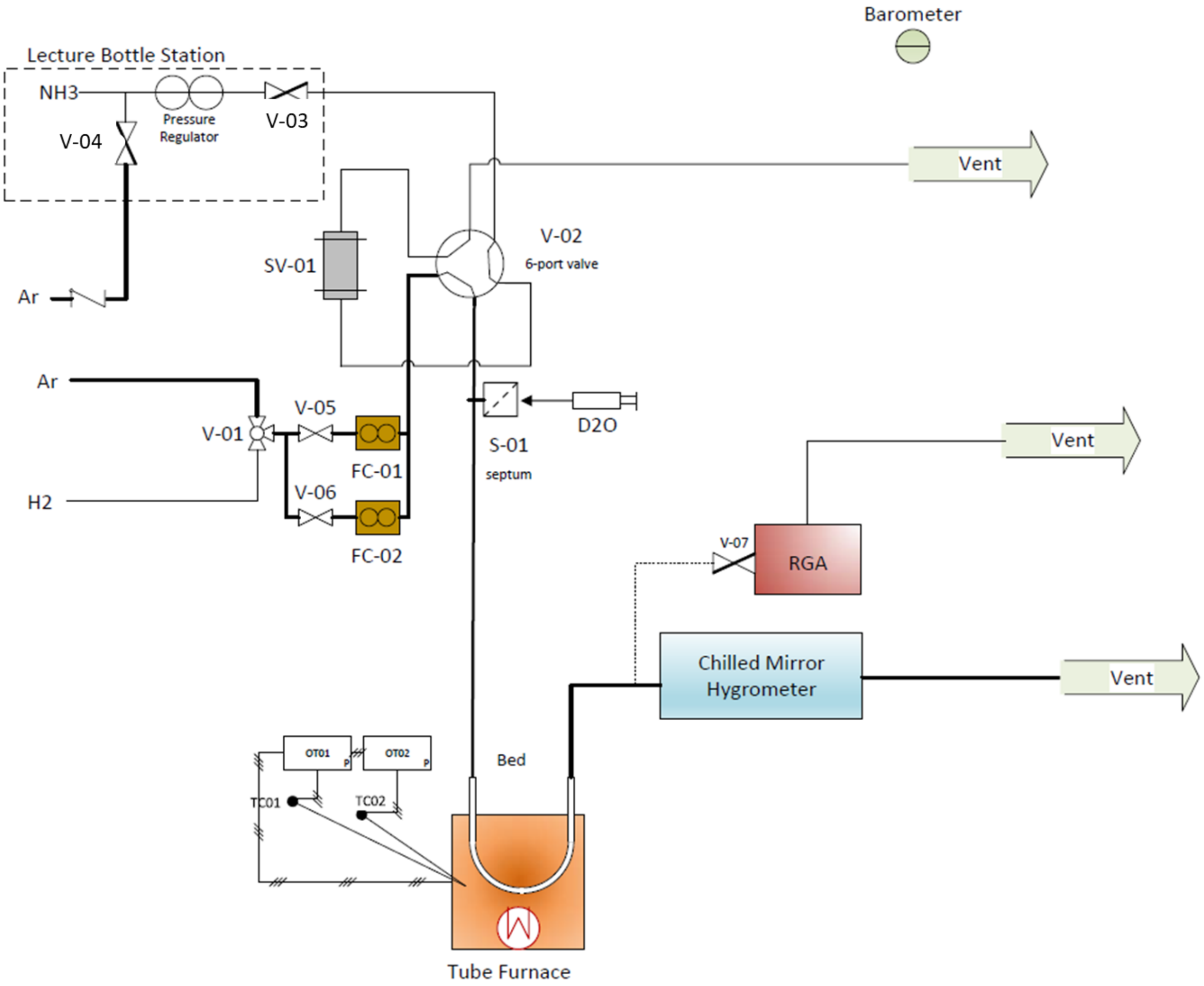

Figure 2-1: Schematic of the RGD manifold.

2.3 Experimental Design

For each material tested, a series of experiments were performed in a specific order to reduce experimental variables. Deuterated samples of water (Aldrich, 99.8 atom% D, Lot # STBH2109) and ammonia (Aldrich, 99 atom% D, Lot # MBBC3735) were used to load the test materials, then the material regenerated with H_2 gas (NexAir, Ultra High Purity) and monitored for concentrations of D in the effluent stream higher than natural abundance. Experiments are continually monitored via RGA data logging with periodic hygrometer data collection. The order of experiments is summarized in Table 2-3. Experimental conditions were followed as described below, unless otherwise stated.

Table 2-3: Experimental procedures.

Test	Procedure
1	Material Blank
2	D_2O/H_2
3	ND_3/H_2
4	$D_2O/ND_3/H_2$

2.3.1 Test 1 – Material Blank

Freshly loaded samples would have H_2 gas passed over at them at 50 sccm for 1-2 hours, to establish baseline H_2 isotopologue data.

2.3.2 Test 2 – D_2O/H_2

Using a syringe, a volume of D_2O would be injected into the system and passed through the sample bed via Ar carrier gas at 50 sccm. After 1-2 hours, H_2 flow (50 sccm) would begin to regenerate the material. RGA data collections would begin prior to injection.

2.3.3 Test 3 – ND_3/H_2

The SV would be filled with ND_3, using pH paper as an indicator as to when the SV was full. Ar carrier gas would move the ND_3 through the sample bed at 25 sccm, allowing approximately 2 hours before introducing H_2 into the system. H_2 flow would be increased to 50 sccm. Ar flow rate reduction was made to reduce the intensity of the exothermic heat of adsorption.

2.3.4 Test 4 – $D_2O/ND_3/H_2$

D_2O would be loaded via injection using Ar carrier gas to move it through the sample bed. After 1-2 hours, ND_3 would be introduced in the same manner as Test 3. H_2 would be passed through the bed at 50 sccm.

2.4 Additional Analysis

Collected samples would occasionally undergo Temperature-Programmed Desorption (TPD) analysis using a Micromeritics AutoChem II 2920. The applied method heated the sample to 700 °C at a ramp of 10 °C/min with a 30 minute hold once at temperature. Mass spectroscopy (MS) data was collected of the desorbed gases using an MKS PerfectEye MS.

3.0 Results and Discussion

The initial experiments performed using the Pt/HY samples (PB-00382-10 and PB-00382-11) allowed for the development of more pointed objectives regarding how each experiment should be performed to maximize and standardize the output of the desired data by the most efficient means possible. Therefore, the first samples analyzed produced scoping results that ultimately allowed for improved data collection for samples analyzed thereafter, albeit also demonstrating active isotopic exchange capabilities.

3.1 5A Molecular Sieves

Following the establishment of the experimental procedure, the Pt/5A samples were tested to create a performance baseline as 5A (uncatalyzed) is commonly used within RGD systems.

3.1.1 (PB-00382-20) 0.624 wt% Pt/5A

The sample bed was loaded with 20.0453 g of 0.624 wt% Pt/5A (PB-00382-20). Experiments were performed back-to-back.

3.1.1.1 Test 1 – Material Blank

The material blank was performed on the loaded sample for approximately 3 hours total, allowing for a stabilized baseline to be collected (Figure 3-1). Focusing only on the isotopologues of molecular hydrogen (masses 2, 3, and 4), a segment of the resulting data was used to determine the baseline concentrations of the effluent gas stream (Table 3-1). It should be noted that the signal-to-noise ratio begins to lessen as the partial pressures become smaller due to sensitivity limitations of the RGA, resulting in less accurate values at lower concentrations, as observed with the mass 4 trace in Figure 3-1. The collected data was compared to data collected from passing H_2 through the sample bed without containing a sample. The resulting data suggests negligible levels of isotopic exchange without inclusion of deuterium containing moieties on the sample material.

Table 3-1: Material Blank resulting concentrations of the hydrogen isotopologues for sample 0.624 wt% Pt/5A (PB-00382-20).

Mass	Concentration (%)	H_2 feed gas w/o Sample (%)
2	97.94	98.58
3	1.96	1.41
4	0.10	0.01

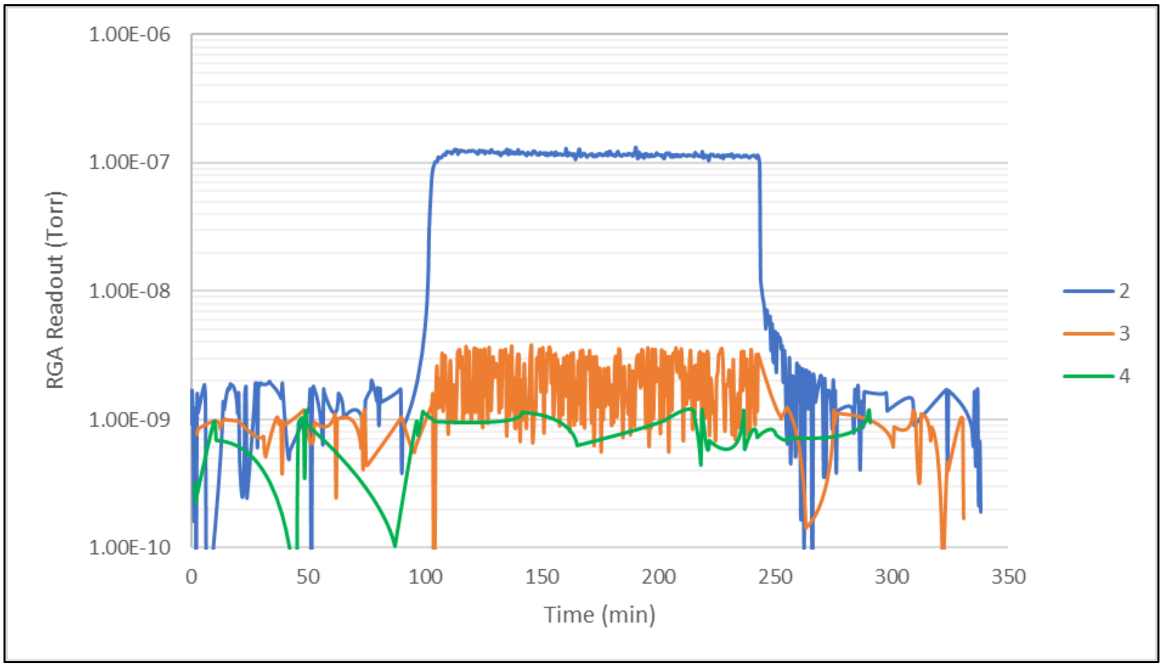

Figure 3-1: Material Blank for 0.624 wt% Pt/5A (PB-00382-20).

