

Yes, Virginia there is Heat, but It is Likely of Chemical Origin

D. A. Kidwell¹, D. L. Knies², K. S. Grabowski², and D. D. Dominguez¹

¹Chemistry Division, Naval Research Laboratory, Washington, DC 20375

²Materials Science and Technology Division, Naval Research Laboratory, Washington, DC 20375

E-mail: David.Kidwell@nrl.navy.mil

Abstract. Gas loading of palladium particles <2 nm in size produces anomalous amounts of heat in a reproducible manner. This heat is produced in the presence of deuterium but not in the presence of hydrogen. Control experiments have ruled out the excess heat was due to impurities in the deuterium that were absent in the hydrogen. Because the system is simple and mostly reversible, all extra heat must be of chemical or some other origin. Neither radiation nor nuclear “ash” was found to correlate with the anomalous heat. In some matrices, the likely source of the anomalous heat is D-H exchange with the water present in the matrix, where an approximate third increase of the expected energy from calculations can account for most of the excess heat. In other matrices, no simple explanation of the excess heat can be made.

1. Introduction

Palladium electrochemically loaded with sufficient amounts of deuterium has been reported to produce anomalous amounts of heat that may be nuclear in origin.¹ The complete requirements for heat production have not been determined. However, one criterion for having a high likelihood of producing heat appears to be that the D-Pd ratio must be above 0.9.² Electrochemical loading of palladium can reach these high levels, which correspond to 10⁵ to 10⁶ atmospheres³ of deuterium overpressure in bulk palladium – a challenge for simple gas pressurization. Pressure alone appears to be insufficient, because Isaac, *et al.* had pressurized palladium with deuterium in a diamond anvil cell and saw no radiation emitted.⁴ Although a temperature change was observed, it was attributed to instrumental drifts.

Most of these claims of excess heat have been dismissed as experimental error rather than nuclear chemistry because almost any conventional nuclear event, such as D-D fusion, should produce some form of radiation (X-rays, neutron, gamma rays) or transmuted atoms (nuclear “ash”). Given the amount of heat claimed, these should be easily detectable.⁵ No convincing evidence of radiation nor transmutations have been reported⁶ and the calorimetry results are sometimes called into question.⁷

As unidentified sources of anomalous heat appear to be the major signature of this process, we investigated the heat production in a gas loading system - a simpler system than electrochemical loading - with the goals of: (1) reproducible heat production, (2) careful attention to heat measurements and energy losses and inputs, and (3) understanding of substrate matrix preparation and instrumentation.

Gas loading experiments have the advantage that the system can be reversible – the heat generated upon pressurization due to the work of pressurization of the gas and the uptake of hydrogen/deuterium into the palladium matrix and spillover of that hydrogen to the support is subsequently taken-up upon evacuation. Any net energy (endothermic or exothermic) from a pressurization/depressurization cycle must come from an irreversible event such as a chemical reaction. Typical reactions and processes that must be considered are the initial reduction of PdO to Pd metal and water, water absorption by the matrix,⁸ oxidation of the hydrogen/deuterium by adventitious oxygen in the gas or absorbed on surfaces, water in the gas binding to the matrix, the Joule-Thompson effect⁹, a change in the matrix lattice with pressure, or D-H exchange with water in the matrix or surface hydroxyls. Most chemical reactions produce gaseous materials that can be monitored by sampling the gas in the cell, or they consume the pressurization gas and cause a pressure drop and thereby signal their presence. Thus, all the reactions listed above should make themselves known, or their effect (such as a change in lattice structure) should quickly be lost during

pressurization/depressurization cycles. Additionally, except for D-H exchange, pressurization with deuterium should produce similar amounts of heat as pressurization with hydrogen *i.e.* any chemical isotope effect should be small.

