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Research Article

Mechanisms for Heat Generation during Deuterium and Hydrogen Loading of Palladium Nanostructures

O. Dmitriyeva [*], R. Cantwell and M. McConnell
Coolescence, LLC, Boulder, CO, USA

G. Moddel
University of Colorado at Boulder, CO, USA

Abstract

Our group has confirmed excess heat production and isotope effects in alumina and zeolite powders containing highly dispersed Pd nanoparticles. Varying the pressures and loading rates produced correlations between the exothermic and endothermic aspects of the experiments. It was shown that the generated power is proportional to the pressurization rate times a quantity Φ, which is the energy content of what we called "fuel". There are two types of fuels, both of which can trigger the reaction that can be either exothermic or endothermic depending on the gas used in the experiment (deuterium or hydrogen). Observed heat generation during the pressurization phase is most likely of a chemical nature.

Keywords: Excess heat, Gas-loading, Isotope effect, Nanoparticles, Palladium

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1. Introduction

Recent studies of deuterium loading of palladium nanostructures demonstrated consistent and repeatable excess heat production [1–4]. Our group conducted a series of experiments on gas loading in Pd-enriched alumina and zeolite matrices to (1) confirm the excess heat production in the systems and (2) investigate heat generation mechanisms and their contribution to the overall excess heat production.

In previous work [5], we have successfully demonstrated (1) excess heat production in Pd-loaded alumina and zeolite matrices, (2) excess heat tapering off with repeated runs possibly due to Pd nanoparticle agglomeration, (3) excess heat generation at low Pd–D ratios, and (4) the amount of excess heat produced depending linearly on pressure (quantity of deuterium provided).

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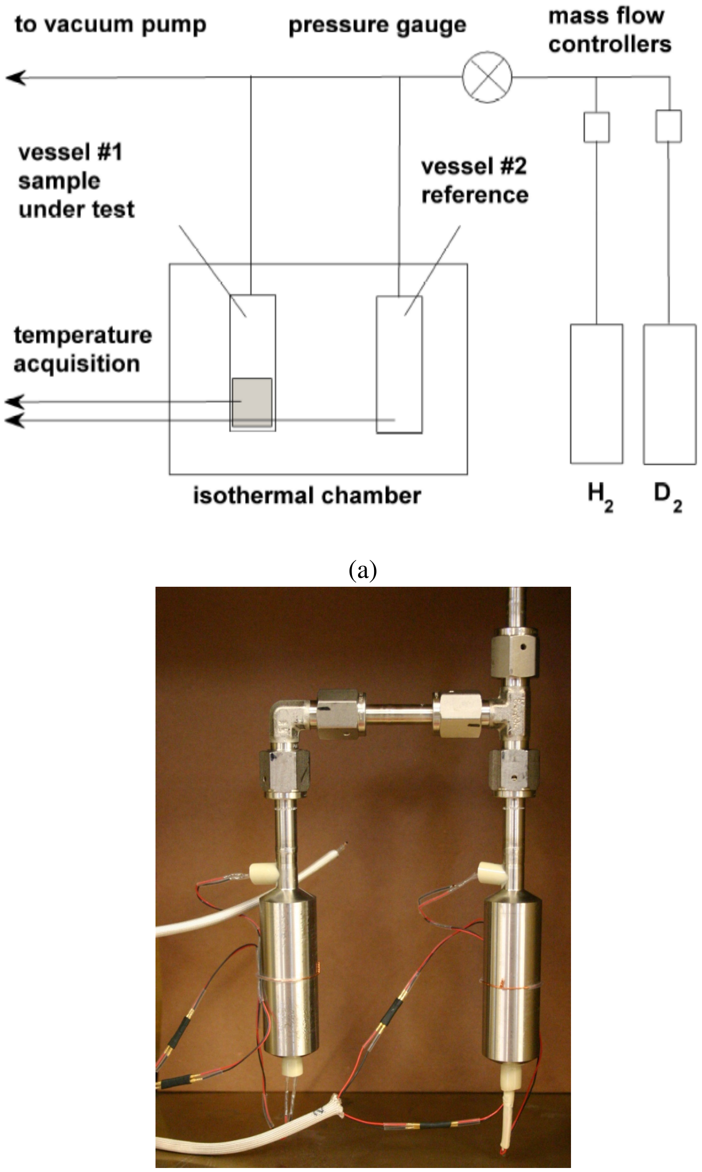
[*] E-mail: olga.dmitriyeva@colorado.edu; Also at University of Colorado at Boulder, CO, USA