3.1.1.2 Test 2 – D_2O/H_2

Without further sample preparation after the material blank experiment, the sample was loaded with 1.4 mL D_2O, constituting one third of the materials known capacity of approximately 20% by mass. After flowing Ar gas through the system for approximately 1 hour at 50 sccm, verifying that very little moisture (~173 ppm) was observed in the effluent stream, H_2 flow started (50 sccm). The resulting spectrum (Figure 3-2) demonstrated a large isotopic exchange based on the observed partial pressures of masses 3 and 4, assumed to be HD and D_2, respectively. Unfortunately for this experiment, data collection was not able to capture the whole regeneration process due to an error with the RGA. From the collected RGA data, no water was observed in the effluent stream, as depicted by masses 18, 19, and 20 in Figure 3-3. This result was not surprising as the volume of water loaded was only a third of the estimated capacity of the zeolite. Data collected from the hygrometer (Figure 3-3) demonstrated a small increase in moisture of 173 to 769 ppm (converted from Dew Point of -37.2 to -22.9 °C).

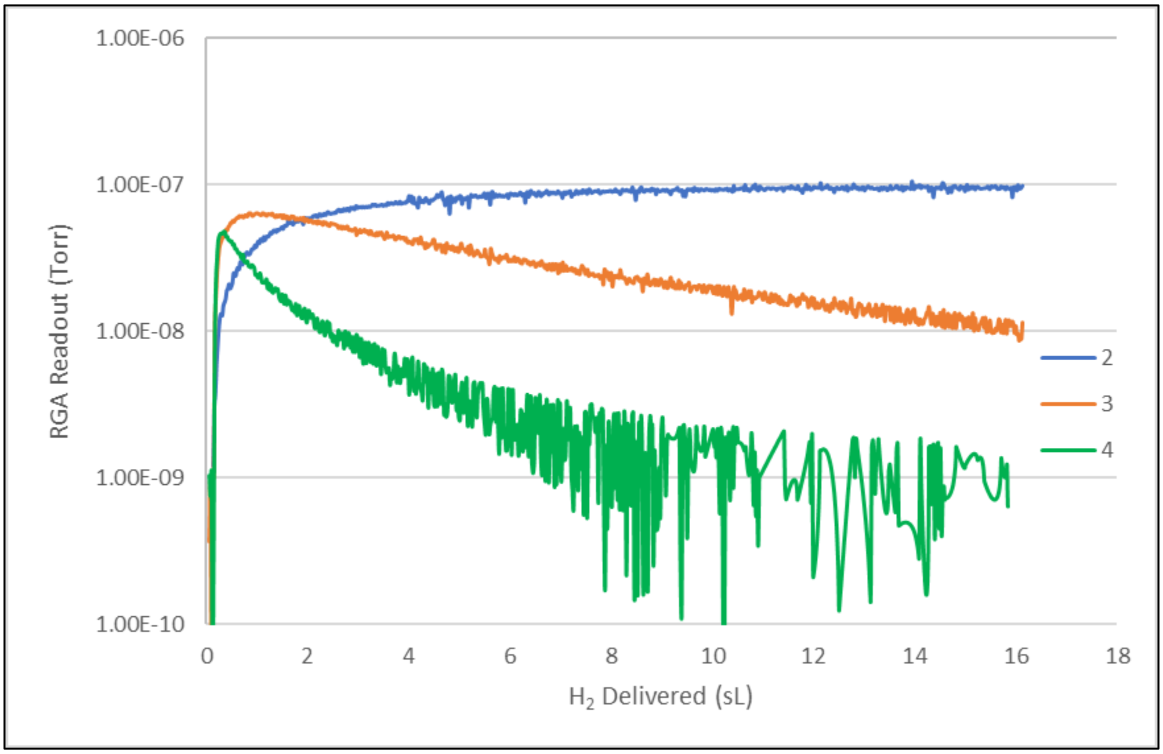

Figure 3-2: RGA trace of the D_2O/H_2 experiment for sample 0.624 wt% Pt/5A (PB-00382-20).

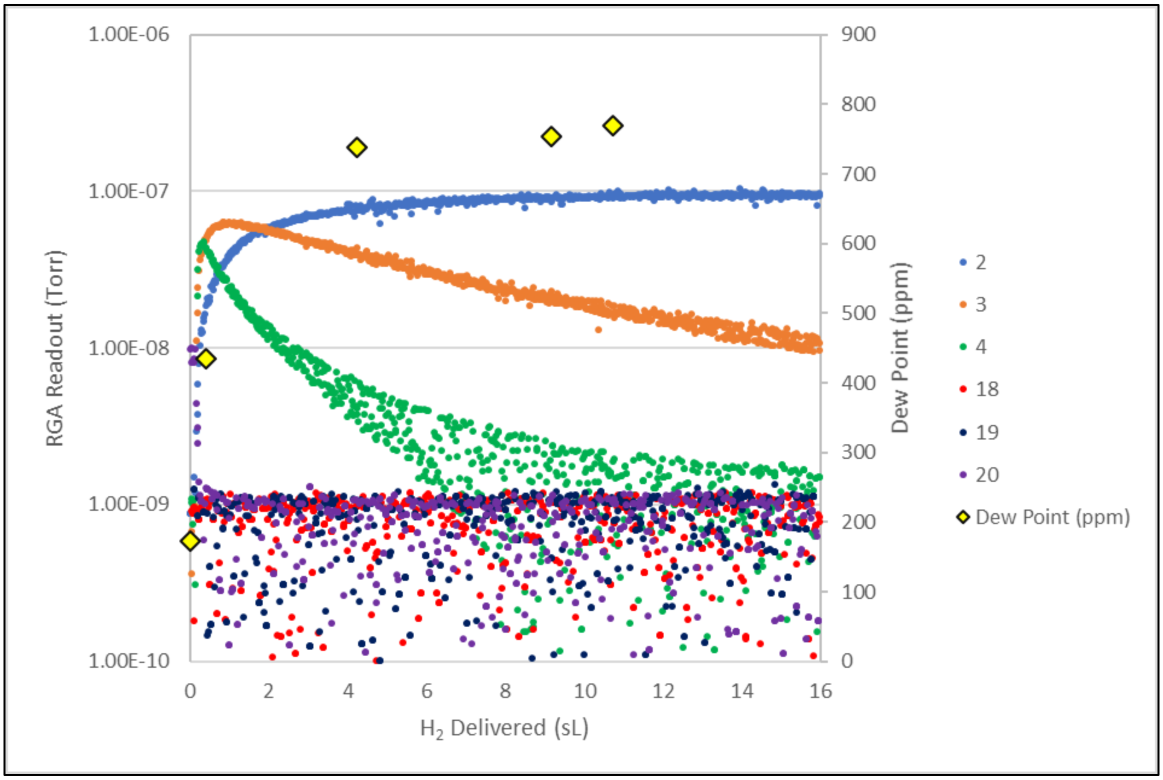

Figure 3-3: RGA trace of the D_2O/H_2 experiment for sample 0.624 wt% Pt/5A (PB-00382-20), including masses 18, 19, and 20 and hygrometer data.

3.1.1.3 Test 3 – ND_3/H_2

This experiment was performed without material bakeout or other material preparation performed after the previous experiment. Similar to the D_2O/H_2 experiment, the material demonstrated good isotopic exchange characteristics based on the effluent stream being laden with masses 3 and 4, assumed to be a mixture of HD and D_2 (Figure 3-4). After delivery of approximately 55 sL of H_2 through the 20 g sample, the material appeared fully regenerated based on the final mass concentrations in the effluent stream when compared to those of the initial material blank test (Table 3-2). Although, the material appeared nearly completely regenerated by 30 sL H_2, suggesting a smaller quantity of regeneration gas could be used to regenerate ~97% of the material.

Table 3-2: Final hydrogen isotopologues as compared to the initial material blank.

Mass	Concentration at 30 sL H_2 (%)	Concentration at 55 sL H_2 (%)	Material Blank Concentration (%)
2	96.98	97.90	97.94
3	3.03	2.19	1.96
4	0.01	0.08	0.10

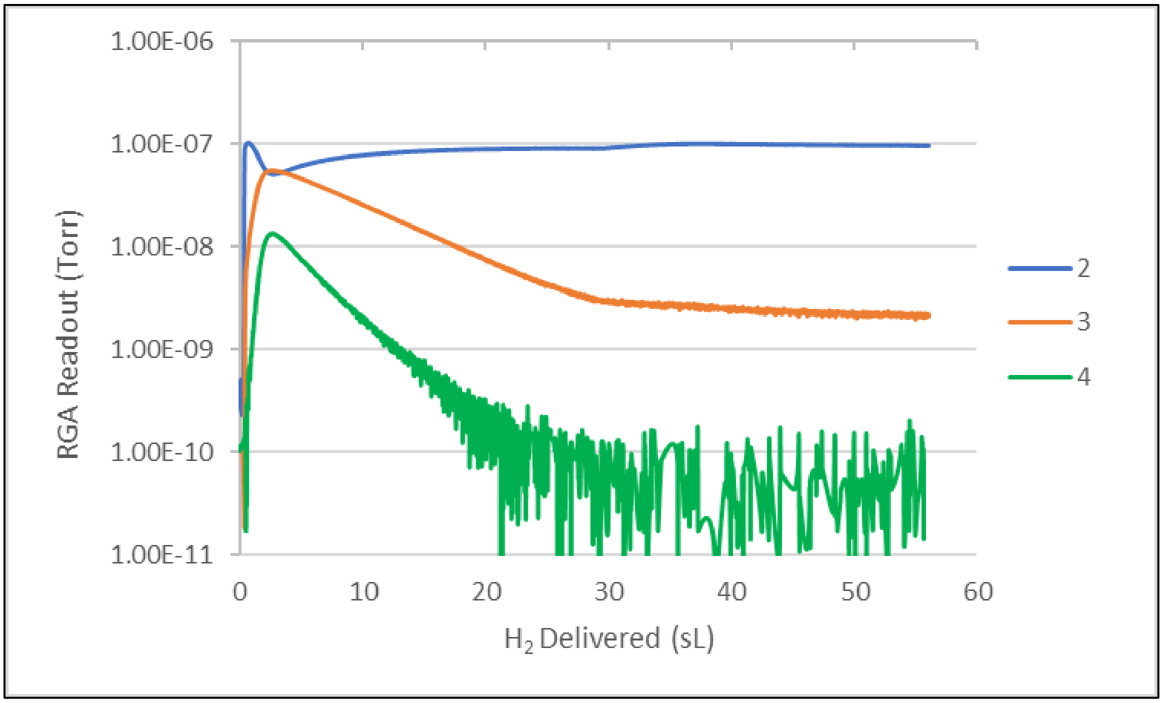

Figure 3-4: RGA trace of the ND_3/H_2 experiment for sample 0.624 wt% Pt/5A (PB-00382-20).

This data can be further extrapolated and applied to an existing RGD bed, containing 65 lbs. of material (Figure 3-5). Assuming the same rate of isotopic exchange and a standard 1A cylinder containing 2400 psig H_2, it can be calculated that roughly 6 full cylinders would be required to remove >95% of the deuterium on the material, as shown in Table 3-3. After 8 cylinders, removal of all deuterium becomes too H_2 expensive.