The consideration that the D/Pd ratio must be near 0.9 for anomalous heat to appear² puts constraints on the size of the palladium particles for gas loading at reasonable pressures. In 1908, Paal and Gerum reported H/Pd of 0.98 measured volumetrically at atmospheric pressure using palladium black prepared with hydrazine.¹⁰ Since that report, most H/Pd ratios on pressurized palladium particles fall in the range of 0.6-0.8 at room temperature (similar to bulk palladium) – increasing at lower temperatures and decreasing at higher temperatures.³ Recently, two groups have reported that they can reach H/Pd ratios near one by decreasing the particle size on certain supports, but this ratio appears to be highly size dependant.^{18,19} A summary of data calculated from Huang, *et al.*, is shown in Table 1.

Table 1. Estimated particle sizes and H/Pd ratios as calculated from the data in reference 19. Note the sensitive dependence of the loading ratio with particle size and the rapid increase in particle size with percent Pd. The more chemically accessible particles (> 5 nm) show a loading similar to bulk palladium of 0.6.

Preparation	Estimated Particle Size (nm)	Heat of Hydrogen Adsorption (kJ/mole)	Ratio H:Pd @ 0.2 bar
Pd Powder	9	94	0.55
1.86% Pd/SiO ₂ (IW)	~4	92	0.68
1% Pd/SiO ₂ (SG)	1.1	131	0.9
0.5% Pd/SiO ₂ (SG)	1	183	1.05

It is difficult to prepare palladium colloids less than 5 nm in diameter as palladium tends to catalyze its own growth.^{11,12} Possibility, Paul and Gerum had a procedure to prepare sufficiently small palladium particles that they absorbed large amounts of hydrogen.¹³ Rather than prepare palladium colloids with their inherent irreproducibility, we focused on preparing nanoparticles in an oxide matrix where the growth is limited by the pore size and availability of atoms. We focused on zeolites because the pore size is about 1 nm and should allow growth of more uniform particles. Also, zeolites are thermally stable so that the high temperatures potentially reached by the particles during pressurization do not degrade the support and the zeolites should help isolate the particles and prevent their coalescence with pressure/temperature cycling.

This paper describes the preparations of some matrices that show an anomalous amount of irreversible heat produced in gas loading and discusses that this heat could be due to Deuterium-Hydrogen (D-H) exchange. Trace levels of neutrons and tritium above background have been seen in some gas loading experiments by other authors.¹⁴ Long term heat also has been reported by other authors that is difficult to explain using conventional chemistry.^{15,16,17} We have been unable to confirm any of these observations in our gas-loading systems.

2. Experimental

We constructed our own data acquisition interface so that we had control over all the design parameters. Two basic systems were designed (GC oven and Hart calorimeter) with a common data acquisition interface. Each component and some of the design parameters will be discussed elsewhere. The deuterium gas was from various suppliers over the course of this project and of varying cylinder ages (which affect the tritium impurity concentrations). The main suppliers were Cambridge Isotope Laboratories, Inc., Praxair, and Matheson. The source of the gas did not appear to affect the results. In earlier experiments, the deuterium was passed through Supelco gas purifiers to remove water and oxygen and produced comparable results to unpurified gases. For the results reported here, all gases were used directly. Weak X-Rays and intense light emission has been observed from these matrices during pressurization, which will be discussed elsewhere. Briefly, these have been shown to be artifacts of the measurement technique or uncorrelated to heat production and therefore likely of chemical origins.

Preparation of the palladium-loaded matrices.

The majority of the matrices were made using zeolite 13X from Aldrich (cat #283592) and chromatography grade Alumina from Fischer (cat #A-540). Other zeolites were purchased from Zeolyst International. High Alumina

Zeolite (Code name NaKX(2.0)) was a gift from Praxair, Inc. As these other zeolites produced similar data to 13X, they will not be reported here.