In this paper, we report the results of our further investigation of the heat production during different stages of the gas loading process in nanoparticle systems. Detailed analysis is instructive when trying to answer questions about the state of the system and conditions required for excess heat generation.



(a)

(b)

Figure 1. Experimental set-up for excess heat measurements. (a) Block diagram, and (b) stainless-steel vessels inside the isothermal chamber.

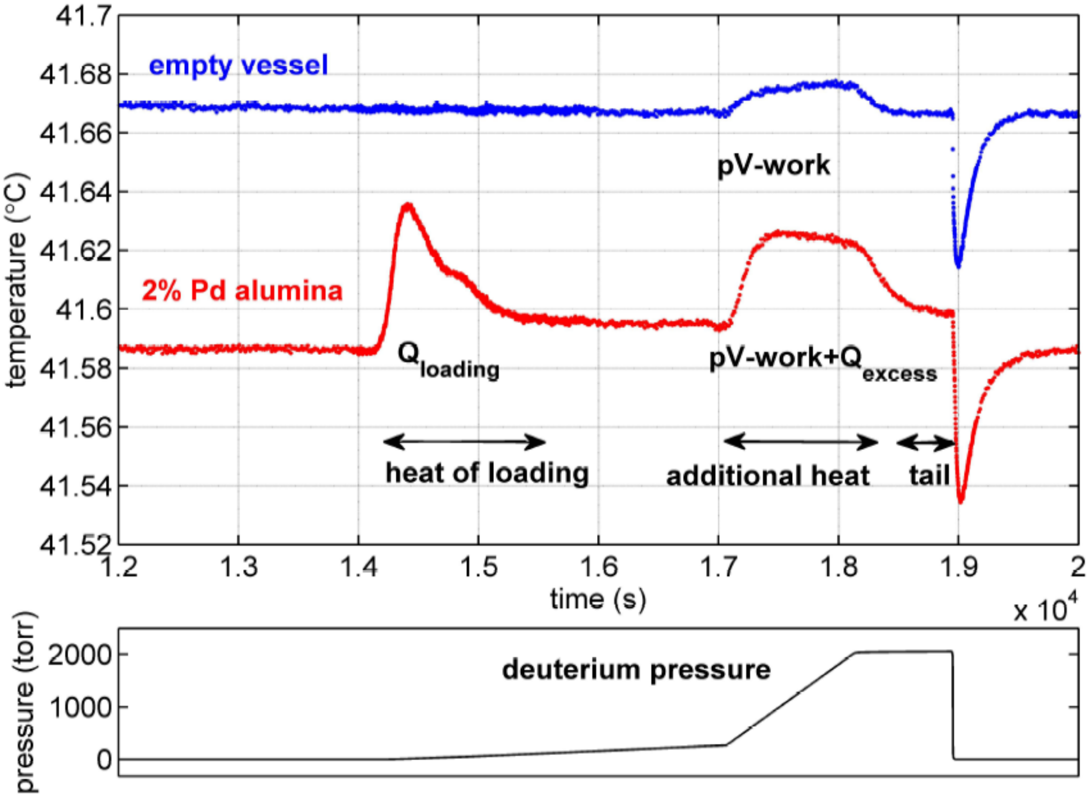


Figure 2. Pressure and temperature change in the system.

