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Thermochimica Acta

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Origin of excess heat generated during loading Pd-impregnated alumina powder with deuterium and hydrogen

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ARTICLE INFO

Article history: Received 5 April 2012 Received in revised form 31 May 2012 Accepted 31 May 2012 Available online 9 June 2012

Keywords: Palladium nanoparticles Gas-loading Excess heat Isotope effect H/D exchange

ABSTRACT

We studied heat production in Pd-impregnated alumina powder in the presence of hydrogen and deuterium gases, investigating claims of anomalous heat generated as a result of nuclear fusion, usually referred to as a low energy nuclear reaction (LENR). By selecting the water isotope used to fabricate the material and then varying the gas used for loading, we were able to influence the amount of heat released or consumed. We suggest that Pd in its nanoparticle form catalyzes hydrogen/deuterium (H/D) exchange reactions in the material. This hypothesis is supported by heat measurements, residual gas analysis (RGA) data, and calculations of energy available from H/D exchange reactions. Based on the results we conclude that the origin of the anomalous heat generated during deuterium loading of Pd-enriched alumina powder is chemical rather than nuclear.

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1. Introduction

Anomalous heat generation in palladium-based materials in the presence of deuterium has been a subject of active research since 1989[1]. More recently attention has been focused on gas loading in a variety of Pd-nanoparticle materials [2–5] because they have consistently exhibited anomalous heat production. Some researchers have associated this anomalous heating with deuteron-deuteron nuclear fusion in the Pd lattice [2]. While some of the experiments showed a correlation between generation of excess heat and a nuclear fusion ash product (⁴He) [2], the results have not been replicated and the search for radiation was also unsuccessful [6]. Therefore, the origin of the excess heat produced by these systems is still unknown.

In our study we tested the variety of Pd-infused oxide materials. Even though our fabrication methods might be different from those used by other groups, the resulting material structure (Pd nanoparticles impregnated into oxide powders) is similar. The fabricated material was subjected to hydrogen and deuterium pressurizations to study heat generation mechanisms.

In previous work we demonstrated (1) excess heat production in Pd-loaded alumina and zeolite powders, (2) excess heat

* Corresponding author at: Department of Electrical, Computer, and Energy Engineering, University of Colorado, Boulder, CO 80309-0425, USA. Tel.: +1 7205659690. *E-mail address:* olga.dmitriyeva@colorado.edu (O. Dmitriyeva). tapering off with repeated runs [7], (3) excess heat generation at low Pd–D ratios (4), and the amount of excess heat produced depending linearly on pressure (quantity of deuterium provided). In this paper we report the results of gas-loading experiments in hydrogen and deuterium-rich materials that provide strong evidence for the source of the heat production.

In the absence of reproducible production of nuclear ash during gas-loading experiments, we looked for a conventional chemical process that could account for the excess heat generation. Palladium in nanoparticle form is known to act as a catalyst that supports the spillover effect, which is a dissociation of hydrogen or deuterium molecules on the surface of Pd [8,9]. We started our experimental work with the assumptions that (1) Pd nanoparticles initiate a spillover effect, (2) deuterium and hydrogen atoms are transferred from the metal to the alumina support, (3) remaining water that is trapped in the material along with OH and OD groups on the face of the alumina support is engaged in a hydrogen/deuterium (H/D) exchange reaction. The explanation of anomalous heating using the concept of H/D exchange was first proposed by Kidwell et al. [5]. This H/D exchange is a chemical reaction and can be either exothermic or endothermic. Using enthalpy of formation [10–13] we calculate heat associated with possible H/D exchange reactions shown in Table 1.

As shown in the table, the reaction can be either exothermic (negative value) or endothermic (positive value). If the source of the anomalous heat in Pd nanosystems is the H/D-exchange reaction then by controlling the particular water isotope in the material and exposing it to either hydrogen or deuterium we should be able to

^{0040-6031/\$ -} see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.tca.2012.05.037

Table 1

Exothermic and endothermic heat associated with H/D exchange chemical reactions.

Chemical reaction	Heat (KJ/mol)
OH + D = OD + H	_4
$H_2O + D_2 = HDO + HD$	-4
$H_2O + D_2 = D_2O + H_2$	-8.3
OD + H = OH + D	4
$D_2O + H_2 = HDO + HD$	4.3
$D_2O + H_2 = H_2O + D_2$	8.3

demonstrate both exothermic and endothermic heat production in the system. Results are discussed in the following sections.