Two variations were employed to prepare the palladium loaded matrices – wet impregnation for alumina^{18,19} and ion exchange for zeolites.^{20,21,22} Palladium chloride came from several sources but for large scale preparations, it was synthesized by dissolving Suisse 99.95% Pd in *aqua regia* and evaporating to dryness. The palladium-amine solution was prepared fresh each time by dissolving 1 g PdCl₂ in 16 mL of water + 4 mL of concentrated HCl and warming. To this deep red solution was slowly added 20 mL of concentrated ammonium hydroxide (an excess ammonia is used but the reaction is in an open beaker so some ammonia is lost). A pink precipitate formed that slowly redissolved upon warming to generate the light yellow Pd(NH₃)₄Cl₂. If the ammonia concentration is too low, Pd(NH₃)₂Cl₂ may form instead.²³ The percentage palladium is based on palladium metal where PdCl₂ is assumed to be 60% Pd metal by weight. Typically 100 g of zeolite powder was placed in a 500 mL flask with 200 mL of distilled water and the required amount of palladium solution. The flask was refluxed overnight. The zeolite was filtered and washed three times with warm water. The material was either air dried overnight then dried at 120°C or dried at 120°C directly. Air drying overnight appeared to produce material with the best characteristics especially when the palladium concentration was decreased below 0.25%. Allowing the water to be slowly lost may preserve the zeolite crystalline structure. The palladium loaded alumina was made by wet impregnation. Alumina (100 g) was placed in a 500 mL flask and slurried with water. The palladium solution was added and the excess water removed on a RotoVapor system under aspirator pressure to a semi-dry, flowing powder. This was air dried overnight and then dried at 120°C for varying lengths of time. Upon oven-drying, the zeolites lost approximately 15% of their weight and the alumina about 11%.

When samples were dried at 450°C they initially were pink and quickly became yellow when cooled in air or in a desiccator. The palladium in these samples reduced to the nanoparticles faster than the matrix dried at 120°C, but drying the matrix at higher temperatures (450°C) appeared to be detrimental for excess heat production.

Higher loading appears to decrease the percentage of heat produced (see Figure 1), likely by growing larger particles. This particle size effect sets apart our approach from that of Kitamura, *et al.*, where he employed high loading 6-30% and high heat that produces multi-nanometer palladium particles.^{16,24} We have tested material produced using Kitamura's recipe¹⁶ with our protocols. Although the heat generated is large because the percentage of palladium is large, we see neither excess heat nor long-term heat. Why our results should differ from that of Kitamura is unknown but similar results to ours have been presented by Hioki and colleagues.²⁵ However if the hypothesis is correct that <2 nm particles are necessary for anomalous heat generation, their production can be difficult and may depend on the exact sample preparation conditions or impurities in a given preparation.

Pressurization and Depressurization Cycles.

A picture of the manifold and peripheral equipment used with the Hart calorimeter is shown in Figure 2. The automated valves are controlled by a custom LabView program that is managed by macros. A summary of the macros for the pressurization and depressurization of the sample cell are given in Table 2.

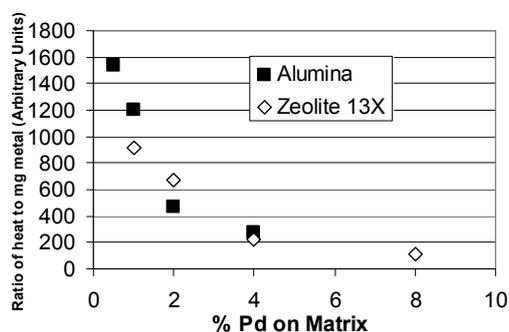


Fig. 1 – Effect of palladium loading of the matrix on excess heat produced. These samples were tested in the GC oven system, which produces relative heats only. The second pressurization cycle with deuterium was used in the calculations. Because these samples were run at different times, direct comparison between matrices is not possible. The percentage Pd on zeolite may vary from the nominal value depicted due to losses during washing.