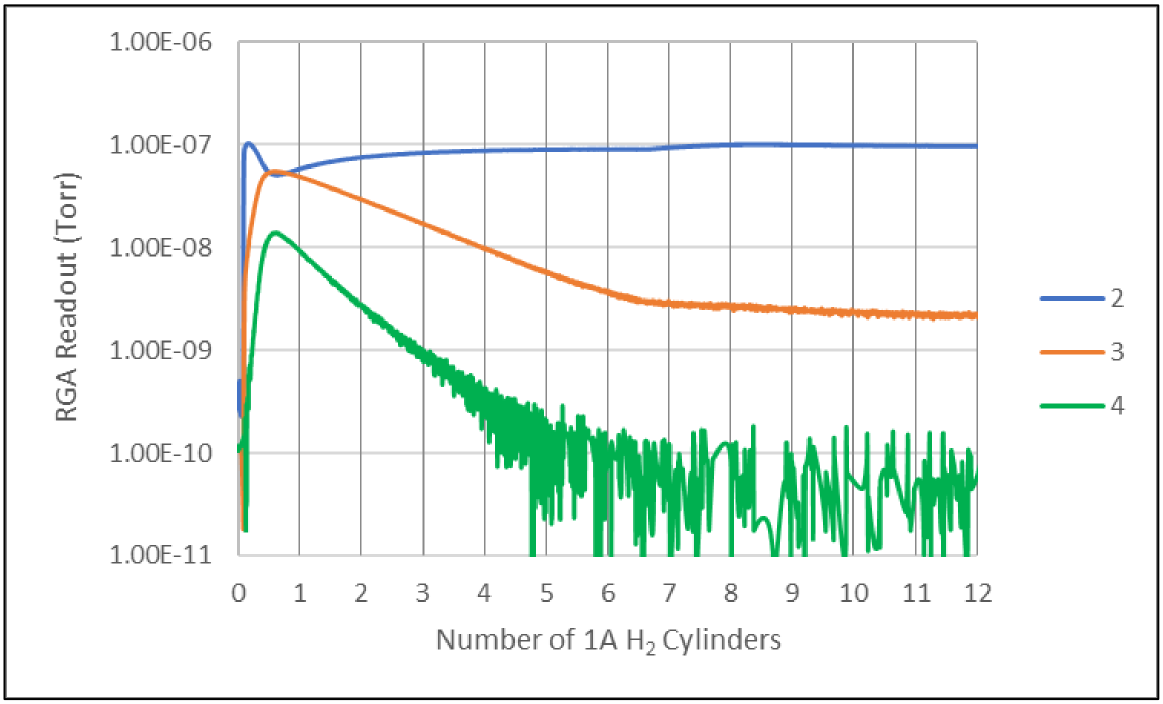

Figure 3-5: Projected consumption of 1A H_2 gas cylinders required for complete deuterium removal for the 0.624 wt% Pt/5A (PB-00382-20) sample after loading with ND_3.

Table 3-3: Extrapolated number of 1A H_2 gas cylinders required to reduce deuterium concentrations on material.

Number of 1A Cylinders	Mass Concentrations (%)		
	2	3	4
1	50.42	41.77	7.81
2	70.30	27.18	2.52
3	82.45	16.72	0.83
4	89.73	9.91	0.36
5	93.93	6.00	0.06
6	96.06	3.92	0.02
7	96.94	2.99	0.08
8	97.48	2.52	0.00
9	97.68	2.28	0.03
10	97.63	2.28	0.09

As a side note, it was noted that after 30 sL H_2 had been delivered (at the 600 minute mark after H_2 flow started), there was a release of additional gas suspected to be ammonia, as determined by the increased masses observed in the RGA spectrum (Figure 3-6). With the uptick in mass 15 observed in the effluent stream, masses 16 and 17 were assigned to ammonia rather than the possibility of residual water from the previous experiment. By assuming the desorbed masses to belong to moieties of ammonia and its respective fragments, the following identities have been assigned and listed in Table 3-4. The effluent stream may have shown an influx of NH_3 and its respective molecular fragments. As of this time, the reasoning behind this event is unexplainable and requires additional experiments to confirm repeatability and elaborate on the suspected cause.

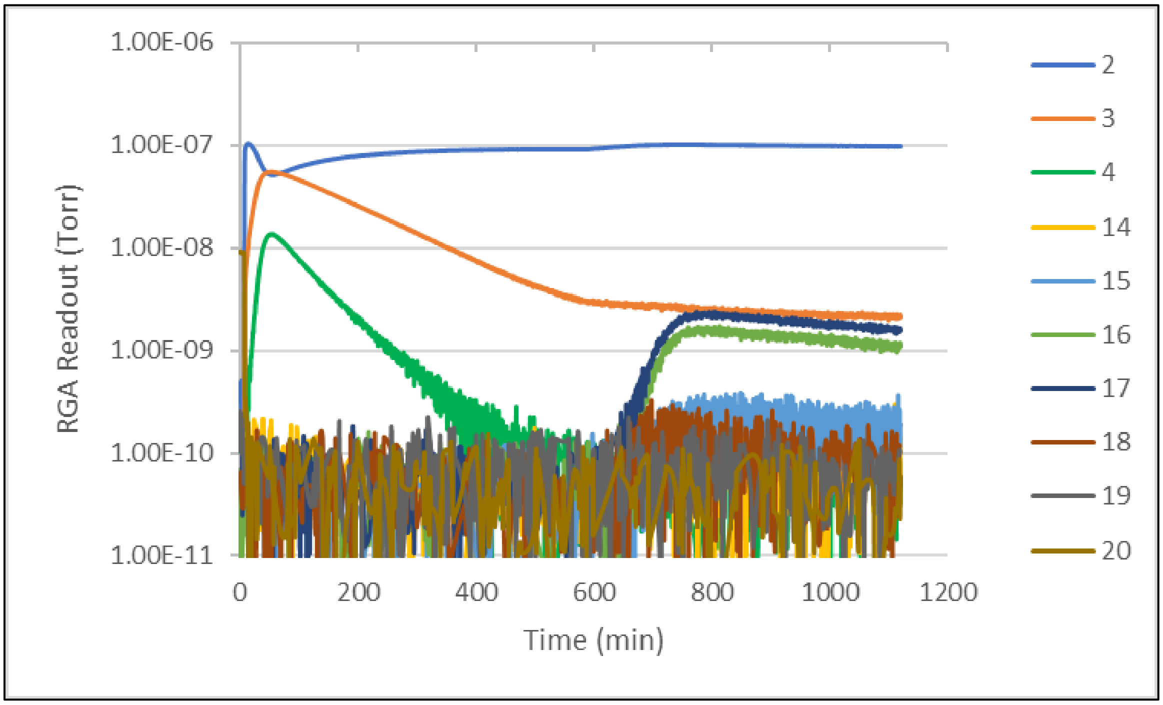

Figure 3-6: RGA trace of the ND_3/H_2 experiment for sample 0.624 wt% Pt/5A (PB-00382-20) depicting evolution of masses 14 through 20 over time.

Table 3-4: Assigned identities to masses pertaining to ammonia and water molecular fragments.

Mass	Ammonia Fragments	Water Fragments
14	N^+	
15	NH^+	
16	NH_2^+, ND^+	O^+
17	NH_3^+, NHD^+	OH^+
18	NH_2D^+, ND_2^+	H_2O^+, OD^+
19	NHD_2^+	HDO^+
20	ND_3^+	D_2O^+

3.1.1.4 Test 4 – $D_2O/ND_3/H_2$

In the same manner as Tests 2 and 3, the sample was loaded with 1.4 mL D_2O and approximately 1500 mL ND_3. The material demonstrated isotopic exchange with the H_2 gas, as depicted in Figure 3-7. However, much like the results of Test 3, the RGA also detected a large amount of ammonia being desorbed as soon as the H_2 was introduced. Figure 3-8 shows a small segment of the first 10 sL H_2 delivered to the sample. Almost immediately, masses corresponding to the various isotopologues of ammonia were observed.

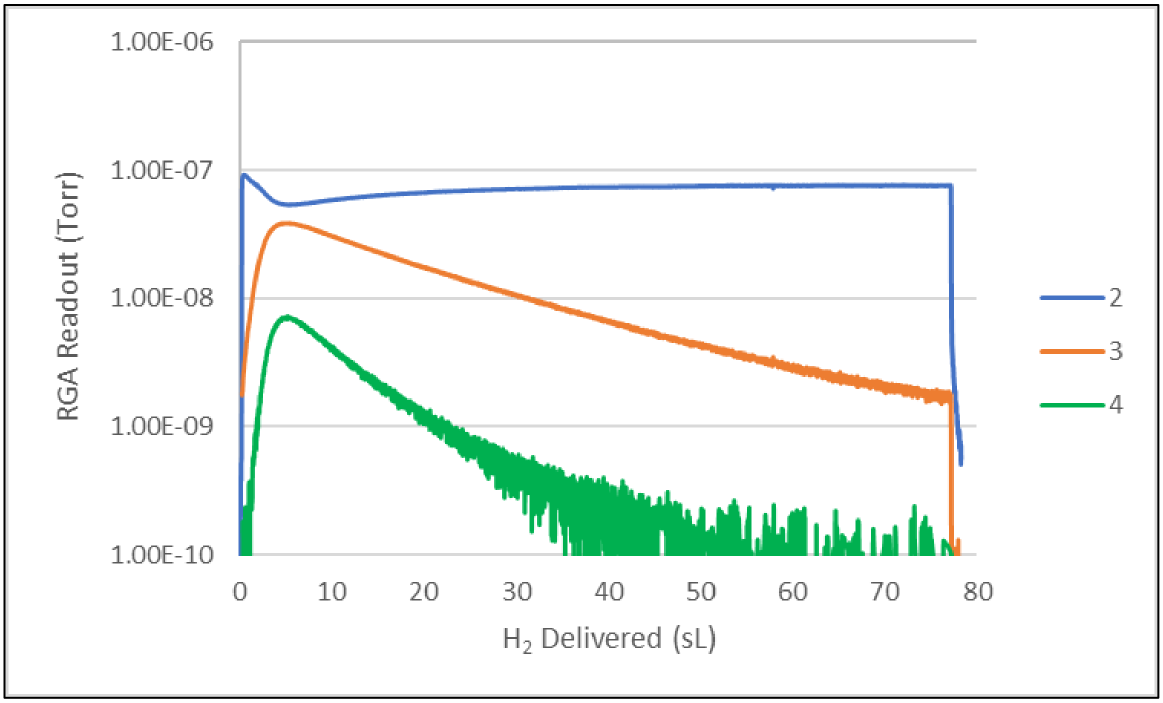

Figure 3-7: RGA trace of the $D_2O/ND_3/H_2$ experiment for sample 0.624 wt% Pt/5A (PB-00382-20).