2. Experimental Procedure

Powder zeolite samples containing 2.0% by weight of Pd were prepared from molecular sieves 13X (Sigma–Aldrich P/N:283592) by cationic exchange for $[Pd(NH_3)_4]^{2+}$ ions in a $[Pd(NH_3)_2Cl_2]$ solution [6,7]. The samples were then washed with de-ionized (DI) water and dried in air at room temperature. Alumina samples containing 2.0% of Pd by weight were fabricated by the incipient wetness method similar to Ref. [8] by impregnating hot $Pd(NH_3)_2Cl_2$ solution into 80–200 mesh Al_2O_3 (Fisher Scientific P/N: CAS 1344-28-1). Alumina slurry was then dried in air at room temperature without washing in DI. Neither zeolite nor alumina samples were calcinated. Prior loading into an experimental apparatus, all the samples were baked in a vacuum oven at 120°C for 24 h.

Figure 1a shows the block diagram of the experimental set-up. It consists of an HP 5890A gas chromatograph (GC) oven that is capable of maintaining the temperature ±10 mK. The temperature of the oven is set to 313 K (40°C). Temperature changes that exceed background temperature fluctuations are associated with exothermic or endothermic heat generated in the system.

Two stainless steel vessels are placed inside the oven and connected to the gas line. One vessel contains 6 g of material. Another vessel remains empty and used as a reference.

Hydrogen, deuterium, and argon are supplied through the gas lines. H_2 and D_2 are introduced to the system through an oxygen-removing hydrogen purifier. The D_2 gas is 99.8% pure and the H_2 gas is 99.99% pure. Argon is used to fill the system while the vessels are exchanged and new material is loaded.

Temperature is registered by thermistors, glued with epoxy to the bottom and the neck of the vessels (Fig. 1b).

The flow of gas into the system is regulated using a mass flow controller and can be set anywhere between 0.2 and 10 sccm. The system is pressurized up to 2000 torr. Evacuation of the gas lines is done manually by opening the vent valve towards the pump.

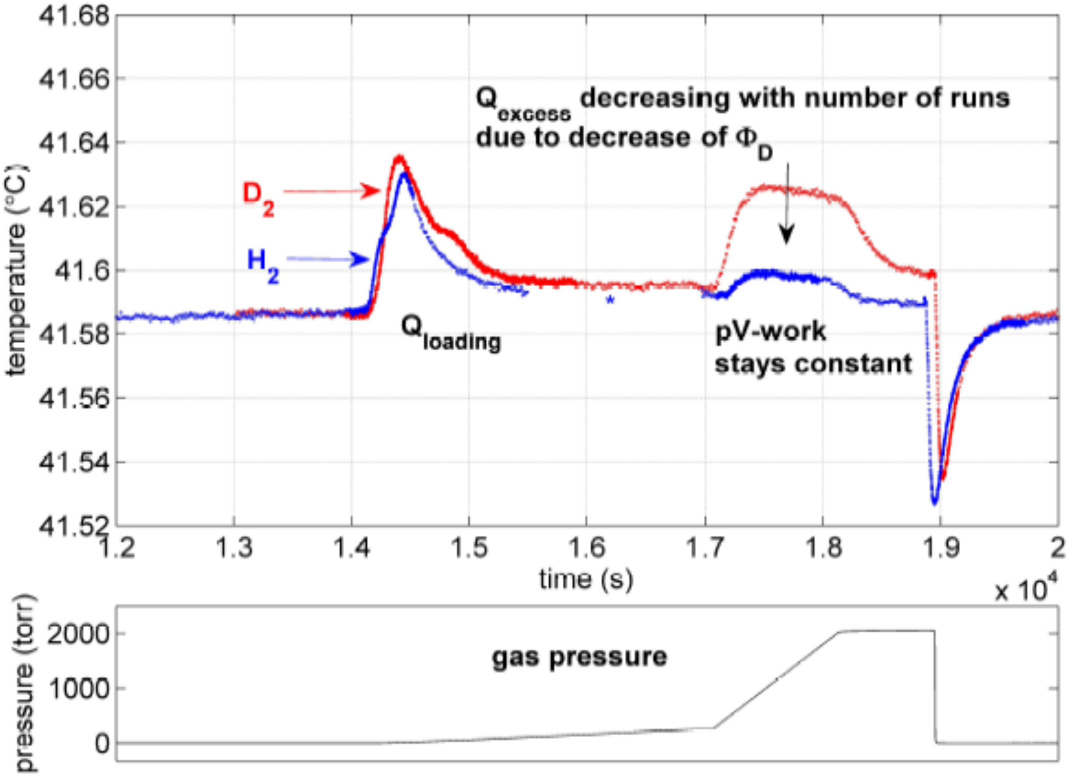


Figure 3. Pressure and temperature change in the system for deuterium and hydrogen pressurization. * The time scale for the hydrogen run was split in order to align the slow and fast pressurization intervals with corresponding intervals from the deuterium run.