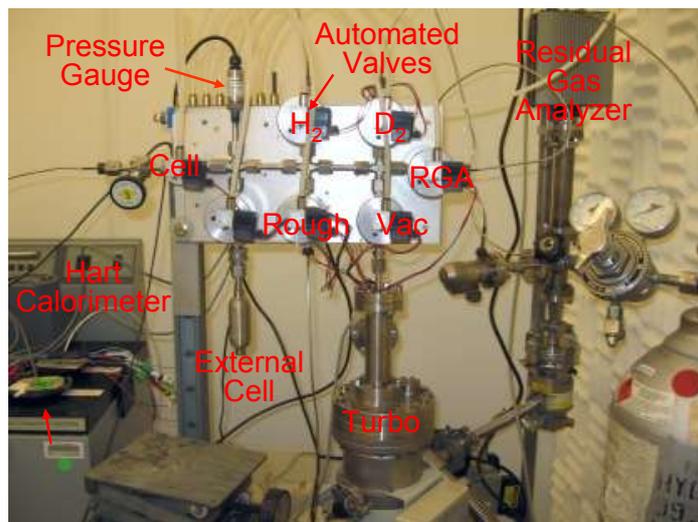


Fig. 2 – Photograph of the manifold and peripheral equipment.

Table 2- Pseudo-macros used to control the automated valves. The timing is in ticks x10, which are acquisition cycles somewhat over a second in length and related to time. The macros in this table were simplified for illustration purposes. The depressurization cycle was done in steps to more accurately measure the D-H exchange. This measurement will be discussed in a subsequent paper.

Pressurization Macro	
Ticks x10	Action
0-120	Close all valves
140	Open RGA
160	Open D2 into manifold
180	Open Cell and fill
1080	Close Cell
1100	Close RGA
1120	Close D2

Depressurization Macro	
0-120	Close all valves
140	Open RGA
160	Open Cell
960	Close Cell
1000	Rough-out the manifold
3000	Close Rough
3020	Open Cell
3100	Close Cell
7000	Rough-out the manifold
9000	Close Rough
9020	Open Cell
9100	Close Cell
13000	Rough-out the manifold
15000	Close Rough
15020	Open Cell

3. Results and Discussion

Figure 3 shows a reversible gas-loading system - five pressurization/depressurization cycles with helium on a Pd-alumina matrix. Integration of all five cycles gives a total heat of $0 \pm 1\text{J}$. The average measured heat of pressurization from the five cycles is $-13.4\text{J} \pm 0.1\text{J}$, whereas the calculated heat of pressurization from PV work is -13.4J .²⁶ This example shows that our approach can have good accuracy and precision. In some matrices, we can directly observe the heat of pressurization because the chemical reduction and subsequent uptake of deuterium is delayed. The delayed chemical reduction is also seen in the pressure recordings, where a pressure drop is observed when the reduction occurs. Like helium, if matrices are initially pressurized with hydrogen, the hydrogen also shows reversible chemistry, where $\text{heat}_{\text{in}} = \text{heat}_{\text{out}}$.²⁷

In contrast to the reversible heat from pressurization with helium (Figure 3) or hydrogen (Figure 4a), is pressurization by deuterium as shown in Figure 4b. With deuterium, the heat released during pressurization (-76.6J) is not equal to that absorbed during evacuation (26.4J) for a difference of -50.2J .²⁸

In one test series, the matrix was cycled many times and the integrated heat ($\text{heat}_{\text{in}} + \text{heat}_{\text{out}}$ and thus excess heat) is shown in Figure 5. The heat from the first pressurization was large due to chemistry occurring. The abrupt decrease in heat after 11 cycles has an unknown cause but it may be due to depletion of a chemical reactant or growth of the palladium nanoparticles above a certain size where anomalous heat is no longer generated.