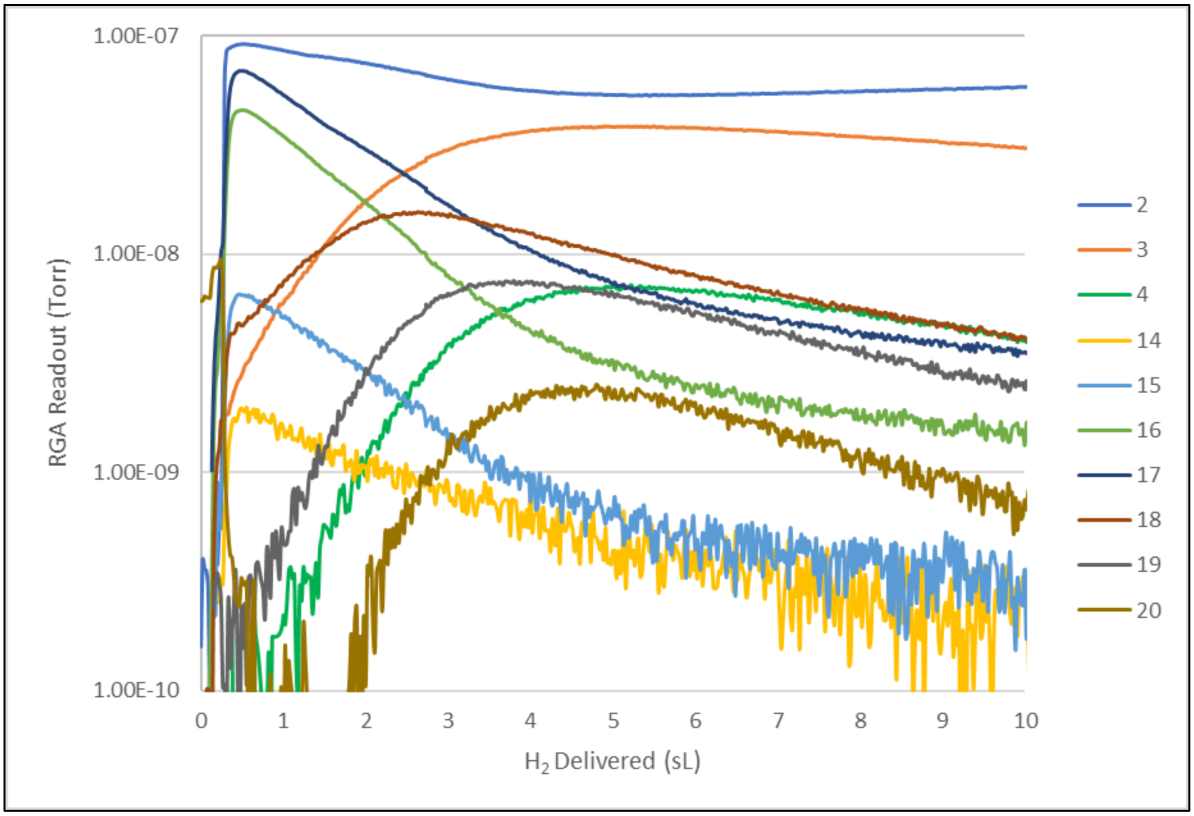

Figure 3-8: RGA trace of the $D_2O/ND_3/H_2$ experiment for sample 0.624 wt% Pt/5A (PB-00382-20) depicting evolution of masses 14 through 20 over the first 10 sL of H_2 being delivered.

As a post-experimental analysis of the test material, TPD analysis was performed. Collecting a sample from the inlet and outlet sides of the sample bed, each sample was analyzed. It is believed that due to the reduced loading sizes of the water and ammonia, the bulk of it would be found closer to the inlet side of the sample bed and the material near the outlet side should show lesser quantities. Any quantity of water or ammonia may be a sign that either was desorbing during the process and traveling through the sample bed only to readsorb near the outlet.

The TPD-MS sample from the inlet side of the sample bed (Figure 3-9) demonstrated a gross saturation in the detector for masses 18, 19, and 20. For masses 15 and 16, the detector was not saturated as indicated by the curves in the lines. Mass 14 is sporadic due to low concentrations. This information suggests that the bulk of the gas coming off is water vapor, due to the saturation of the detector. This would also suggest that ammonia had desorbed during Test 4, supported by the RGA data provided above. The TCD signal shows a large desorption around 300 °C with a slight broad shoulder around 500 °C, where water is the first to desorb followed by ammonia. These desorption temperatures are in good agreement with previously observed desorption experiments.[3,4] The slight discrepancies may be attributed to differing heating ramps between samples and instruments used.

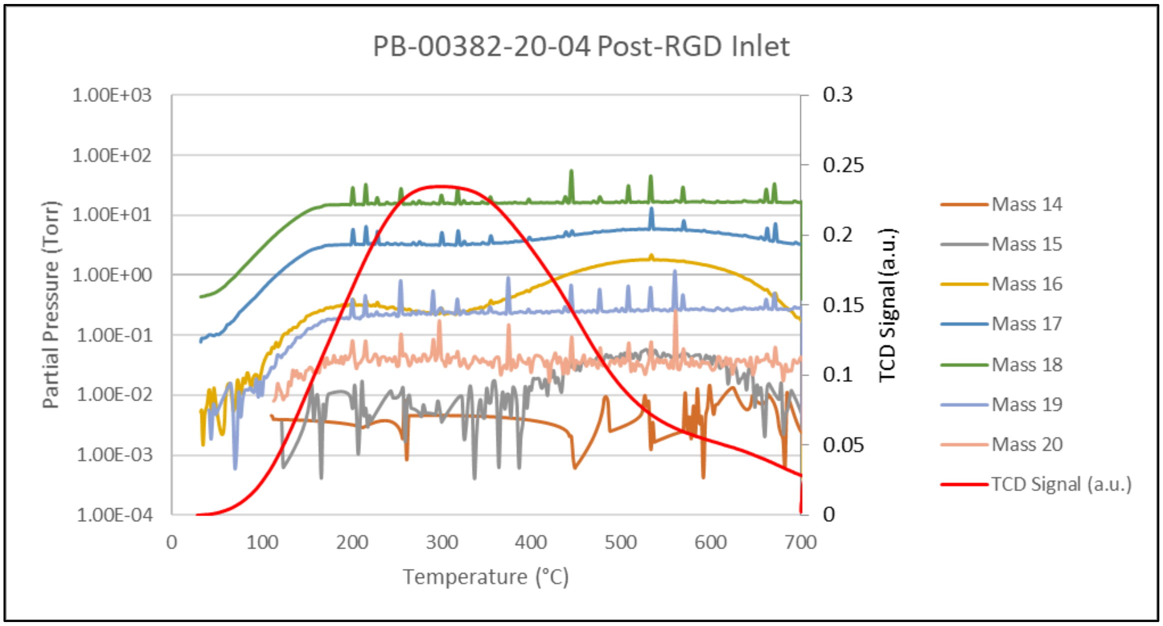

Figure 3-9: TPD-MS results from 0.624 wt% Pt/5A (PB-00382-20) inlet side of sample bed after Test 4.

Figure 3-10 tells a similar story where masses 18, 19, and 20 saturate the detector while masses 15, 16, and 17 appear to be lesser in concentration. Again, the TCD signal depicts peak desorption around 250-300 °C and a small shoulder has appeared at approximately 500 °C. Peak deconvolution may help to provide more accurate peak positions.

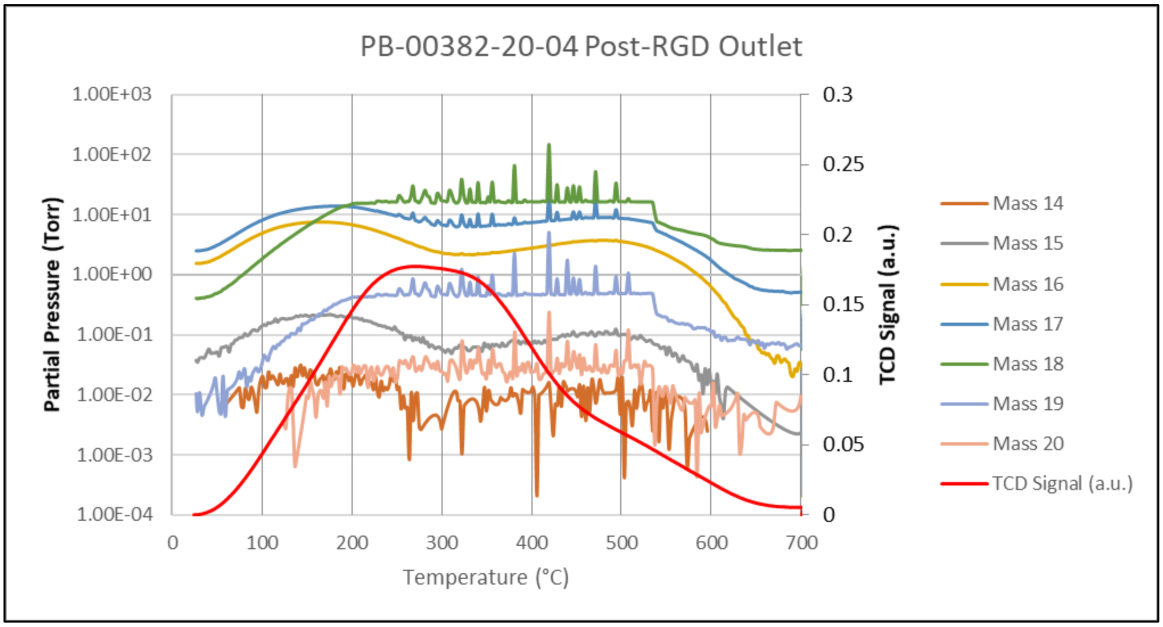

Figure 3-10: TPD-MS results from 0.624 wt% Pt/5A (PB-00382-20) outlet side of sample bed after Test 4.

3.1.2 (PB-00382-21) 1.115 wt% Pt/5A

The sample bed was loaded with 21.6402 g of 1.115 wt% Pt/5A (PB-00382-21) and the experiments were performed back-to-back, in the same manner described above.

3.1.2.1 Test 1 – Material Blank

The material blank experiment was performed for approximately two hours, generating H_2 baseline data by passing H_2 gas over the test sample. The resulting data (Figure 3-11) produced steady enough levels of masses 2, 3, and 4 that a representative baseline could be determined. Using a small section of data in the plateau regions of the experiment, hydrogen isotopologue concentrations were determined and listed in Table 3-5. The results were found to be in good agreement with sample 0.624 wt% Pt/5A (PB-00382-20) (Table 3-1).

Table 3-5: Material Blank resulting concentrations of the hydrogen isotopologues for sample 1.115 wt% Pt/5A (PB-00382-21).