2. Experiment

2.1. Material fabrication

Table 2 lists different catalysts we used throughout our studies. Incipient wetness and ionic exchange methods were used to prepare 2.0 wt% Pd samples from different Pd precursors. In addition to the materials fabricated in our laboratory, we experimented with a commercially available catalyst from Acros Organic. Comparing the properties of individual catalysts is beyond the scope of this paper. Samples showed some limited variation during gas-loading experiments. However, regarding the phenomena investigated here they all responded similarly.

For this study we used 80–200 mesh Al₂O₃ powder (Fisher Scientific P/N: CAS 1344-28-1) that was baked in vacuum at 350 °C for 12 h to remove residual water. Powder samples containing 2.0 wt% of Pd were fabricated by impregnating alumina powder with hot $Pd(NH_3)_4Cl_2$ or $Pd(ND_3)_2Cl_2$ in H_2O - or D_2O -based solutions, forming a slurry. This slurry was later dried either in air or in an argon atmosphere at room temperature without calcination. Prior to loading into the measurement apparatus, all the samples were baked in a vacuum oven at 120 °C for 24 h. This prebaking step results in 2% of weight loss due to water evaporation based on the thermogravimetric analysis (TGA). Some water is still trapped in the material even after prebake. We discuss this in more details in Section 3.4.

The fabrication method we described produces nanoscale Pd clusters on the surface of the alumina support, as shown in the transition electron microscope (TEM) image on Fig. 1. Measurements taken from multiple images show the particle size distribution maximum to be 5 nm.

Two different approaches were taken to loading Pd into the alumina powder. Our goal was to make two materials: one rich in hydrogen with very little deuterium, and the other rich in deuterium with very little hydrogen. The first fabrication method used hydrogen-based chemicals and water. The other method used deuterium-based chemicals and heavy water with the fabrication done in an argon atmosphere to minimize H₂O exposure from the air.

The fabricated materials were then loaded into our experimental apparatus and exposed to deuterium and hydrogen using the scheme presented in Table 3. During the loading there was a 2 min period during which the samples were exposed to air, which have resulted in some contamination of the deuterium-based material

Table 2

List of the catalysts. *Samples used in this study.

Sample/method	Precursor	Reference
5% Pd-on-alumina/commercially available 2% Pd-on-alumina/incipient wetness 2% Pd-on-zeolite/ionic exchange *2% Pd-on-alumina/incipient wetness *2% Pd-on-alumina/incipient wetness	Not applicable H ₂ PdCl ₄ Pd(NH ₃) ₄ Cl ₂ Pd(NH ₃) ₄ Cl ₂ Pd(ND ₃) ₄ Cl ₂	Acros Organic [14] [5] [5]



20 nm HV=100.0kV Direct Mag: 73000x Philips CM100

Fig. 1. TEM image for a 2.0 wt% Pd-impregnated alumina sample prepared using a Pd(NH₃)₄Cl₂ precursor. Dark spherical spots represent Pd particles.

by hydrogen. However, the majority of the water, trapped in the deuterium-based material was still in D₂O form (discussed in Section 4).

Anomalous heating that is observed during deuterium loading of Pd material but not during hydrogen loading is an isotope effect. We hypothesize that the isotope effect demonstrated in a number of gas loading experiments [3–7] is a manifestation of the H/D exchange chemical reaction, where deuterium is introduced into material saturated with H_2O and OH-groups (experiment 2 in Table 2). If our hypothesis is correct then an endothermic reaction should be observed during experiment 4 in Table 2. Little or no heat should be seen in experiments 1 and 3, where the material was prepared with the same isotope that was later introduced into the apparatus in gaseous form. The results of these experiments are discussed in Sections 3.1 and 3.2.

2.2. Experimental setup

Fig. 2a shows the block diagram of the experimental setup. The system was enclosed in an isothermal chamber (an HP 5890A gas chromatograph oven). The temperature of the oven was set to 313 K (40 °C). Temperature changes that exceeded background temperature fluctuations were associated with exothermic or endothermic heat generated in the system.

Two removable stainless steel vessels (Swagelok P/N: SS-4CS-TW-25) were placed inside the oven and connected to the gas line. One vessel contained 6 g of material, and the other vessel remained empty as a reference.

