Mesoscopic Catalyst and D-Cluster Fusion

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Abstract: Discussions with brief summary of the Kobe group’s experiments are given. Phenomenological modeling on mechanisms are made for explaining observed anomalies in D(H)-overloading and high heat-power release rates from nano-palladium-particles and binary metal PdNi nano-particles dispersed in/on ZrO₂ ceramics supporter flakes under D(H)-gas loading at room temperature. Roles of PdO layer and Pd-ad-atoms (incomplete outer shell) of nano-Ni-core are modeled as mesoscopic catalysts which have sub-nano-holes (SNH) on nano-particle-surfaces. SNH may realize strong sticking force for D(H)-gas to dissociate and diffuse rapidly into inner local lattice sites. During the beginning process, 4D/TSC cluster fusions with 1watt/g-Pd(or PdNi) may happen on surface. By the very over-loading (x>1) states in the later region of Phase-I and in the Phase-II after saturation, TSC formation inside nano-particles may be strongly enhanced by the non-linearly coupled QM oscillation (high free energy states of deuterons in local Bloch potentials) under the deep mesoscopic global collective potential well.

Keywords: Pd nano-particle, binary PdNi nano-particle, D(H)-gas-loading, anomalies, over-loading, high heat-power, mesoscopic catalyst, D-cluster

1. Introduction

Very rapid MD(H)x over-full loading (x>1) under near “zero pressure” of D(H)-gas and anomalously large released heat (0.6-2.0 eV/D(H)) in Phase-I period are reproducibly observed for Pd/ZrO₂ (PZ) and Pd/Ni/ZrO₂ (PNZ) samples by our group¹³. By the forced oxidization (5-10% PdO or MO formation) of used PZ and PNZ samples, a surprising recovery of performance on the loading ratio (x>1) and heat release level (0.9-1.5eV/D(H)) has been repeatedly observed ¹³. To study dynamic behavior of D(H)-sorption (adsorption/absorption) from the start, time-dependent measurements³⁵ of the evolutions for D(H)/M ratios and η-values (dynamic released energy per a D(H)-sorption) have provided quite interesting data, namely the very large dynamic isotope effects, which suggest some “nuclear effects” taking place at least partially⁴. In the present paper, we propose and discuss mechanisms to answer why such “chemical + nuclear” anomalies take place in “mesoscopic” particles dispersed in metal-oxides (ceramics) powders (flakes).

Special roles of the PdO surface layer⁴ and the ad-atoms of Pd on the Ni nano-core are modeled to gain an understanding of the generation of surface sub-nano-holes (SNH). SNH may trap D(H)-clusters on the surface with deep adsorption potential, providing seeds of 4D/TSC-induced 4d fusion (23.8MeV/³He-product)⁴. It enhances D(H)-diffusion into Pd (and the Ni nano-core of binary alloys) lattice sites of nano-particles, and at the end of Phase-I realizes the x>1 state with a “very deep (1.5-1.8eV for PZ and about 0.6eV for PNZ)” global potential for trapping (GPT) of mesoscopic catalyst which generates anomalous chemical heat for D(H)-gas absorption at room temperature. In GPT there holds local shrunken Bloch potentials for PdD(H) or NiDₓ(H₁) lattice to induce the non-linearly coupled D(H)-oscillation mode that strongly enhances the dynamic TSC (tetrahedral symmetric condensate; transitory Bose-Einstein-Condensate) formation probability inside the nano-particle⁴. Binary-metal nano-particles with incomplete-shell/core, dispersed in ceramics supporter flake, are promising for providing very large (x>3.0) loading and long lasting high level heat-power in repeatable use.
2. Examples of anomalous data observed

Brief summary is given in this section to show typical anomalies obtained by using PZ, PNZ-I and PNZ2B samples. D(H)-gas charging experiments were done for the virgin-as received-samples (#1 runs), the forced de-oxidization samples (#2 runs) and the forced oxidation samples (#3 runs), after baking process. Runs without the baking process are labeled as #1A and #1B. Desorption runs by evacuation are labeled as #1d and #1Ad. Using the twin system, simultaneous runs for D-gas and H-gas charging were made for measuring time-dependent D(H)-loading rates, heat-powers, gas-pressures, neutron counts (by a $^3$He counter) and gamma-ray counts (by an NaI counter). No meaningful increases of neutron and gamma-ray counts over natural background were observed for all runs reported here. Heat-power evolution data and gas-pressure data can be classified to two regions, namely the phase-I and the phase-II. In the phase-I interval, major heat release happens with “near zero” gas-pressure and rapidly increasing D(H)-loading rates, while in the phase-II we observe saturated states of D(H)-loading and low level excess heat for D-charging only sometimes.