Mass	Concentration (%)	H_2 feed gas w/o Sample (%)
2	98.00	98.58
3	1.96	1.41
4	0.04	0.01

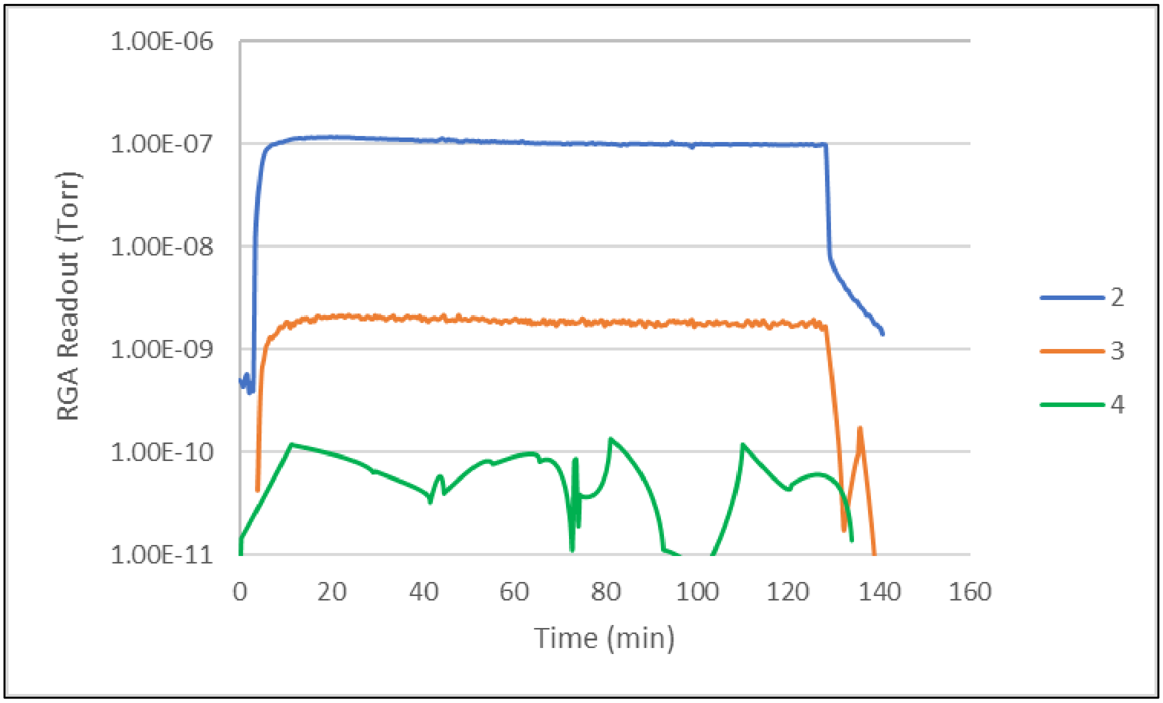

Figure 3-11: RGA trace of the H_2 material blank for sample 1.115 wt% Pt/5A (PB-00382-21).

3.1.2.2 Test 2 – D_2O/H_2

The experiment began promptly after concluding the material blank test, with the addition of 1.4 mL D_2O injected into the system. Ar gas was allowed to move the water through the sample for 2 hours before introducing H_2, verifying very little moisture (~114 ppm) in the effluent stream. Once H_2 flow began, masses 3 and 4 quickly increased then slowly tapered off as deuterium concentration on the material decreased. After delivery of approximately 60 sL H_2 through the 21 g sample, the partial pressures had stabilized, the isotopologue concentrations were determined and summarized in Table 3-6, demonstrating that the test material had been nearly completely regenerated.

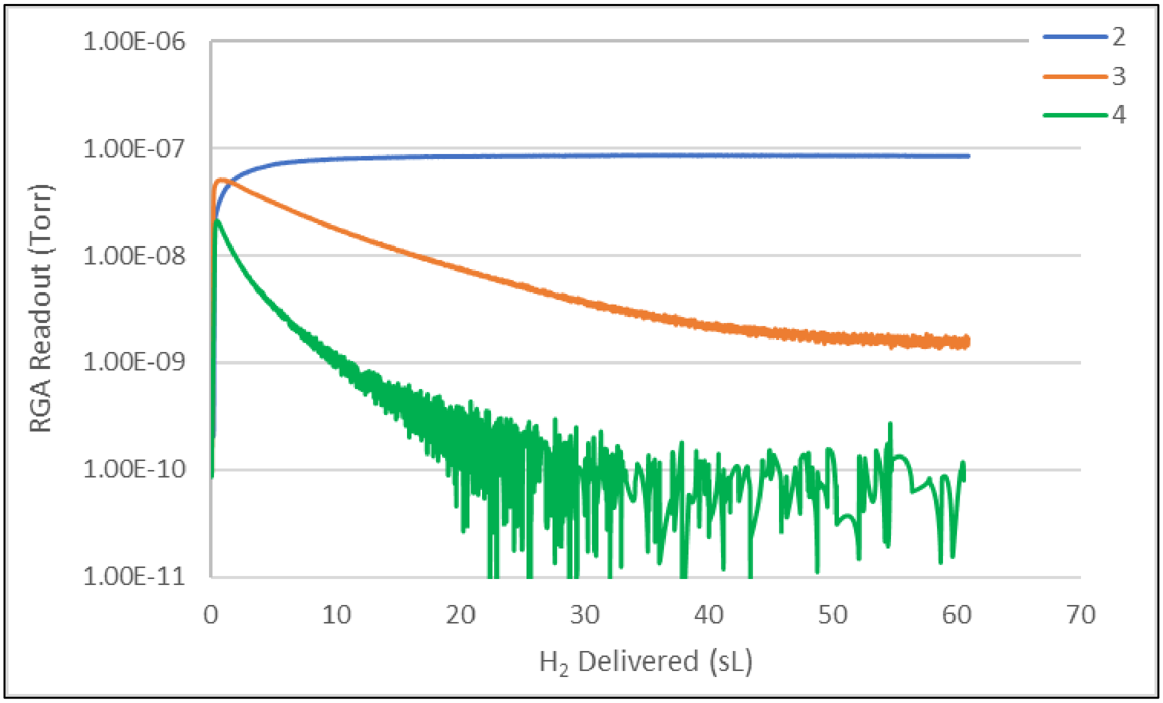

Figure 3-12: RGA trace of the D_2O/H_2 experiment for sample 1.115 wt% Pt/5A (PB-00382-21).

Table 3-6: Hydrogen isotopologues concentrations after completion of Test 2, in comparison to Test 1 and H_2 feed gas.

Mass	Test 2 Concentration (%)	Test 1 Concentration (%)	H_2 feed gas w/o Sample (%)
2	97.76	98.00	98.58
3	2.17	1.96	1.41
4	0.07	0.04	0.01

Due to the experiment being allowed to proceed overnight, dew point data collection was sparse. Therefore, only RGA data was used to determine if any moisture had evolved during the isotopic exchange process. Based on data presented in Figure 3-13, there was no evidence supporting water desorption from the test material.

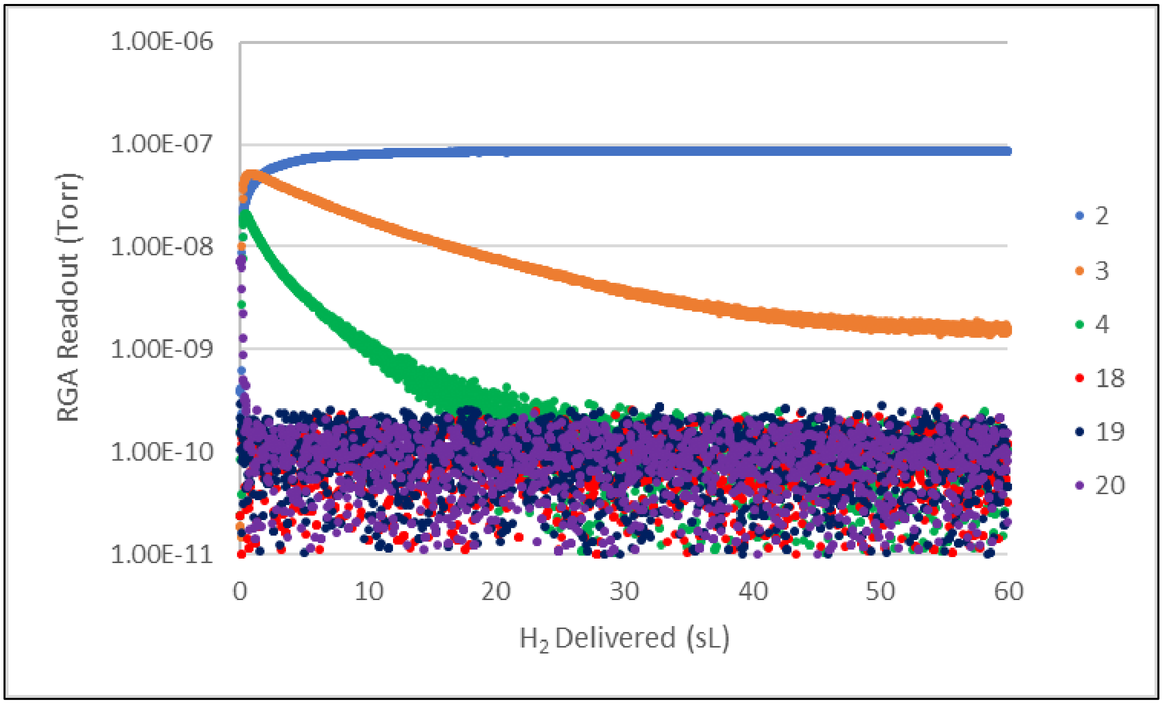

Figure 3-13: RGA trace of the D_2O/H_2 experiment for sample 1.115 wt% Pt/5A (PB-00382-21), including masses 18, 19, and 20.

After Test 2 had completed, a bakeout was performed *in situ* and the effluent stream was monitored via RGA. The bakeout was performed stepwise, using a 0.5 °C/min heat ramp, to ensure that the test sample would not be damaged in the process. The first step heated the material to 150 °C (0-250 min), the second step increased the temperature to 250 °C (251-500 min), then the final step reduced the temperature to 20 °C, allowing the furnace to return to ambient temperature gradually with data collection ongoing. The resulting data (Figure 3-14) showed that the bulk of the water desorbed once the material started to warm to 150 °C (250-minute mark) and had ceased by the 500-minute mark. In the figure, mass 20 was purposely left out to avoid confusion with the Ar carrier gas used during the bakeout.