Hydrogen, deuterium or argon could be supplied through the gas line. H_2 and D_2 were supplied through an oxygen-removing hydrogen purifier. The D_2 gas was 99.9% pure and the H_2 gas was 99.9% pure. Typical run consisted of (1) pressurization by hydrogen or deuterium, (2) a period of time when system stays under pressure, (3) an evacuation step. There was a section of the pipeline connected to the vessels that was shared by both gases. However, the pressure of the gas in the pipeline during the pressurization step is

Table 3

Four types of experiments having different combinations of material and gas, and our expectation of exothermic or endothermic reaction in Pd-loaded alumina powder.

Experiment number	Material and gas	Expected outcome
1	H-rich material and H_2 gas	No heat
2	H-rich material and D ₂ gas	Exothermic heat
3	D-rich material and D ₂ gas	No heat
4	D-rich material and H ₂ gas	Endothermic heat



Fig. 2. Gas loading system for excess heat measurement: (a) schematic of the setup, (b) vessels inside the isothermal chamber.

nine orders of magnitude higher than during the evacuation, which makes the residual gas contribution negligible. Argon was used to fill the system while the vessels were exchanged and new material was loaded, in order to minimize air exposure. During the loading process the material was exposed to atmosphere for not more than 2 min.

The flow of gas into and out of the system was regulated using mass flow controllers and could be set anywhere between 3.4×10^{-4} and 1.69×10^{-2} Pa m³/s. The system was pressurized up to 1.6×10^5 Pa. Evacuation of the system was done using a turbo-molecular pump. A residual gas analyzer (SRC RGA200) was connected to the system. RGA data was collected during evacuation, first by discrete sampling every 3 min at 2.7×10^3 Pa through a capillary tube and then every 5 min during pump-out when the pressure in the system was below 20 Pa.

The initial gas pressurization was a "reduction run", where Pd was reduced to its metallic form. The reduction runs were always done with the same gas as the subsequent runs. Temperature was measured using thermistors, glued with epoxy to the bottom and the neck of the vessels, shown in Fig. 2b. We used a Sensor

Scientific Inc. glass probe $10 \text{ k}\Omega$ thermistors p/n: SP43A10310. System control, temperature, pressure and RGA data acquisition was done using LabView software.

Heat released or consumed by the system during gas load/unload cycles resulted in temperature changes that were measured by the thermistors. Since our system was not a direct calorimetric setup, additional calibration and data manipulation was done to convert the temperature change into power. The excess power generated by the system is described by the calorimetric equation [15]:

$$P = C_p M \frac{dT}{dt} + k_C \Delta T$$

where C_pM is equivalent heat capacity of the system, k_C is heat transfer coefficient, and ΔT is temperature change. The $C_p M$ and $k_{\rm C}$ are parameters of the specific system and experimental protocol. Once determined for a given configuration, they can be used for subsequent runs on the same system. The technique we used to calibrate our system is described in Ref. [15] in conjunction with isoperibolic calorimetric measurements. The vessel, filled with blank alumina, was pressurized with hydrogen. In this case the only heat source is the heat dissipated due to the gas compression. Using the known vessel parameters we then linked the measured temperature change to the heat of compression. During pressurization some of the heat is dissipated due to conduction. That allowed us to calculate the heat transfer coefficient $k_{\rm C}$ When pressurization is complete, it takes a certain time for the system to come back to the state of thermal equilibrium. This process is governed by both, heat conduction and equivalent thermal mass $C_p M$ constants. The value of $C_n M$ is derived based on temperature decay slope. For the configuration used in this research, the calculated parameters were $k_C = 0.65 \text{ W K}^{-1}$ and $C_p M = 103.2 \text{ J K}^{-1}$. The scatter in measured heat values that was derived from over 30 runs was 1.4 J.

Initially the system was checked using alumina powder with no Pd added in the presence of both hydrogen and deuterium. We found that the exothermic heat, due to work of pressurization (pVwork) and endothermic heat, (recovery of pV work) during evacuation offset each other. This means that system was not producing any excess heat, as expected.