System control, temperature and pressure data acquisition was done using LabView software.

The calculations of the exothermic and endothermic heat are done by integrating the temperature data from the bottom thermistors over a period of time when the temperature of the system is changing with respect to the baseline. Heat is proportional to the temperature deviation times time, and is shown in units of °C sec.

Initially, the system was checked with alumina and zeolite powders without any Pd added. The heat produced by a process is proportional to the integration of temperature deviation over time. In the presence of hydrogen and deuterium we found that the exothermic heat due to the work of pressurization (pV-work) and endothermic heat (recovery of pV-work) during evacuation balanced each other and no excess heat was produced.

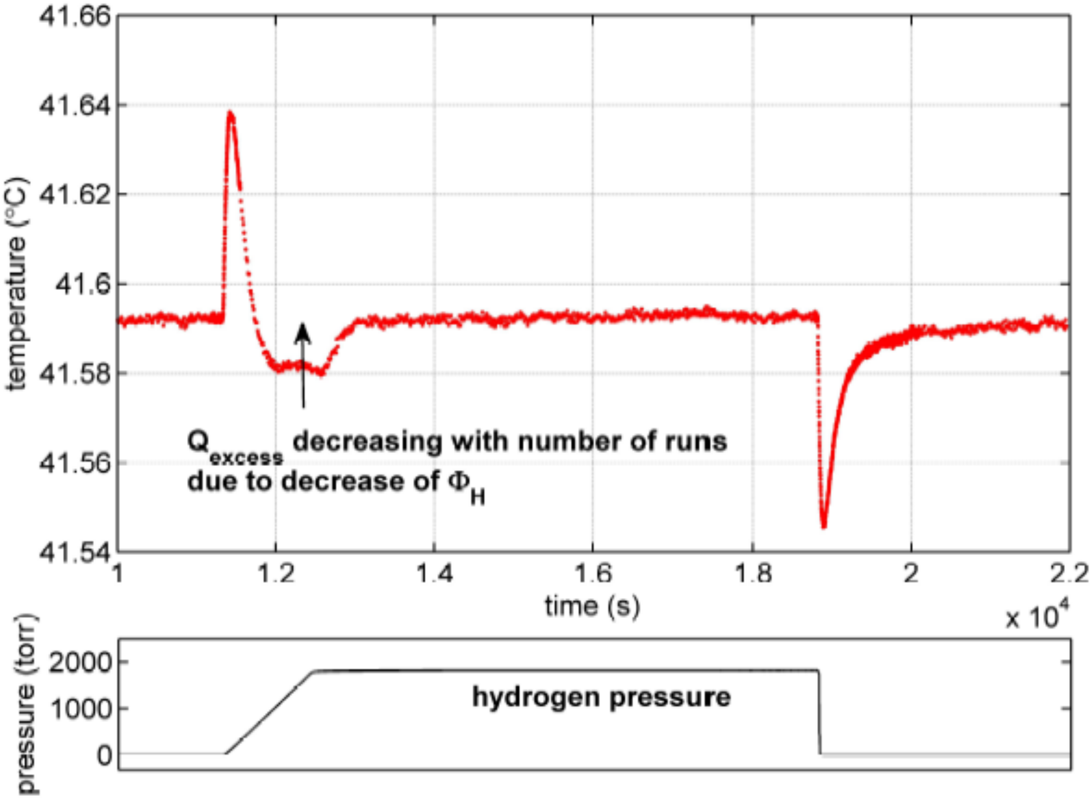


Figure 4. Pressure and temperature change in the system during hydrogen pressurization following 14 deuterium runs.

3. Results and Discussion

3.1. Excess heat generation

Figure 2 shows the typical run done with a 2% Pd-loaded alumina matrix in the presence of deuterium gas.