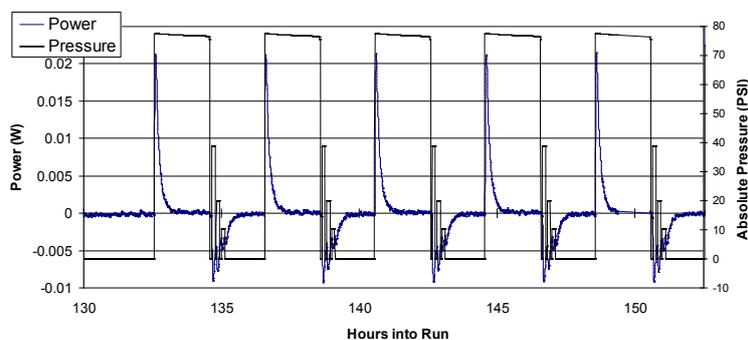


Fig. 3 – Pressurization/Depressurization Cycles Showing Reversible Heat. Pressurization of Pd on alumina with helium: $\text{heat}_{\text{in}} = \text{heat}_{\text{out}}$. The pressurization and depressurization cycles are given in Table 2. The automatic, membrane valves leak deuterium slightly if the pressure is reversed from the normal flow path. To minimize this leakage in the sample cell, the sample cell valve is closed after pressurization and the manifold pressurized. The slight decrease in pressure in the manifold, which is read by the pressure transducer, is due to a leak from the manifold into the turbo system, not due to consumption of the helium in a chemical reaction.

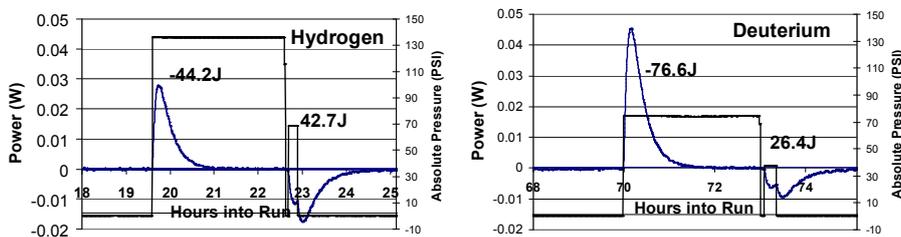


Fig. 4 – Comparison of Hydrogen and Deuterium pressurization cycles. The matrix was 0.5% Pd on zeolite 13X. The hydrogen was pressurized first to avoid possible reverse D-H exchange. Deuterium pressurization shows irreversible heat whereas hydrogen pressurization integrates to near zero (-2.5J). The pressure for hydrogen was larger, but this extra PV work is recovered in the depressurization cycle. In this case, the depressurization cycles were done in two steps rather than four as in Figure 3.

Figure 6 shows a pressurization/depressurization series ($\text{heat}_{\text{in}} + \text{heat}_{\text{out}}$) using zeolite 13X with 1% palladium loading. In this case, the pressurization and depressurization cycles were rapid, which was detrimental to production

of excess heat (see below). The heat decayed with time in a fairly linear manner. More importantly, pressurization with hydrogen produced an endothermic reaction rather than zero (recall that all reversible heat from PV work and hydrogen uptake by the matrix is accounted). This indicates that chemistry must be occurring and, in the case of pressurization with hydrogen, H-D exchange

Consider the reactions in Scheme 1. Palladium-loaded zeolites are known to catalyze D-H exchange.^{29,30} If D-H exchange was occurring in our system, then the chemistry would be exothermic until all the protons in the H₂O and zeolite hydroxyl groups were exchanged. Then, this irreversible energy (due to chemistry) would stop. Pressurization with hydrogen would reverse the exchange making normal water and be endothermic (reverse reactions in Scheme 1). Upon restarting deuterium pressurizations, heat should be produced as the H₂O present would be reconverted to D₂O. Partial restoration of heat appears to occur, as illustrated in Figure 6.

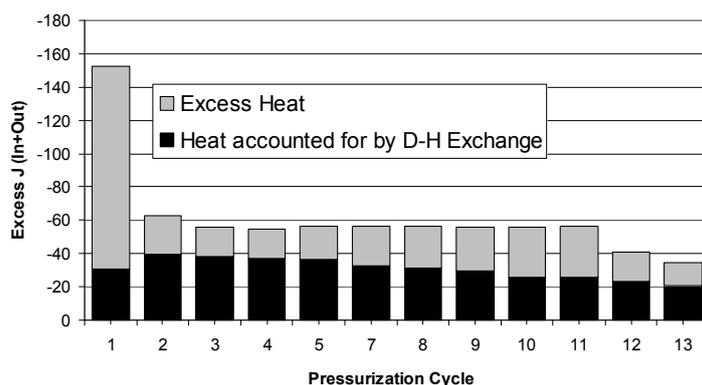
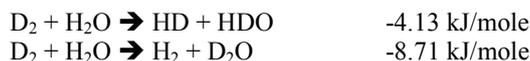


Fig. 5 – Integrated heat for each cycle for 15.42 g of 1% Pd on alumina. The alumina was dried at 120C for 3 hr before use. Note that the calculated heat from D-H exchange (dark bars) is not a constant fraction of the total heat. From step 9 and on, the evacuation time was increased to 10 hr from 6 hr.