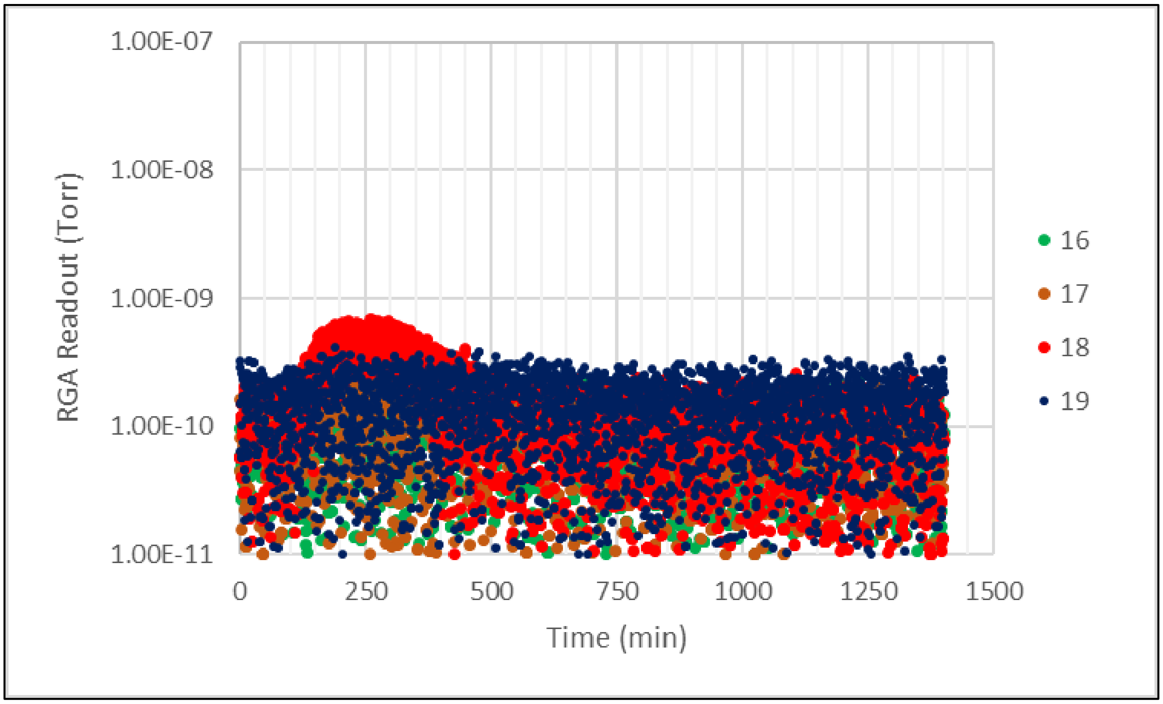

Figure 3-14: RGA trace of bakeout performed on sample 1.115 wt% Pt/5A (PB-00382-21) after Test 2.

3.1.2.3 Test 3 – ND_3/H_2

After the material had returned to room temperature with a continued flow of Ar carrier gas, the material was loaded with ~1.5 L ND_3 at a rate of 25 sccm using Ar carrier gas. After two hours, H_2 flow had started, resulting in immediate evidence of isotopic exchange, as shown in Figure 3-15. During this time, there was no evidence via RGA to suggest that any ammonia had desorbed from the material. This is in direct contrast with what was observed for the 0.624 wt% Pt/5A Test 3 (Figure 3-6) where it was observed that ammonia was released once the material appeared to be essentially free of deuterium. The difference between this sample and the 0.624 wt% sample, aside from catalytic loading, is the presence of water on the material. This sample underwent a small bakeout prior to loading with ammonia and therefore, may have played a role in the retention of the adsorbed ammonia however, additional experimentation is required to fully confirm this event with both samples, as noted above.

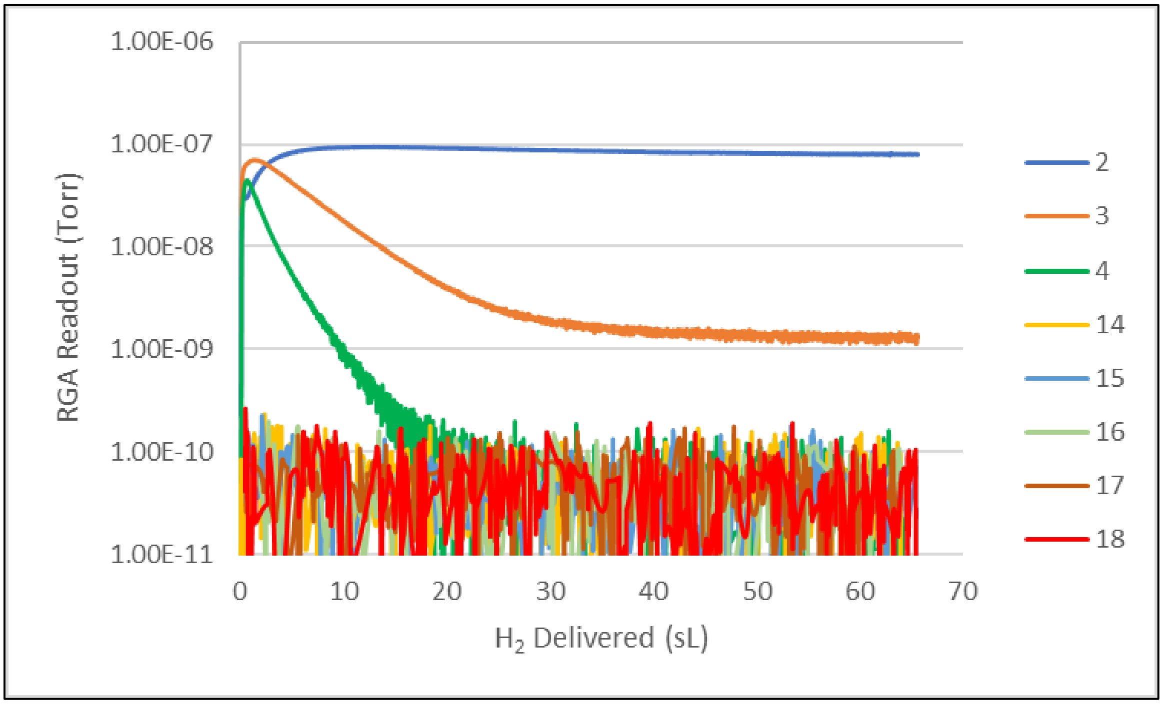

Figure 3-15: RGA trace of the ND_3/H_2 experiment for sample 1.115 wt% Pt/5A (PB-00382-21).

3.1.2.4 Test 4 – $D_2O/ND_3/H_2$

This experiment proceeded without any material alteration or preparation (e.g. bakeouts). The standard 1.4 mL D_2O was injected into the system and dispersed at 50 sccm using Ar carrier gas for ~80 minutes, demonstrating very little moisture in the effluent stream (~32 ppm). The sample was then loaded with ND_3 delivered at 25 sccm using Ar carrier gas for ~2 hours. Twenty minutes into the ND_3 loading on to the sample (100-minute mark in Figure 3-16), a small amount of mass 14 was observed in the RGA trace. At the 150-minute mark, masses 16 and 17 had spiked to nearly $1x10^{-7}$ Torr with notable amounts of masses 15, 14, and 18 as well. It is believed that the material may have been saturated with water and ammonia at this point and the observed ammonia isotopologues belonged excess/unbound gas exiting the system. Although it should be noted that mass 17 was in the greatest concentration and suggests the effluent stream consisted of mainly NH_3. At the 515-minute mark, there was another uptick in observable ammonia in the form of mass 18, 17, and 16, coupled with masses 14 and 15 to a lesser extent. This event corresponds to the introduction of H_2 (Figure 3-17), after allowing some time for the detectable ammonia levels in the effluent stream to return to lower concentrations before its start.

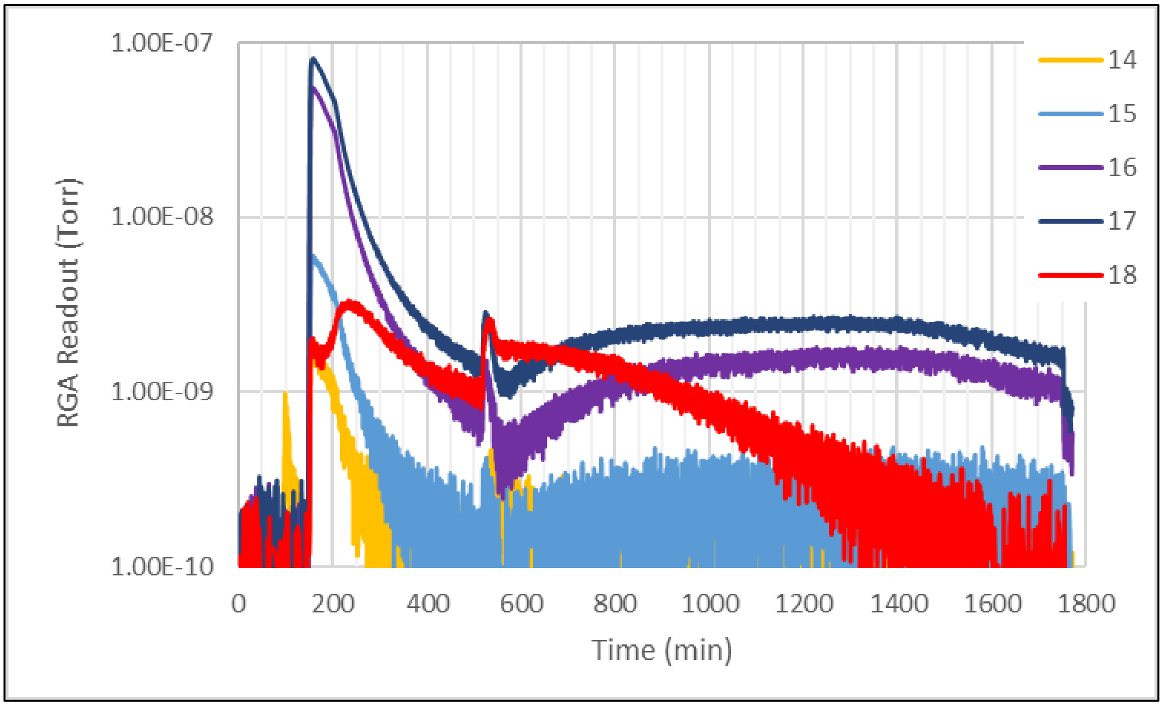

Figure 3-16: RGA trace of the $D_2O/ND_3/H_2$ experiment for sample 1.115 wt% Pt/5A (PB-00382-21), focusing on ammonia isotopologues and respective fragments.