2.1 Anomalies by PZ samples

PZ sample is made of 34.6%Pd + 65.4%Zr material plus oxygen-atoms to form nano-Pd/ZrO$_2$ powder. Sizes in 8-10nm diameter of Pd-nano-particles were analyzed by TEM. Detail of experiments is written in Ref.5. Integral heat data in the phase-I for the PZ samples are shown in Fig.1 for time-order of runs.

Integrated Heat Data (Phase-I) for D-PZ11 and H-PZ12

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Fig.1 Integral heat data in phase-I obtained by PZ samples

Heat values of #1 runs by virgin samples are anomalously large, compared with known values for bulk-Pd metal as observed in later sorption/desorption runs (#3A, #3Ad, and so on). The runs (#2) after the forced de-oxidization of PZ samples gave similar values to the bulk ones. Observed maximum D(H)-loading ratios, $x=[D(H)]/[Pd]$, for #1 run was over-full loading $x=2.0$ (H and D), while $x=0.45$ (H) and 0.60 (D) for the #2 runs. Surprisingly the #3 runs after the slight oxidization (speculating...
5-8% PdO surface layer formation on Pd-nanoparticles\(^5\) showed “full” recovery of heat-level and over-full loading ratios (x = 1.4 for H and 2.0 for D). Heat levels by the D-gas-charging, especially for the #3 run are significantly higher than those of the H-gas-charging. However the desorption runs (#3d) gave much smaller absolute values of heat-absorption (endothermic reaction). In usually known data for bulk Pd give almost same values of heat levels (regarded as binding energies of D(H)-atoms in metal lattice) between the sorption (adsorption plus absorption) exothermic heat and the desorption endothermic heat. It is a common sense of “chemistry” in hydrogen in metal. Why did such large isotopic effects happen?

In Fig.2, we show isotopic ratios of \(\eta\)-values\(^3,5,6\), which are dynamic data of D(H) binding energies (plus alpha for D!) in Pd-nano-particles during the time-dependent sorption process.

![Fig.2 Dynamic isotopic ratios of \(\eta\)-values for virgin PZ samples](image)

In usual chemistry sense, the ratio should behave around 1.0 and may have about 10% or less isotopic effect, because the binding energies are reflected as almost the same electron-bonding energies between D(H)-atoms and metal lattice-atoms for D- and H-isotopes. Therefore, we are interested in the time-intervals where the ratios deviated much over the 1.0 “chemical line”, as it may show the information of some nuclear-origin energy induced by deuterons. In Fig.2, we notice that the interval for \(\eta\)-ratio \(\gg\) 1.0 appears already in the beginning of D(H)-gas charging. The ratio is as large as 6.5 in the very beginning. It is a surprise and has never been expected in the past Cold Fusion (electrolysis) experiments which required very long “waiting time”. The other large ratios in the later time interval after 200 minutes need our careful study due to the difference of gas-flow rates between D- and H-charging. In addition, we observed sub-phases (the phase-Ia and the phase-Ib)\(^3,5\), reason of which should also be investigated further.

### 2.2 Anomalies by PNZ-type samples

Before PNZ runs, we tested NZ sample (35.8%Ni and 64.2%Zr) to have no measurable D(H)-loading and heat levels at room temperature (around 20 deg C). Then we tested PNZ-I sample (10.5%Pd,
25.3% Ni and 64.2% Zr) to get anomalously large D(H)/Pd ratios and heat-levels\(^3\), which were however proportional to the amount of contained Pd-atoms and looks independent of the amount of Ni. The third trial using PNZ2B sample (4%Pd, 29%Ni and 67%Zr) has given us the surprising results\(^6\), showing very large loading ratios \([D(H)]/[M=0.125Pd + 0.875Ni]\), over 3.0 and anomalously high heat levels. What is the reason of such drastic change between the experimental results for NZ, PNZ-I and PNZ2B? Why can the much smaller amount of Pd atoms in PNZ2B induce the great and anomalous loading and heat effects?