3. Results

In all our experiments we used a two-step pressurization technique: slower pressurization at a rate of 8.5×10^{-3} Pa m³/s up to 3.3×10^4 Pa and faster pressurization at a rate of 1.69×10^{-2} Pa m³/s from 3.3×10^4 Pa up to 1.6×10^5 Pa [7]. Two-slope pressurization is needed to separate the processes of PdD and PdH formation (heat of loading Q_{loading}) from the heat due to work of pressurization (*pV* work)

The temperature changes we observed during gas loading/deloading cycles were interpreted as:

- (a) heat of deuterium or hydrogen loading/deloading in palladium Q_{loading}.
- (b) heat of pressurization/depressurization pV work,
- (c) excess heat, either exothermic or endothermic Q_{excess}.

During the slower pressurization step we observed only Q_{loading} because the *pV* work was negligible due to the low incoming gas flow rate. During the faster pressurization step we observed *pV* work and $\pm Q_{\text{excess}}$ components.

The expression for heat generated during pressurization is

 $Q_{\text{loading}} + (pV \text{ work}) + Q_{\text{excess}}$



Fig. 3. Power in/out and pressure during hydrogen and deuterium runs on H-rich material as a function of time. These hydrogen (experiment 1) and deuterium (experiment 2) runs are both the second pressurization runs in a sequence of runs following the initial reduction runs.

Both the Q_{loading} and pV work were recovered during evacuation of the system, producing

$$-Q_{\text{loading}} - (pV \text{ work})$$

Summing up these two expressions leaves Q_{excess} , which can be either exothermic or endothermic depending on the material fabrication method and the gas running into the system.

3.1. Isotope effect on H-rich material

Data from experiments 1 and 2 in Table 3 along with the reference data for the empty vessel are shown in Fig. 3. All the curves are for the second pressurization, after the palladium was reduced to its metallic form.

There are several differences in the signals generated by the empty reference vessel, the loaded vessel exposed to hydrogen, and the loaded vessel exposed to deuterium:

- (1) Q_{loading} for deuterium is close to Q_{loading} for hydrogen calculated as the areas underneath the curves in Fig. 3. For deuterium loading this energy is (-12.9J) and for hydrogen it is (-11.4J). The amount of Pd by weight is 0.12 g. If we assume that the gas loading ratio of Pd and D/H is 0.86 [16], then the maximum possible energy released due to the PdD formation process is (-16.6J) and due to PdH formation is (-18.0J). Exothermic heat is represented by negative values and endothermic heat by positive. The deuterium run shows a slightly elevated baseline that is caused by additional heat generation. We will discuss this effect in Section 4.
- (2) During the faster pressurization step:
 - (i) deuterium loading shows significant excess heat production (-23.9])
 - (ii) hydrogen loading shows only a pV work component, similar to the one generated with the reference vessel (-2.9 J).
- (3) The double endothermic spike during pump out is due to a discontinuity in the evacuation process at 2.7×10^3 Pa introduced by collecting the RGA data (deloading of hydrogen and deuterium from Pd at 40 °C occurred at approximately 4×10^3 Pa [14]). The heat associated with gas deloading from Pd is 13.4J for the deuterium run and 12.9J for the hydrogen run.



Fig. 4. Power in/out and pressure during deuterium and hydrogen runs on D-rich material as a function of time. Both the hydrogen (experiment 4) and deuterium (experiment 3) runs are the second pressurization runs in a sequence of runs following the initial reduction runs.

Earlier we found [7] that power generated during the faster pressurization step is proportional to the slope of pressurization (dp/dt) times a quantity Φ , which is the energy content of the fuel remaining in the system:

$$\frac{Q_{\rm excess}}{\rm time} \propto \Phi \cdot \frac{dp}{dt}$$

The fuel in the material can be exhausted or replenished (discussed in Section 3.3).

So far we have experimentally demonstrated excess heat production and an isotope effect in H-rich material: excess heat generated during deuterium loading (experiment 2 from Table 3), and no excess heat when the same material is loaded with hydrogen (experiment 1 from Table 3).

3.2. Isotope effect on D-rich material

Now we move to a discussion of experiments 3 and 4 from Table 3. Data from the second pressurization are shown in Fig. 4. The key points here are:

- (1) During the slower pressurization step, the deuterium and hydrogen runs show Q_{loading} values that are close to each other (-15.3 J and -11.2 J respectively), released due to the PdD and PdH formation processes.
- (2) During the faster pressurization step:
 - (i) The deuterium run still shows excess heat (-9.7 J), but the absolute value is more than two times smaller than for H-rich material (-23.9 J), as shown in Fig. 3.
 - (ii) The hydrogen run shows endothermic heat during the faster pressurization step (5.4 J). The plot does not show a large endothermic dip because the heat of pressurization and the endothermic reaction heat are close in magnitude and almost compensate each other.
- (3) The double endothermic spike during pump-out is the same as discussed previously (10.4J for deuterium run and 8.2J for hydrogen run).