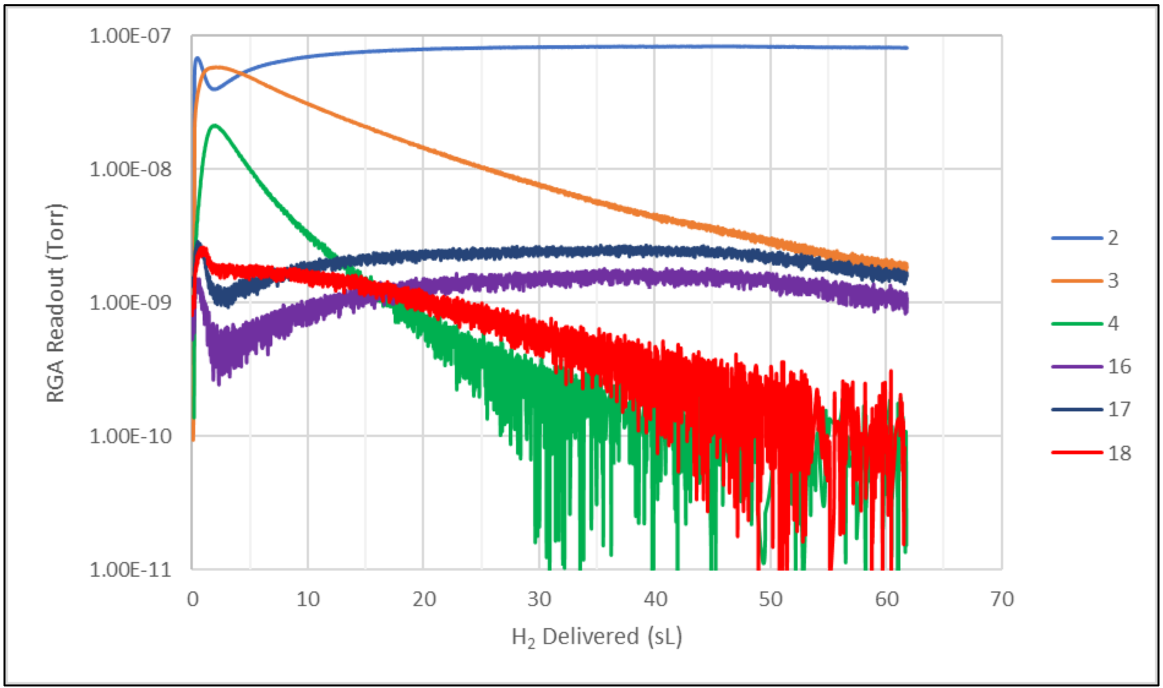

Figure 3-17: RGA trace of the $D_2O/ND_3/H_2$ experiment for sample 1.115 wt% Pt/5A (PB-00382-21), depicting H_2 introduction into system.

The steady decline in the partial pressure of mass 18 (assumed ND_3) coincides with the decline of masses 3 and 4 while there appears to be a period of increased desorption of masses 16 and 17. This would suggest that the desorbed moieties are the protium-containing isotopologue of ammonia as there is active exchange on going.

After the analysis, samples collected from the inlet (Figure 3-18) and outlet (Figure 3-19) of the sample bed were analyzed via TPD-MS. Similar to the resulting data from the 0.624 wt% Pt/5A sample, the sample collected from the inlet produced a spectrum showing detector saturation of masses 18, 19 and 20 and a massive TCD signal around 250-300 °C, suggesting that water had not previously desorbed during Test 4. Further downfield at roughly 500 °C, a small shoulder appears on the TCD trace, coupled with masses 14, 15, 16, and 17 desorbing in detectable amounts, proposing the desorption of chemisorbed ammonia, as also supported by previous studies.[3,4] The small increase in the masses 15 and 16 traces at roughly 175 °C suggest the desorption of residual ammonia physiosorbed on the material.

The outlet side of the sample bed appeared to be less concentrated in both water and ammonia, based on the degree of detector saturation. Masses 14, 15, 16, and 17 begin desorbing between 150-200 °C, signifying a sizable concentration of physiosorbed ammonia to be present on the outlet side of the sample bed. This phenomenon can be rationalized by the ammonia on the inlet side of the sample bed desorbing during Test 4, only to be readsorbed further down the bed by unsaturated catalyzed 5A. These elevated traces in Figure 3-19 continue on to approximately 500 °C before dropping off, as the remaining quantities of chemisorbed ammonia. The TCD trace shows a significant desorption around 300 °C however, the intensity of the signal is less than that of the inlet trace, supporting the notion of a lesser water content in the material as a result of stronger coordination and a reluctance to desorb during Test 4.

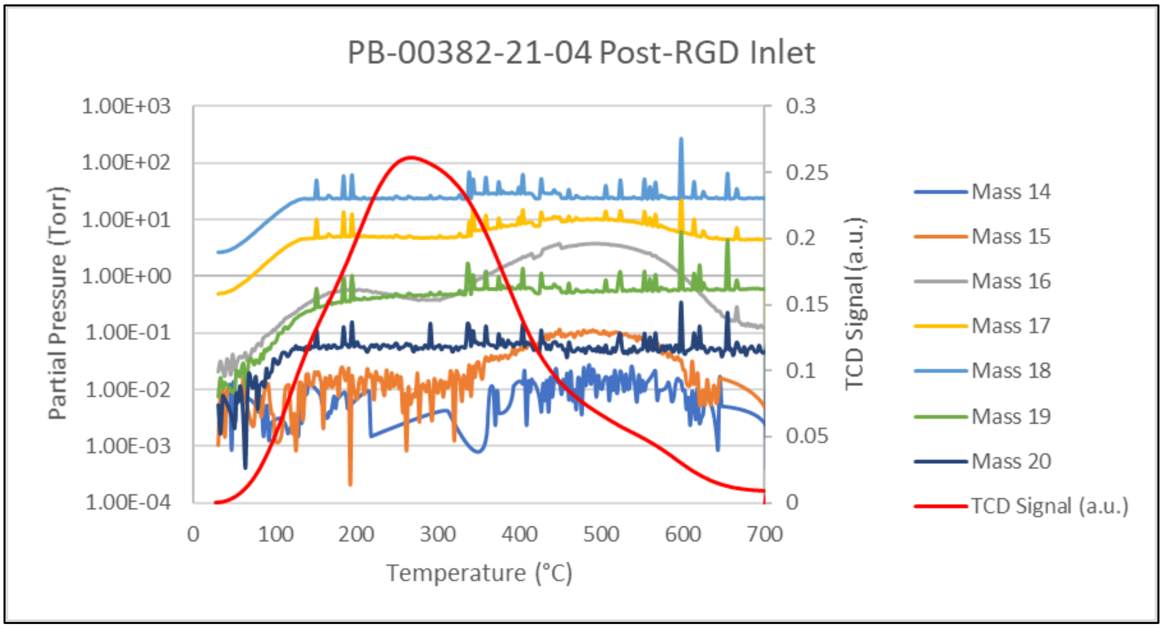

Figure 3-18: TPD-MS results from 1.115 wt% Pt/5A (PB-00382-21) inlet side of sample bed after Test 4.

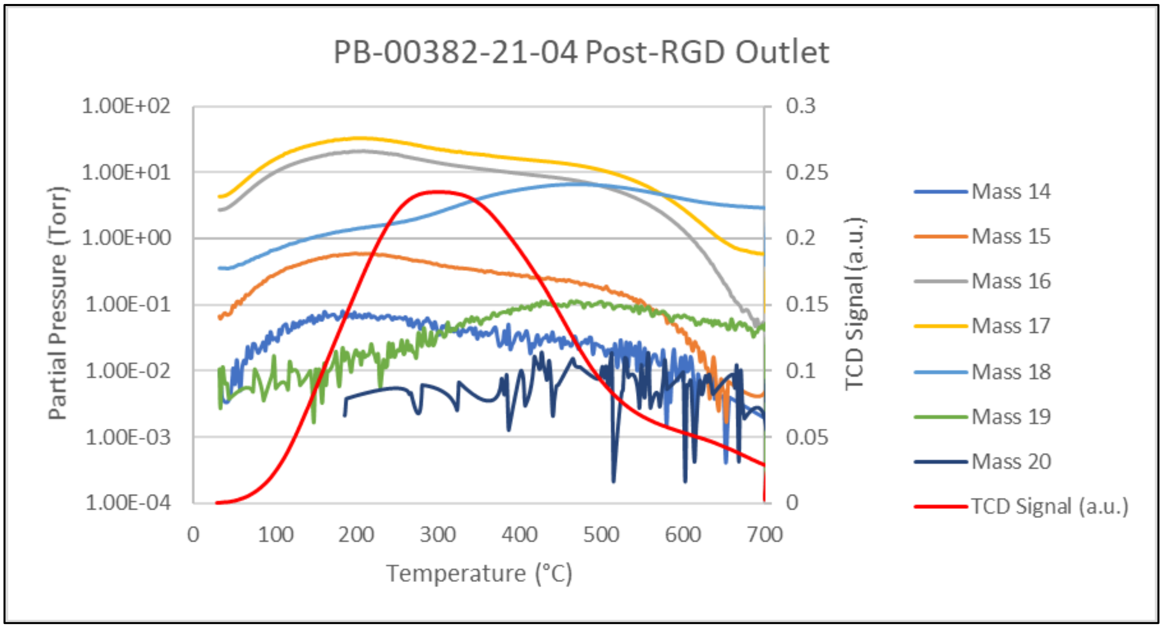

Figure 3-19: TPD-MS results from 1.115 wt% Pt/5A (PB-00382-21) outlet side of sample bed after Test 4.

Ignoring the desorption of anything but masses 2, 3, and 4, the resulting data can again be extrapolated and applied to existing RGD details (Figure 3-20). Making the same assumptions regarding rate of isotopic exchange, RGD material content mass, and H_2 quantity contained in a 1A gas cylinder, it may require up to 10 1A cylinders to regenerate ~95% of the material (Table 3-7).

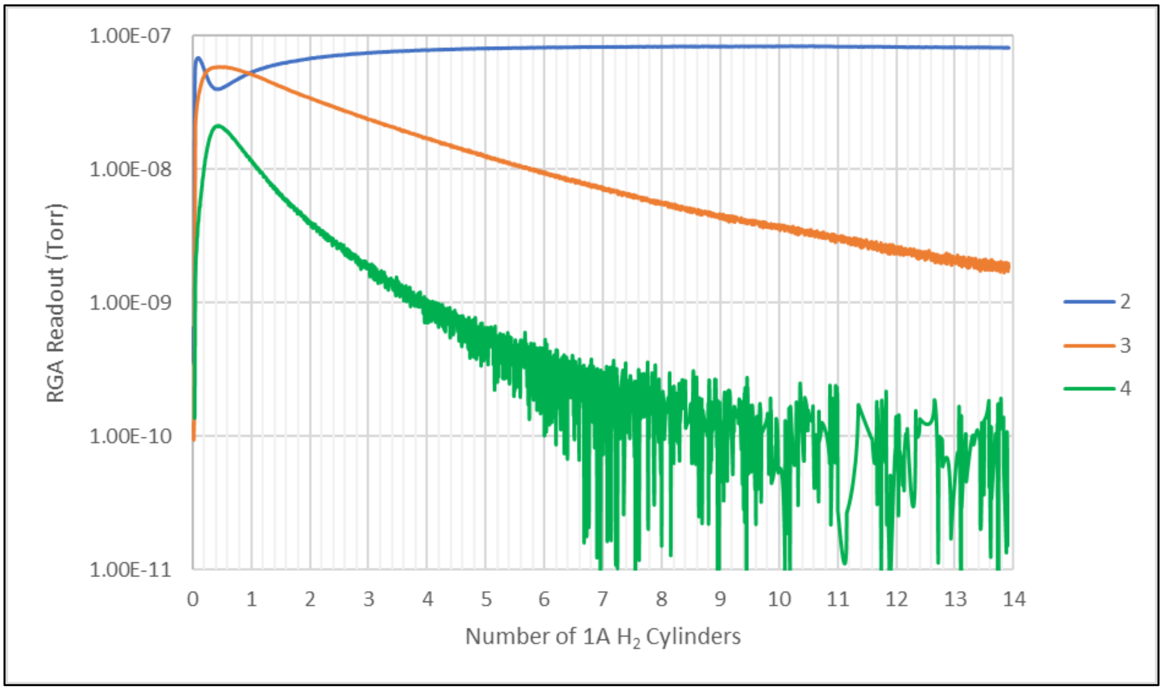

Figure 3-20: Projected consumption of 1A H_2 gas cylinders required for complete deuterium removal for the 1.115 wt% Pt/5A (PB-00382-21) sample after loading with D_2O and ND_3.

