Summary of the latest results of gas loading experiments

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Aim and Background

BG:

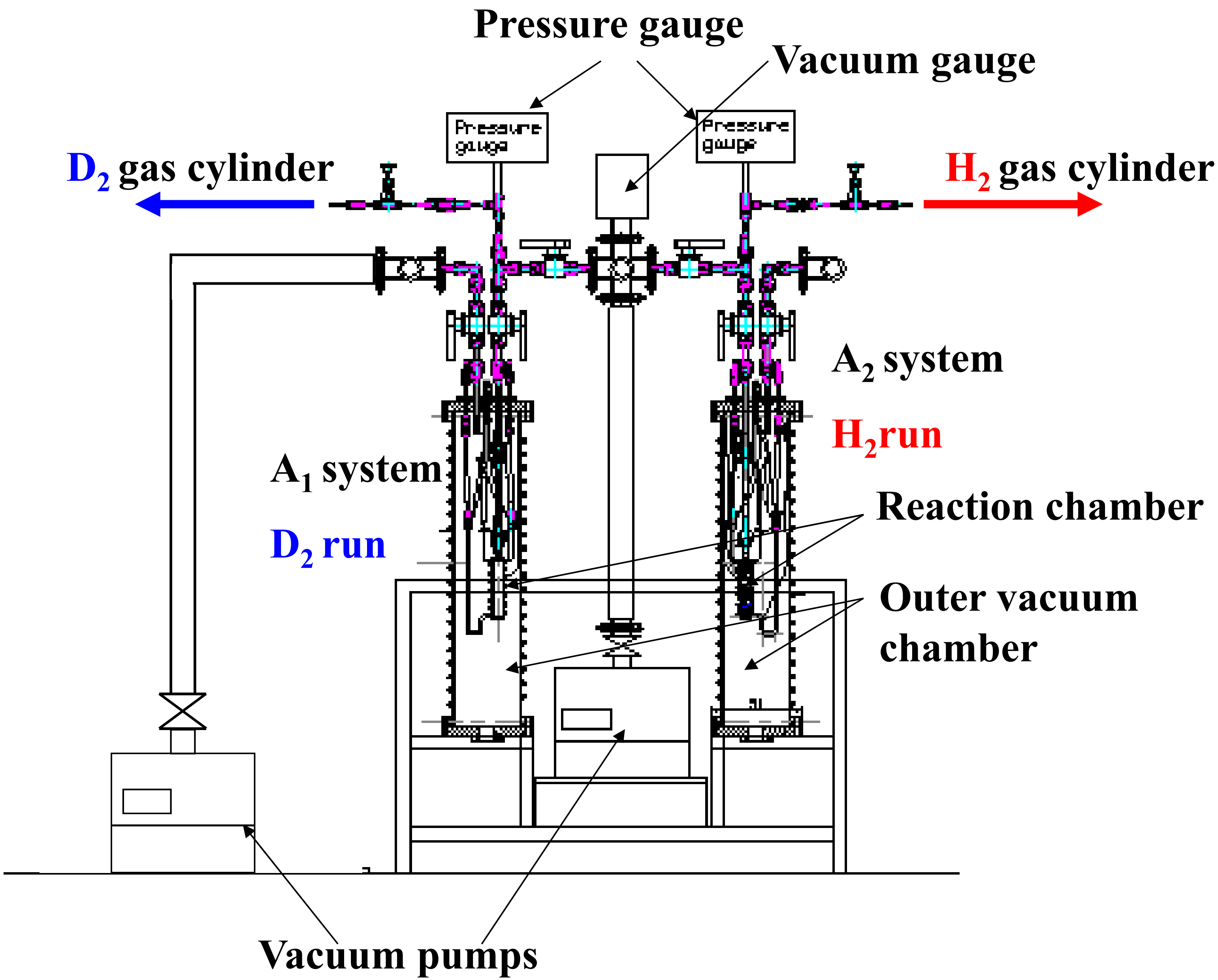
Anomalous heat evolution accompanied by ^{4}He generation, which is difficult to explain by chemical reactions, was reported using Pd/ZrO_2 nano-composite samples exposed to gas-phase hydrogen isotopes [Y. Arata, et al.; The special report on research project for creation of new energy, J. High Temperature Society, No. 1, 2008].