D-H exchange should produce a signature in the gas phase because the excess gas overpressure (cells were typically filled to ~5 bar) would be enriched in HD or H₂. This enrichment should be observable using the in-line RGA (see Figure 2). When we first took gas samples, very little D-H was observed. Given the amount of deuterium present and the percentage of HD formed, we concluded that at most 7 J of excess heat could come from D-H exchange. However, later we sampled the gas in pulses (see Table 2 and Figure 5) that allowed sampling at various pressures.³¹ The lower pressure samples were enriched in HD and H₂ and these percentages were used in calculating the excess heat shown in Figures 5 and 6. With these updated numbers, D-H exchange can account for 60-62% (average for initial FDeuterium 7-16 60.7% ±0.56%, n=10) of the heat as calculated from the heats of formation in the pressurization series shown in Figure 6. Other sources (or sinks) of heat can come from the hydrogen bonding of the water and hydroxyls in the zeolite. One complication is that normal water forms stronger hydrogen bonds than does D₂O.^{32,33} Converting normal water to D₂O should absorb heat and make the discrepancy even larger. Thus, the source of this discrepancy is unknown.

Scheme 1. Possible D-H exchange reactions and the calculated enthalpy. Exchange of the hydroxyls on surfaces should have similar thermochemistry.



Although the calculations of the energy from D-H exchange using the values in Scheme 1 do not quantitatively agree with the measurements, D-H exchange is the dominant mechanism to explain Figure 6 because: (1) the percentages of excess are constant, (2) the hydrogen is negative – also by a constant amount, although slightly different (64.3% ±0.87%, n=15) than that of the deuterium, (3) after the hydrogen pressurization/depressurization cycles, the deuterium returns to similar heat and similar percentage of D-H exchange (after = 60.9% ±0.33% n=4) as was observed initially, and (4) the total heat from D-H exchange of the first 22 pressurization cycles is consistent with the amount of water possible in the zeolite (total = -288 J, 0.6 g water, 4.4% water).