A two-slope pressurization is needed to separate the processes of PdD formation (heat of loading-Q_{loading}) from the heat due to work of pressurization (pV-work). The first slope corresponds to a 0.5 sccm gas input flow and second slope to 10 sccm.

There are several differences in the temperature signal between the data from the reference (empty) vessel and the vessel loaded with material. These differences are summarized in Table 1.

Based on the data from the Table 1 we can write equation for the exothermic and endothermic portions of heat generated in the material:

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

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

As for excess heat produced during the fast pressurization step we can say that the power generated is proportional to the slope of pressurization times a quantity Φ, which is the energy content of the "fuel":

$$Q_{\text{excess}}/\text{time} \propto \Phi \frac{\mathrm{d}p}{\mathrm{d}t}.$$

The fuel in the material can be exhausted or replenished (discussed further in Section 3.3). Along with nanoparticle agglomeration this leads to the decrease of excess heat production with an increasing number of runs.

3.2. Isotope effect

Anomalous heating, which is observed during deuterium loading of Pd nanostructures but not during hydrogen loading, is called an "isotope effect". The isotope effect has been attributed to the nuclear nature of the excess heat generation due to deuteron–deuteron fusion inside Pd lattice [9].

We have designed an experiment where one of two identical samples are subjected to hydrogen and the other to deuterium using the same two-step pressurization technique (Fig. 3).

Heats of PdD and PdH formation (Q_{loading}) are similar. Endothermic heat, which consists of $-Q_{\text{loading}} - (pV \text{ work})$, is the same for both materials. However, there is an isotope effect: extra heat is generated during the fast pressurization step with deuterium gas.

3.3. Fuel production within the system. Recharging

The results demonstrated in Section 3.1 suggest the existence of a fuel in our system that supports the reaction. Earlier experimental data have shown that repeated runs deplete this fuel [5]. However, the fuel can also be replenished in the system. To demonstrate this process we switched our system to hydrogen gas after multiple deuterium runs. Figure 4 shows the effect of hydrogen pressurization on 2% Pd-loaded zeolite powder that was subjected to 14 deuterium runs in which there was exothermic excess heat production.

During fast pressurization the process became endothermic. Fuel was generated during deuterium runs and supported the endothermic reaction in the presence of hydrogen.

Figure 5 shows the values of excess heat (exothermic and endothermic) due to switching of the gas from deuterium to hydrogen and back to deuterium. Exothermic excess heat was partially recovered after hydrogen pressurization. In

Table 1. Exothermic and endothermic heat generated during deuterium pressurization.

Pressurization step	Reference (empty) vessel	Material loaded vessel
Slow 0–66 min	The temperature of the empty vessel does not change because the heat of pressurization dissipates faster than it is generated.	Heat of loading we call Q_{loading}
Fast 66–80 min	pV-work	pV-work and extra heat we call Q_{excess}
Constant pressure 80–90 min	No temperature change	Excess heat, in the "tail". Excess heat associated with the tail typically disappears after 3–4 cycles.
Depressurization	Endothermic heat due to recovery of pV-work	Endothermic heat due to recovery of pV-work and Q_{loading}

other words, the system was recharged with more fuel during the hydrogen runs. Similar results were reported by the Naval Research Lab [2].

The fact that excess heat was recovered only partially may be explained by Pd-particle agglomeration. Smaller diameter particles produce more heat [2,10]. We suggest that repeated deuterium or hydrogen loadings of Pd material make the Pd nanoparticles cluster together [11] and reduce the active surface area of the Pd [12]. This process of agglomeration induces permanent damage to the system, and cannot be fixed by alternating the introduced deuterium and hydrogen gases.