Aim and method:

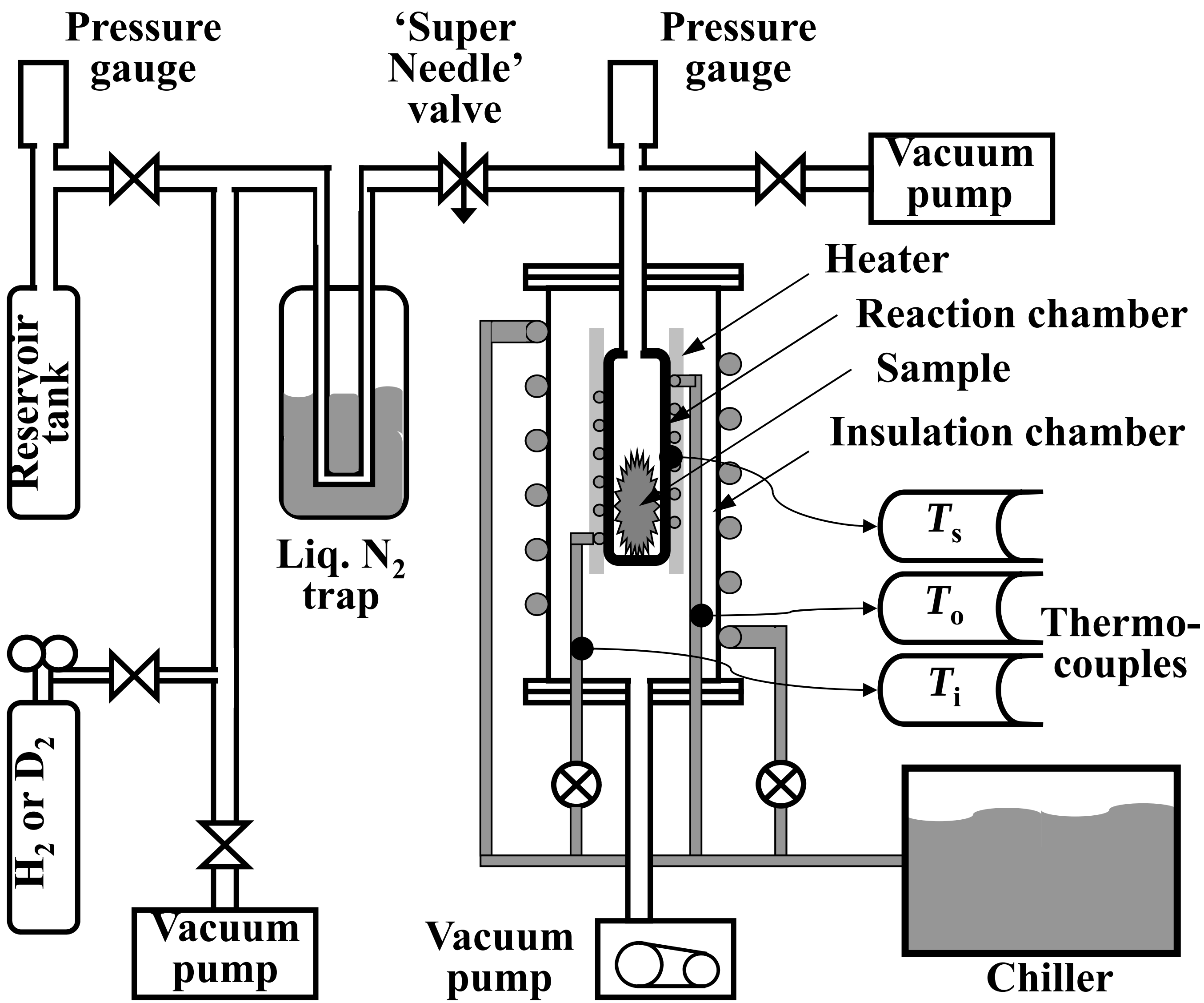
To find **the underlying mechanism** of the claim and to develop **more efficient materials** for the heat evolution, an experimental facility consisting of a twin hydrogen-isotope absorption / adsorption system and a nuclear diagnostic system has been constructed in 2008 [1].