In Fig.3, we show an example of raw data for the #3 (forced oxidization) run using PNZ2B samples.

\[\text{Fig.3: Raw data of } D(H)/M \text{ ratios, heat-powers and gas-pressures for the PNZ2B(3,4)#3 runs}\]

We see significant isotopic effects in D(H)/M evolutions, heat-power-levels and gas-pressures for about 15 hours twin-cell run. Maximum loading ratios exceeded the 3.0 line. We can see “excess heat-power” for the D-gas charging in the later time region (the phase-II\(^2\))? reproducibility of which shall be further confirmed. In Fig.4, we show data of heat-powers and \(\eta\)-values. We see a little bit delay of starting D(H)-gas sorption just in the beginning, where bumps of gas-pressures and short endothermic heat-power (especially for the D-sorption) are observed. The reason for these transient phenomena in the starting period is unknown. Correspondingly, \(\eta\)-values in the beginning are small and rising up with delays (see Fig.5): this trend is very different from that for the PZ samples that gave a sharp spike of \(\eta\)-values only for the D-gas charging in the beginning time interval. The observed \(\eta\)-values for all runs (#1, #2 and #3) of the PNZ2B samples gave the same trend of delay (please compare Figs. 5, 6 and 7).
Fig. 4: Evolutions of heat-powers and η-values for the #3 runs of PNZ2B samples after the forced oxidization

We see the η-values by the D-gas charging increase more and more as time elapses, while those by the H-gas charging keep almost constant values (about 0.6eV per one H-atom sorption) until about 300 minutes (5 hours). Data for H after about 350 minutes became poor in accuracy due to decaying
heat-power level (approaching to zero and difficult to calculate \( \eta \)-values there). The sudden and large peak of \( \eta \)-values for D just after 300 minutes might be by chance and unknown happening. The data for isotopic ratios of \( \eta \)-values are shown in Fig.5.

**Fig.6:** Data for isotopic effect on \( \eta \)-values for the #2 (forced de-oxidization) runs of PNZ2B samples

These data for the #3 runs of PNZ2B may suggest a gradually enhancing nuclear effect as time elapses. In Fig.6, we show the data of isotopic ratios of \( \eta \)-values for the #2 (forced de-oxidization) run of
PNZ2B samples. We observed very large (near 3.0, see Fig.8) maximum D(H)/M loading ratios and as high heat levels as those of the #1 virgin runs for PNZ2B. It is drastically different aspect from the results of PZ samples. The forced de-oxidization, namely complete reduction of oxygen atoms from the sample did work for the anomalous over-loading and high heat-level effect, in the case of binary (Pd-Ni) nano-particles dispersed in/on ceramics (ZrO₂) supporter flakes. What is the reason?

In Fig.7, we show the data of isotopic ratios of η-values for the virgin (#1) runs of PNZ2B samples. These two data (Figs. 6 and 7) show the existence of local time regions where η-values for the D-gas charging are larger as much as 50% which are already difficult to explain by the isotopic effect of usual chemical reactions. In addition, behaviors of the ratios are very time-dependent, although we expect rather constant ratios near 1.0 for any chemical reactions.

In Fig.8, we summarized observed maximum loading ratios for PNZ2B samples, for the initial series of #1 to #3 runs and the reused series runs.

![History of Maximum Loading Ratios for PNZ2B](image)

**Fig.8: Observed variation of maximum D(H)-loading ratios for the first series runs (3,4) and the reused series runs (5,6) of PNZ2B samples**

We see anomalously high loading ratios around 3.0 for #1, #2 and #3 runs, and still high values around 2.0 for reused samples. The PNZ2B sample has a tough life for D(H)-absorption and high heat release. It is a nice indication for industrial application of this CMNS effect in energy production/transfer systems. Observed maximum loading ratios showed similar values between the D-gas loading and the H-gas loading, so that we see no isotopic effect in loading.

In Fig.9, we show the data of Q1, mean released energy per a D(H)-atom sorption for the PNZ2B samples. The Q1 data correspond to the time-averaged η-values with heat-power weighting functions. The observed Q1 values for the D-gas charging have given “always” larger values than those for the H-gas charging. The excess values (differences) might be attributed to some nuclear effect caused by deuterons. The excess values are significant for the (3,4)#3, the case of forced oxidation, and the (5,6)#1, the first run of reused samples. These may be hints for further trials to enhance the excess
energy. The mean “chemical” binding energy is expected to be given by the data of the H-charging. We have had maximum value of 0.6eV by the (3,4)#2 run and the minimum value in Fig.9 is 0.35eV. Probably, the sub-nano size structures on surface D(H)-adsorption sites are changing from run to run.

Fig.9: Data of mean released energy per a D(H)-atom sorption for the first series (3,4) runs and the reused series (5,6) runs of PNZ2B samples

3. Mesoscopic Catalyst and D-Cluster
In order to gain some understanding on what is going on in observed anomalies as summarized in Section-2, we extend here proposal of phenomenological models and related discussions. In Fig.10, we illustrate a feature of making PZ and PNZ type samples.