Therefore, we have experimentally demonstrated significant reduction of exothermic heat in D-rich material in the presence of deuterium (experiment 3 from Table 3) as well as endothermic heat production during the faster pressurization step (experiment 4 from Table 3).



Fig. 5. Excess heat generated in H-rich material during deuterium and hydrogen pressurizations, as a function of run number. We omitted the data from the first run because heat generated during this run was dominated by the reduction of Pd to its metallic form.

3.3. Effect of depleting and replenishing of fuel. RGA data on H/D exchange

In Sections 3.2 and 3.3 we demonstrated material composition (whether fabricated with H-rich or D-rich water) affects the sign of Q_{excesss} . Based on the fact that the reaction can be ether exothermic or endothermic we suggest that the fuel is of two types: it is either H₂O and OH hydroxyl groups with its energy content, $\Phi_D < 0$, or D₂O and OD groups with its energy content, $\Phi_H > 0$ (subscript refers to the reacting gas).

By using H-rich material and switching between deuterium and hydrogen gas we previously found that fuels can be depleted, or replenished within the material during repeated gas loading cycles [7]. Since those data were presented we have calibrated our system as discussed in Section 2.2 to quantify the heat produced. The quantitative data are shown in Fig. 5 for the faster pressurization step for three sets of gas loadings done with deuterium, hydrogen, and again deuterium.

The following processes are evident in the data of Fig. 5:

Depleting fuel Φ_D : During the first set of deuterium runs, D2–D7, we see that the excess heat tapers off with repeated runs.

Generating fuel Φ_H : Switching to hydrogen in runs H1–H5, we observe endothermic heat generation during the faster pressurization step. As the number of hydrogen runs increases, the amount of the endothermic heat decreases in absolute value indicating fuel depletion.

Replenishing fuel Φ_D : After switching back to deuterium in runs D1–D5 (second series), the system is recharged with the fuel Φ_D that supports the exothermic reaction. Notice that the excess heat levels recover only partially.

RGA data confirms the depleting and replenishing processes, as shown in Fig. 6a and b. These data were obtained during the evacuation step for the experimental runs of Fig. 5. The processes evident in the data of Fig. 5 give rise to the following effects in the RGA data of Fig. 6:

Depleting fuel Φ_D : From the first set of deuterium runs, D1–D7 in Fig. 6a, we see the depletion of H₂O from the material. At the same time exchanged hydrogen is released as a result of this reaction as shown in Fig. 6b.

Generating fuel Φ_H : The D₂O concentration increases during runs D1–D7 as H₂O is converted to D₂O through H/D exchange.



Fig. 6. RGA data showing: (a) water isotopes and (b) hydrogen gas isotopes as a function of deuterium and hydrogen run sequence. We omitted the data from the first run because heat generated during this run was dominated by the reduction of Pd to its metallic form.

During the pump-out phase of each run only a fraction of this D_2O is removed, and so it builds up in the system.

Replenishing fuel Φ_D : The H₂O concentration increases during runs H1–H5 as D₂O is converted to H₂O, releasing exchanged deuterium, as shown in Fig. 6b. As in the previous process only a fraction of the H₂O is removed during the pump-out step, and so it builds up in the system.

The ongoing chemical reaction depletes or enriches the material with either H_2O or D_2O , as shown in Fig. 6a. The change of the water isotope concentration in the three sets of runs with different gas shows the depletion or recharging process.

3.4. Calculations

To see whether the heat produced by the system could be due to H/D exchange we calculate the total available heat. We found experimentally that desiccated 2% Pd-impregnated alumina reabsorbs approximately 5.7% of water by weight from air, corresponding to 0.342 g. If all this water is used in the exchange chemical reaction with deuterium, the system is capable of producing -159 J total. This number exceeds by a factor of two the amount of heat measured during the first sequence of six deuterium runs, which is -80.7 J, as shown in Fig. 5.

4. Discussion

Several mechanisms are responsible for heat generation in Pdloaded alumina material at different stages of the gas loading process. While two of them (heat of loading and heat associated with work of pressurization) are reversible, there is an additional source of excess heat that can be either exothermic or endothermic. The experiments that we carried out provide insights into the mechanism for this excess heat.