[1] A. Kitamura, et al.; Physics Letters A, 373 (2009) pp.3109-3112.

$A_1 \cdot A_2$ twin system for simultaneous D_2/H_2 absorption experiments.



Schematic of one of the twin absorption system.



Samples tested

	Pd / (Cu)	Ni	Zr	Si	O	Supplier	
100nmϕ-Pd PP	99.5%, 100nmϕ	---	---	---		Nilaco Corp.	[1],[2]
Pd-black PB	99.9%, 300mesh	---	---	---		Nilaco Corp.	[1],[2]
mixed oxide PZ	0.312 (8nmϕ)	---	0.688	---	(1.69)	Santoku Corp.	[1],[2],[3]
mixed oxide PS	0.054 (2-10nmϕ)	---	---	0.946	(1.95)	Admatechs Corp.	[5]
mixed oxide NZ	---	0.467	0.533	---	(1.53)	Santoku Corp.	[2]
mixed oxide PNZ / PNZII	0.080 / 0.023	0.352 / 0.891	0.568 / 0.292	---	(1.57) / (1.50)	Santoku Corp.	[2]
mixed oxide PNZ2B	0.04	0.29	0.67	---	(1.67)	Dr. B. Ahern	[4]
mixed oxide CNZI	(Cu) 0.08	0.35	0.57	---		Santoku Corp.	[6]

[1] Phys. Lett. A, 373 (2009) 3109-3112.
[2] J. Condensed Matter Nucl. Sci., 4 (2011) 56-68.
[3] J. Condensed Matter Nucl. Sci., 5 (2011) 42-51.
[4] Miyoshi Y.; ICCF16, paper MT-02.
[5] Sakoh H.; to be published in Proc. JCF12.
[6] Miyoshi Y.; to be published in Proc. JCF12.

TEM images of the PZ sample

TEM images of Palladium nanoparticles from Japan (sample # 2)