To apply the formula for power production in the system to exothermic and endothermic processes we rewrite the heat production relation for deuterium runs:

$$Q_{\text{excess}}/\text{time} \propto \Phi_{\text{D}} \frac{\mathrm{d}p}{\mathrm{d}t}$$

and for hydrogen runs:

$$Q_{\text{excess}}/\text{time} \propto \Phi_{\text{H}} \frac{\mathrm{d}p}{\mathrm{d}t}.$$

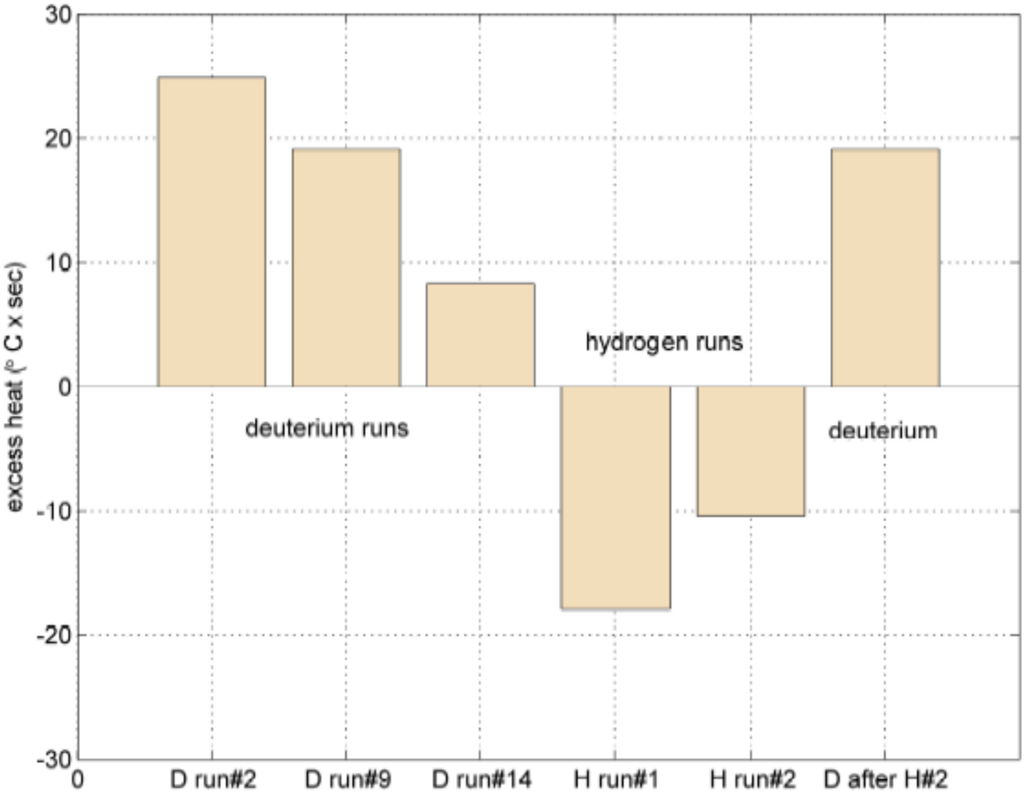


Figure 5. Effect of recharging the system by alternating deuterium and hydrogen pressurizations on 2% Pd-loaded zeolite.

Quantities Φ_D and Φ_H are not the same and we emphasize this fact by assigning different subscripts to them. Φ_D is positive and supports the exothermic reaction in the presence of deuterium while Φ_H is negative and supports the endothermic reaction in the presence of hydrogen.

4. Conclusions

By varying the pressurization rate in our experiments we were able to associate the exothermic and endothermic heat produced by the system with different mechanisms of heat production. We have looked at the heat of palladium loading, the heat of pressurization (pV-work) and the heat induced by a high rate of pressurization of the system.

We have found that heats of PdD and PdH formation are roughly the same and do not contribute to excess heat generation. Some excess heat is produced in the fast pressurization mode. The power of the heat generated during this mode is proportional to the slope of the pressure rise and the energy content of what we have termed fuel.

Fuel can be produced, exhausted or replenished within the system. The concept of fuel can explain the recharging effect, when excess heat is partially recovered by alternating deuterium and hydrogen pressurizations. Depending on the type of the fuel and reacting gas the system can produce either exothermic or endothermic excess heat. Because the system can be recharged with fuel and the sign of heat produced by the system can be reversed, it appears that the heat generated during the pressurization phase is the result of a chemical reaction.

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