We fabricated different batches of material rich in protium or deuterium constituents. H-rich material was virtually free of the deuterons: the material is fabricated in H₂O-based solution and any moisture absorbed from the air also came in H₂O form. We assume our H-rich material was 100% "protonated". D-rich material, however, with all the precautions to prevent the exposure to air was only partially "deuterated". This was confirmed by the nuclear magnetic resonance (NMR) measurements. The NMR showed the concentration ratio of the protons to deuterons in D-rich material to be close to 2.2. Based on this information the material is 70% "deuterated". Using H-rich and D-rich material batches in combination with hydrogen and deuterium loading gases, we were able to demonstrate both exothermic and endothermic heat generation. Hrich material in the presence of deuterium is a source of exothermic heat and D-rich material reacts with hydrogen endothermically. We associate the particular water isotope provided to the system with a fuel. Our RGA results and heat measurements suggest that this fuel was later engaged in the H/D exchange chemical reaction during gas loading, partially confirming the expectations shown in Table 3.

An isotope effect with exothermic heat generation in the presence of deuterium was confirmed for H-rich material (experiments 1 and 2). Most of the heat was generated during the first several runs, followed by the rapid fall off. Calculations presented in Section 3.4 show that this excess heat can be fully accounted for by H/D exchange.

Endothermic heat generation in the presence of hydrogen was demonstrated for D-rich material (experiment 4). While H-rich material produced excess heat during deuterium runs it was shown that the amount of this heat can be reduced (more than two times in our case) by fabricating the material with D-based chemicals and limiting the exposure to the air (experiment 3). The reduction in the excess heat is not greater because D-rich material was only 70% deuterated. Thus the expectation given in Table 2 were confirmed, with the exception that experiment 3 exhibited some small exothermic heat due to water absorbed during exposure to air.

Recharging the material with D- and H-species during its subsequent exposure to deuterium and hydrogen gas is another way of controlling the amount of fuel available for exothermic or endothermic chemical reaction. Using RGA and temperature measurements we demonstrated that fuel can be depleted or replenished in the system by switching between deuterium and hydrogen pressurizations. Excess heat decline can be a result of a combination of fuel depletion, nanoparticle agglomeration [9,17], and/or palladium catalyst degradation [17,18]. The same arguments can be used to explain why the excess heat levels recover only partially during the recharging. Our results on recharging are similar to those reported earlier by Kidwell et al. [5].

We found that the catalyst fabricated from $Pd(NH_3)_4Cl_2$ exhibited long-term exothermic heat in the presence of deuterium and hydrogen gases after the H/D exchange reaction was completed (after 8–10 runs). Based on the RGA data, we concluded that the

source of this heat is the exothermic ammonia-based chemical reaction, which is independent of the H/D exchange reaction we describe here. Acros Organic commercial catalyst and material prepared from H_2PdCl_4 did not show any long-term heat and all excess heat could be accounted for by the H/D exchange reaction.

5. Conclusions

We demonstrated that by choosing whether Pd-impregnated alumina is synthesized with H- or D-constituents the material produced either exothermic or endothermic heat in the presence of deuterium or hydrogen. All other aspects of chemical processing including Pd concentration were the same. We obtained a similar difference between exothermic and endothermic reactions by post-synthesis substitution of one hydrogen isotope for the other during gas alternation experiments shown in Fig. 5. We suggest that Pd nanoparticles catalyze exothermic or endothermic H/D exchange reaction. According to our calculations, the experimentally measured excess heat can be accounted for fully by this chemical reaction. Expected gas products of the reaction are consistent with those observed by RGA analysis of gases emitted during the processes and heat measurements. If instead a nuclear reaction initiated under these conditions was the cause for the excess heat, it would be exothermic only. Furthermore, it would not depend directly on the water isotope used during the fabrication step as long as Pd remained in the same form and concentration and was loaded with deuterium atoms.

In summary, the results of our gas loading experiments of Pd-infused alumina powder are consistent with the excess heat produced being due to an H/D exchange reaction, showing that the origin of the excess heat is chemical. In regard to LENR studies, we would like to emphasize the importance of testing Pd-impregnated oxide systems for their ability to initiate and support the H/D exchange reaction to assess chemical heat contribution.

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