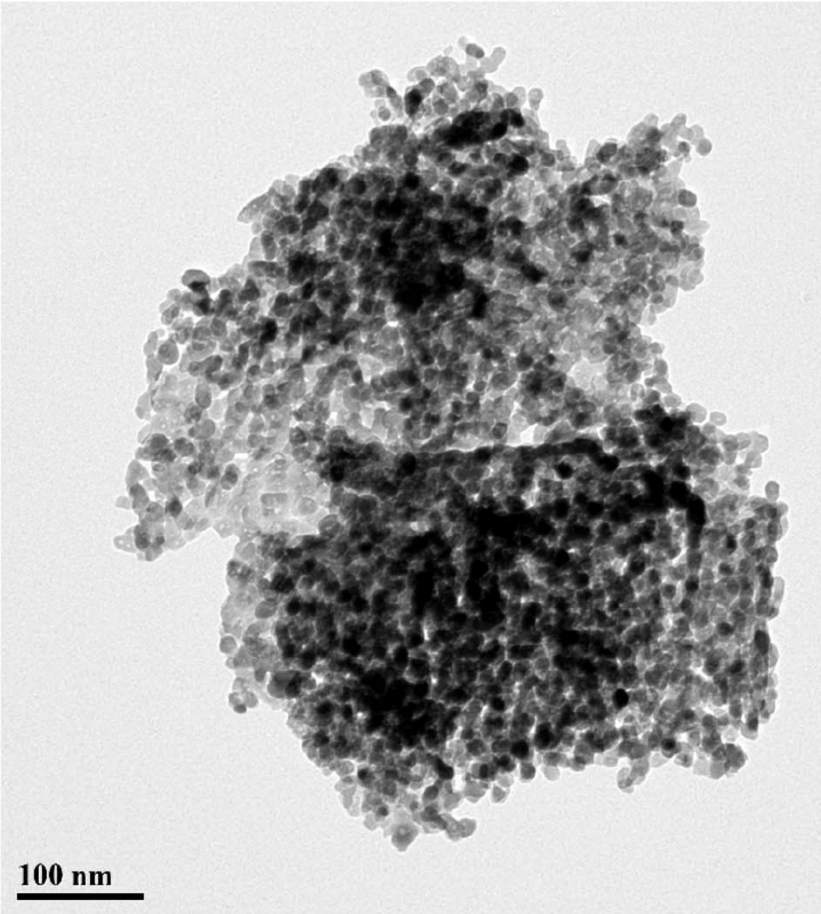
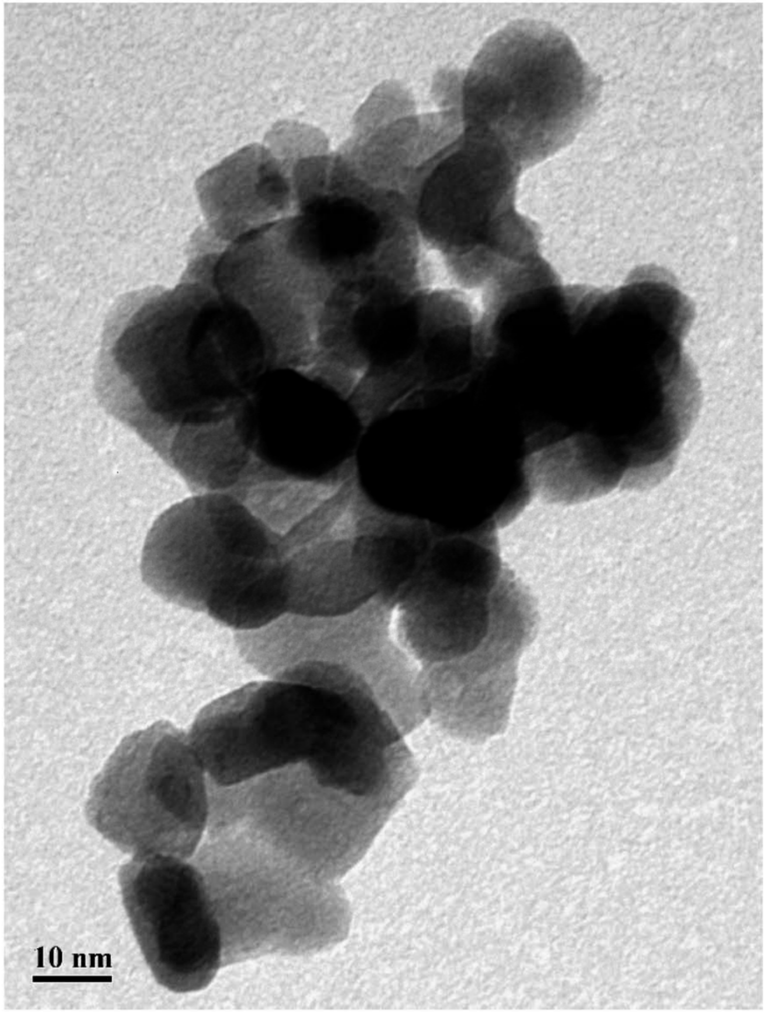