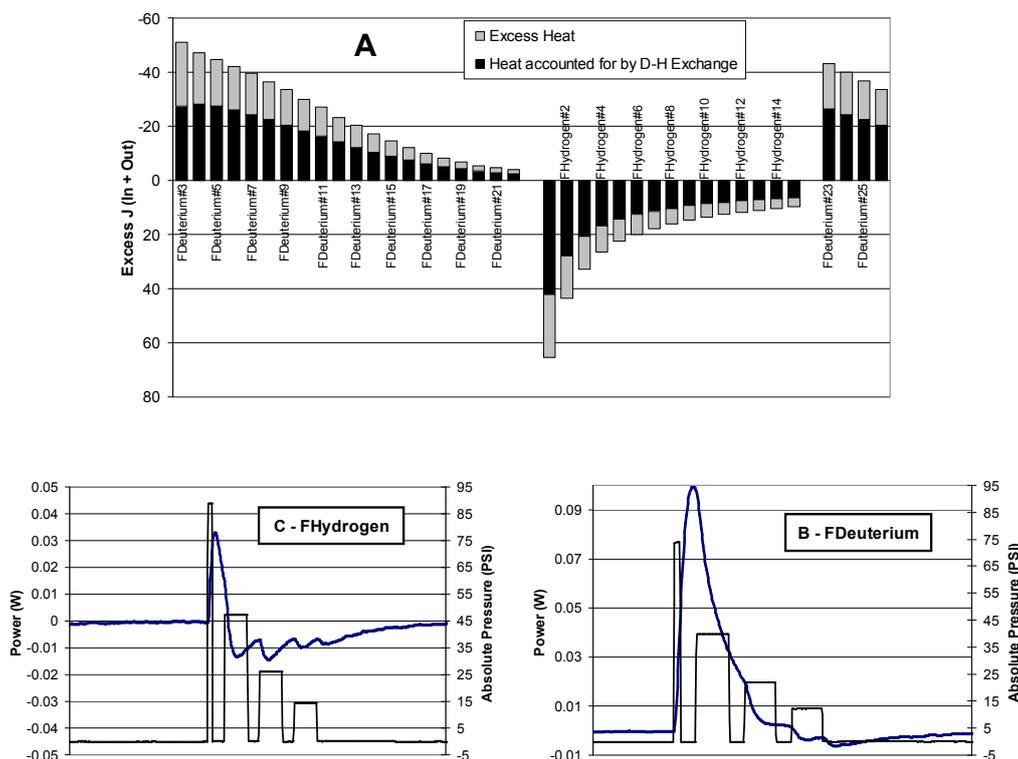


Fig. 6 - (A) Integrated heat for each pressurization/depressurization cycle for 13.5 g of 0.5% Pd on zeolite 13X. This series was started after two normal cycles. The letter F indicates a fast pressurization cycle, which are rapid in-out pulses (which was later hypothesized to be detrimental) where the depressurization period overlaps the pressurization period. Any net positive or negative peak measured is irreversible energy. The depressurization is done in steps (see B & C light lines) to better sample the excess gas with the RGA for calculating the amount of D-H exchange. For an inert gas, the net heat is almost zero. Figure 6 B and C show the cycles for deuterium (cycle FDeuterium #7) and hydrogen (cycle FHydrogen #2). The deuterium cycle is mostly above the baseline – exothermic – whereas, the hydrogen cycle is mostly below the baseline – endothermic. The D-H exchange appears to have a rapid time constant otherwise the heat of pressurization pulse in C should be more evident.

The structure of palladium inside zeolites is complex and depends on preparation conditions.³⁴

We have tried to dry the matrix before the pressurization. However, Type X zeolites contain up to 30% water and can retain considerable water (and OH groups on the surface), except under severe conditions.^{8,35} Also, water and ammonia (left-over from the preparation) may be important to observe anomalous heat generation (they would certainly be important for D-H exchange), as these species can coordinate to the nanoparticles and modify their electronic structure. Heating the zeolites in air to 450°C for 8 hr and adding D₂O reduced the excess heat but did not eliminate it. However, the exchange may have been incomplete and normal water still could have been present.

What is interesting is that the explanation for D-H exchange does not account for the excess heat observed in FDeuterium#3 and FDeuterium#4 (Figure 6). Statistically, FDeuterium#4 at 59.8% of the heat accounted for by D-H exchange is two standard deviations from the mean expected of 60.7%, whereas FDeuterium#3 at 53.8% is 12 standard deviations from the mean. The initial chemical reactions of reduction of the PdO to Pd nanoparticles may take several cycles. Therefore, the excess heat observed in FDeuterium#3 and FDeuterium#4 MAY be due to an incomplete reduction of the PdO rather than unusual chemistry.

Referring to Figure 5, the D-H exchange heat decreases as was observed in Figure 6. This decrease would be expected as the H₂O gets converted to D₂O. However, the excess heat stays the same out to pressurization cycle 11. Thus, in this pressurization series, the D-H exchange is NOT a constant percentage of the total heat, and is not as easily explained as the pressurization series shown in Figure 6. One possibility is that the surface is changing as it becomes more deuterated, and the amount of heat released as H₂O goes to D₂O somehow increases with surface coverage. The major difference between Figures 5 and 6 is in the timing of the pressurization pulses. After many

tests, it appears necessary to restore the particles to their original form without deuterium. This takes considerable time at room temperature given the poor vacuum pumping speed to the cell (Figure 2). Even the 6 hr evacuations used in Figure 5 did not remove all the deuterium from the sample.³⁶ Faster pressurization cycles (2 hr intervals) as used in the sample depicted in Figure 6 would not be sufficient to remove much of the deuterium. Thus, any excess heat due to other causes would no longer be apparent and the D-H exchange reaction would dominate, as in Figure 6.