Fig.10; Illustrative feature of PZ and PNZ samples
Mono-metal (Pd in this case) nano-particles (1-10nm diameter in size) with PdO surface layer are dispersed in/on a flake of ceramics supporter (ZrO$_2$ in our case, and zeolite and gamma-alumina with nano-poles in other group’s experiments). PdO/Pd nano-particles are replaced with binary nano-particles such as Pd$_x$Ni$_y$ “alloy” with x+y=1.0. It is known that binary alloys make a homogeneous lattice of regularly arranged positioning (lattice) of two different atoms. However, as known (see internet googling nano-catalyst) by recent development of nano-catalysts, binary nano-particle makes a outer-shell/inner-core structure and works as “nano-catalyst” because of large “fractal” surface with electron-dangling bonds. Our PdO/Pd nano-particle and Pd$_x$Ni$_y$ binary nano-particle (around 2nm diameter$^2$) are supposed to work as nano-catalysts having the shell/core structure.

In Fig.11, we show schematic pictures of Pd$_x$Ni$_y$ binary nano-particles for the case a) of x=2/8 and y=6/8, which is corresponding to the PNZ-I sample, and the case b) of X=1/8 and y=7/8 which is corresponding to the PNZ2B sample.

![Binary Alloy Metal Nano-Particle Catalyst; Model for PdxNiy](image)

**Fig.11: Illustration of Pd$_x$Ni$_y$ binary nano-particles having shell-core structure**

In the case of a) complete-Pd-shell/Ni-core structure, incoming D$_2$(or H$_2$) molecules will be trapped by dangling bonds of Pd-layer, dissociated into two D atoms and absorbed as making PdD state, which however blocks additional D$_2$ molecules to be trapped and in addition the formed PdD layer also blocks trapped deuterons diffusing into inner Ni-core lattice (fcc structure as Pd). This feature may explain the loading and heat results obtained for the PNZ-I (10%Pd) sample, which does not work well.

In the case of b) “incomplete”-Pd-shell/Ni-core structure, many sub-nano-holes (SNH) can be formed on its surface as illustrated, where we expect increased electron-dangling bonds to stick strongly incoming D$_2$ molecules to dissociate and diffuse into inner Ni core lattice. As we modeled the role of oxygen-atoms in PdO surface layer of PZ sample$^4$, Pd ad-atoms of the incomplete outer shell have a role to generate SNHs for working as “mesoscopic catalyst”. In the case of PZ samples, we need to
supplement oxygen after the #1 run for recovering as oxygen-atoms in PdO layer are gone away by the D(H)-charging. In contrast, Pd ad-atoms on the binary nano-particle remain and are active after the #1 run and revive fully by the forced de-oxidization. This is commonly the reason why PNZ2B samples worked still strongly for the reused series runs (5,6).

As we have already discussed in Ref-4, the surface SNHs are seeds for making 4D/TSC transient Bose-Einstein condensates just from the beginning time of D-gas charging. The anomaly of η-values and their isotopic ratios in the beginning interval in Fig.2 can be explained by the 4D/TSC induced 4d-multi-body simultaneous fusion (break up to two alpha-particles after complex final state nuclear interactions), as causing 1watt per one gram Pd nano-particle nuclear heating by PZ samples4.

In the case of PNZ2B samples, we have observed gradually enhancing trend of η-values as shown in Figs. 4 and 5. We speculate that the anomalously high loading ratios exceeding 3.0 for PNZ2B samples would have suggested the D(H) trapping at T-sites (portion 2.0 of loading ratio) as well as O-sites (portion 1.0 of loading ratio) of Ni fcc local lattice of nano-Ni-core. Remaining component of over 3.0 loading ratio will be attributed to the trapped D-clusters at SNHs on the surface. Such anomalous occupation of T-sites by deuterons will enhance 4D/TSC formation inside Ni-core in the later time interval of Phase-I region and possible in the Phase-II region4.

An image of trapping potential of the mesoscopic catalyst is drawn in Fig.12. The left inserted figure illustrates the periodic Bloch trapping potential for the bulk Pd (same feature with larger valleys for bulk Ni). As we discussed already in our previous paper4, the mesoscopic global potential of meso-catalyst realizes anomalies in very rapid sorption, over-full-loading of D(H), anomalously large “chemical heat, chemical + nuclear combined heat evolution phenomena in the Phase-I interval, and possibly pure nuclear (maybe 4d fusion) heat evolution in the Phase-II region.

For conclusions, please see the abstract on the top.
References:


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