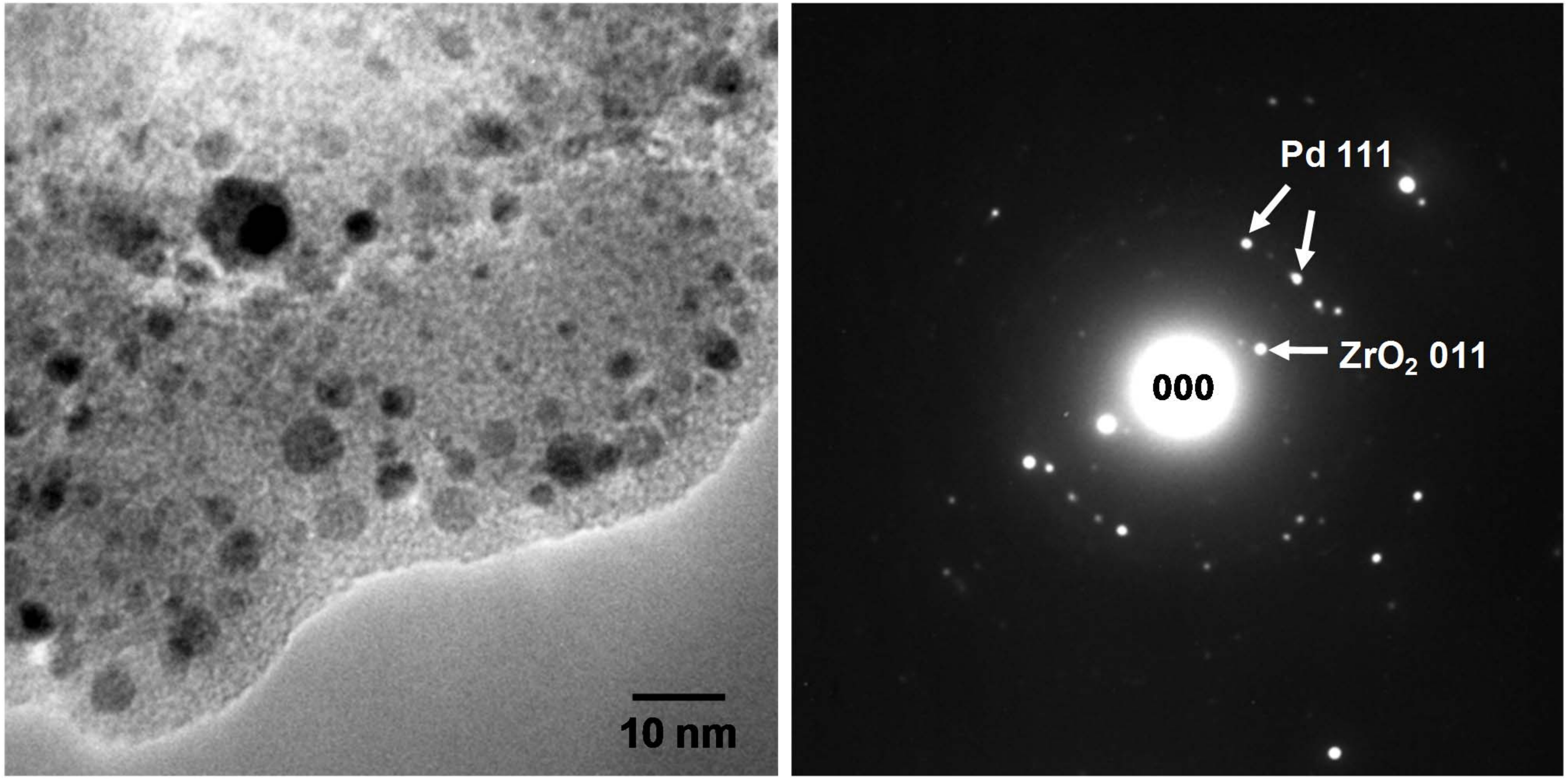