There may be two reasons for why low deuterium levels in the nanoparticles are necessary to observe anomalous heat: (1) upon absorbing deuterium, small particles heat (but this heat is reversible). One can estimate the expected temperature rise. For example, assume that the enthalpy of formation of nanoparticles of PdD is approximately 100 kJ/mole.³⁷ If all this energy were deposited in one second³⁸ and not transferred quickly to the matrix (as the matrix is an oxide insulator), each particle could heat to 3849°C³⁹ – substantially above the melting point of palladium (1554°C). This high temperature would help catalyze conventional chemical reactions, such as D-H exchange, or it may catalyze an anomalous heat production. and (2) some authors have suggested that anomalous heat production is flux driven.² This could require a particle without much deuterium/hydrogen present each time to reach sufficient flux into the particle during pressurization.

These two hypotheses also suggest why small particles are necessary for this effect to be observed. Larger particles would not load to as high of deuterium levels AND would not load as quickly and thereby not reach as high of temperatures.

4. Conclusions

Low concentrations of palladium in oxide matrices appear to produce sub-nanometer palladium particles which allow high and rapid deuterium gas loading at easily reachable pressures. Gas loading produces anomalous amounts of heat in a reproducible manner in the presence of deuterium but not in the presence of hydrogen. This anomalous heat appears to be sensitive to the size of the palladium particles and rate of loading. The excess heat is reduced during repeated pressurization-depressurization cycles, pointing towards a source of chemical energy that is diminished. Alternatively, the particles may grow with repeated cycling beyond a range that is easily loaded with the parameters employed. In some matrices and pressurization conditions, the likely source of the anomalous heat is D-H exchange with the water present in the matrix. In other cases, this explanation is incomplete and other sources of heat must be considered.

Acknowledgements

Funding from the Defense Threat Reduction Agency is gratefully acknowledged. We would like to thank Graham Hubler, Albert Epshteyn, and Andrew Purdy for helpful discussions and suggestions.

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[26] The heat from PV work for expanding He, D₂, or H₂ into a vacuum container of 30 mL can be estimated from the equation Heat = 0.2058(pressure) + 0.1558. The heat is proportional to the size of the container inside the calorimeter (25 mL in this case).

[27] Interestingly, the Zeolite matrices absorb large amounts of Argon and Nitrogen (but not likely to be enough to be useful commercially) at room temperature so that these gases cannot be used to measure chamber volumes.

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[31] Apparently the produced HD and H₂ was bound to the surface and exchanged only slowly with the gas phase. Lower pressures sampled the surface and gave a truer picture of the amount of D-H exchange.

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[36] The pressure is typically in the 10⁻⁵ to 10⁻⁶ torr range after 6-10 hr of evacuation. However, Deuterium evolution is still evident as measured by the RGA, and the time it takes to remove the Deuterium depends on the matrix. Alumina appears to be faster than Zeolites. We considered reacting the trace Deuterium with oxygen to remove it faster, but this could introduce additional chemistry that may confuse the pressurization cycles.

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[38] Unlike some other authors, we pressurize quickly. Modeling suggests that the heat pulse evolved has three components. Based on the appearance of the heat curves from hydrogen pressurization of deuterated matrices, we suggest that the fastest component is the PV work, the next component is D-H exchange and that the slowest component is deuterium absorption by the nanoparticle and spillover onto the surface.

[39] (100 kJ/mole)/(Specific heat capacity of 25.98 J·mol⁻¹·K⁻¹) provides a ΔT of 3849K. This assumes that the heat capacity is constant and heat transfer to the matrix is at a rate much less than the heat production. Both are unlikely situations so this calculation provides an upper limit.