Table 3-7: Extrapolated number of 1A H_2 gas cylinders required to reduce deuterium concentrations on material.

Number of 1A Cylinders	Mass Concentrations (%)		
	2	3	4
1	45.56	44.36	10.08
2	67.81	28.76	3.42
3	74.50	23.60	1.90
4	81.35	17.71	0.94
5	86.15	13.21	0.64
6	89.36	10.28	0.36
7	91.59	8.07	0.34
8	93.47	6.40	0.13
9	94.91	5.07	0.02
10	95.60	4.31	0.09

3.1.3 Control 5A Experiment

To verify isotopic exchange of the catalyzed material, a control experiment was performed using uncatalyzed 5A molecular sieves. The sample bed was loaded with 20.0751 g 5A that had been stored at 110 °C. The material was charged with 1.4 mL D_2O and approximately 1.5 L ND_3 in the same manner as the previous experiments. Very little moisture (~52 ppm) was observed in the effluent stream prior to additional of the ND_3. H_2 was introduced to the system and allowed to flow for approximately 21 hours. Results of the experiment (Figure 3-21) demonstrated no significant increase to the quantity of HD or D_2 in the effluent stream. A small section of the RGA trace was analyzed once the hydrogen isotopologue levels had stabilized, allowing for the collection of the average concentrations. These values were compared to those of the H_2 feed gas, noted in Table 3-8. It was found that the resulting concentrations were identical to that of the 0.624 wt% Pt/5A (PB-00382-20) sample blank and near identical to the 1.115 wt% Pt/5A (PB-00382-21) sample blank.

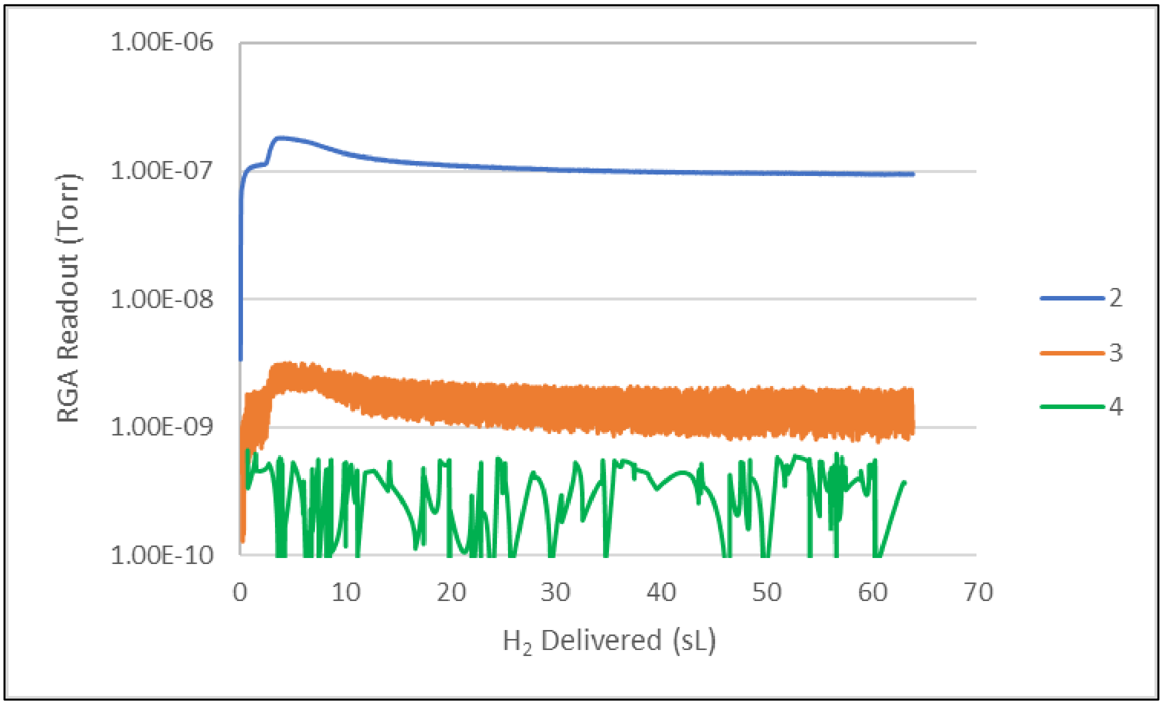

Figure 3-21: RGA trace of the $D_2O/ND_3/H_2$ 5A control experiment.

Table 3-8: Resulting hydrogen isotopologue concentrations from the 5A control experiment, as compared to the H_2 feed gas.

Mass	Concentration (%)	H_2 feed gas w/o Sample (%)
2	97.94	98.58
3	1.96	1.41
4	0.10	0.01

During the experiment, a small increase of mass 2 and 3 were observed after roughly 3 sL H_2 had been delivered to the sample. Upon further examination, the small increase coincided with a significant release of mass 16 and 17, as well as a notable increase in masses 14, 15, and 18, as shown in Figure 3-22. Due to the observance of masses 14 and 15, it is believed that this release belongs to ammonia rather than water. The release of ammonia occurred in roughly the same concentration as previously described in Test 3 – ND_3/H_2 for the 0.624 wt% Pt/5A (PB-00382-20) sample (Figure 3-6). According to Table 3-4, the presence of NH_3, NH_2, ND, and NHD molecular fragments suggest that without catalyst present, isotopic exchange still occurred, just at a much smaller rate and therefore, demonstrating the effectiveness and necessity of including one on the material.

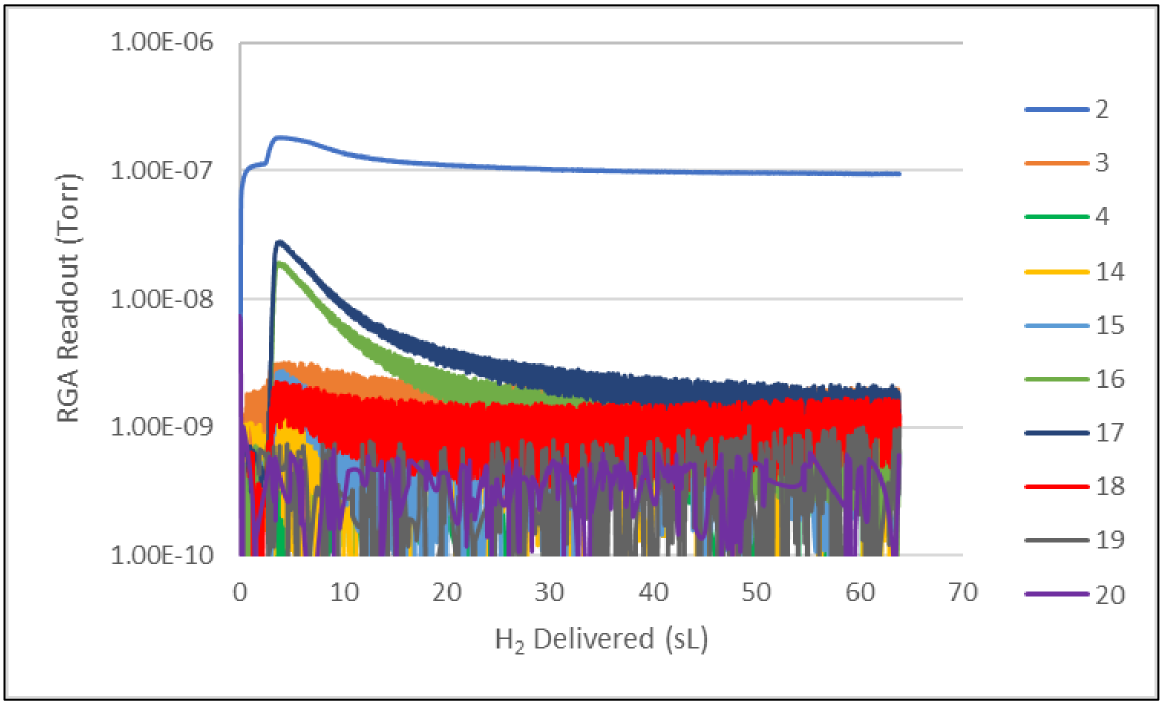

Figure 3-22: RGA trace of the 5A control experiment, depicting masses 14 through 20.

4.0 Conclusions

1. Catalytic isotopic exchange was demonstrated successfully between hydrogen gas and deuterated water and ammonia over Pt loaded zeolites.
2. No significant catalytic isotopic exchange was observed over the 5A zeolite without Pt.
3. Four different zeolites with various Pt loadings were prepared. Within the evaluated samples, Pt/HY and Pt/5A, both appeared equally active in catalytic isotopic exchange as well as moisture and ammonia removal. Further studies are needed to quantify this conclusion.

Tritium removal from tritiated ammonia and tritiated water is possible for future RGD beds using Pt loaded zeolites based on the experiments performed so far.

5.0 References

[1] Xiao, X. S., *"Water Detritiation Development – H/D Demonstration in FY16"*, **SRNL-L2100-2016-00100**, Aiken, SC, Savannah River National Laboratory.

[2] Xiao, X. S., *"Water Detritiation Development – H/D Demonstration in FY17"*, **SRNL-TR-2017-00444**, Aiken, SC, Savannah River National Laboratory.

[3] Thompson, A. B., "*Material Characterization for Impurity Removal by Adsorption",* **SRNL-L2100-2016-00084**, Aiken, SC, Savannah River National Laboratory.

[4] Beaumont, P. R., James, D. W., Poore, S. R., Steedley, J. A., *"Recovered Gas Dryer Material Characterization Testing for End of Life Disposition"*, **SRNL-TR-2019-00227**, Aiken, SC, Savannah River National Laboratory.