Image at 25000X magnification



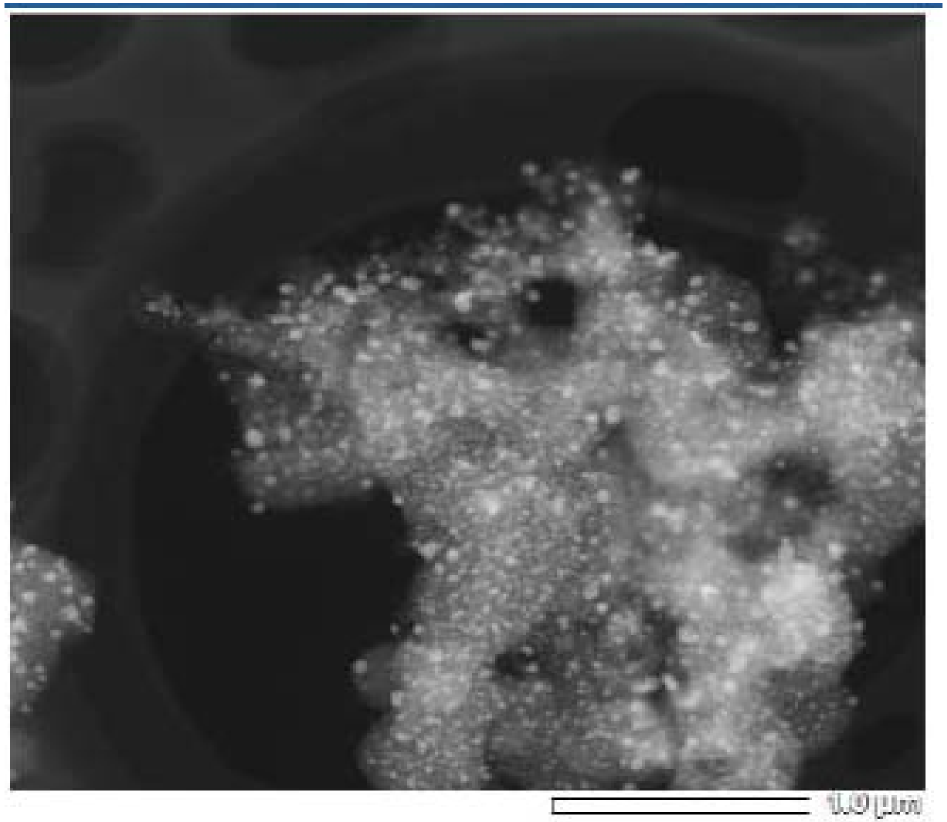
Sample prepared by Snatoku Corp.
TEM analysis by Prof. R. Duncan, Univ. Missouri, Colombia

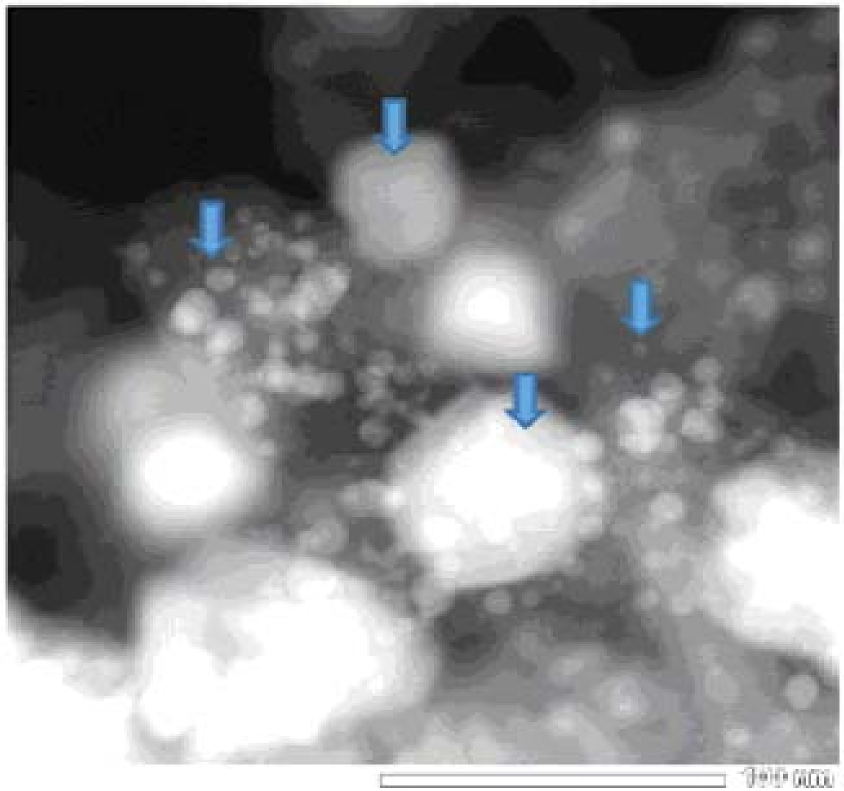
TEM images of a sample similar to PNZ2B



TEM analysis by Prof. Oku, Univ. Shiga Prefecture

TEM images of the PSII sample





Contained Pd:
9.2 wt%

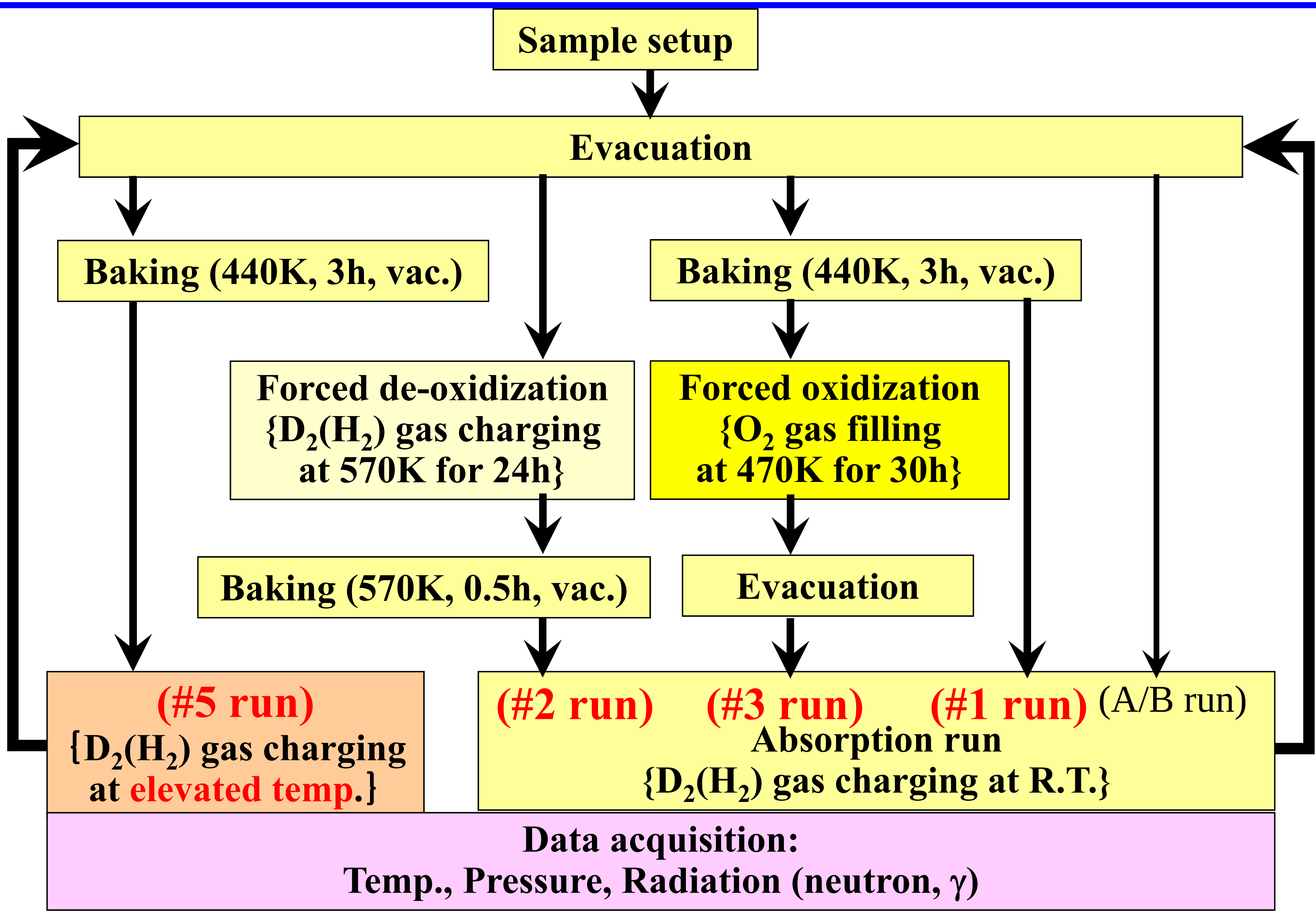
Size of porous silica:
4 µm

Pd particle size:

3-10nm: 90%
20-150nm: 10%

Courtesy of Admatechs Co. Ltd.

Experimental procedure



Summary of the runs at R.T.

PZ: 8-nmϕ Pd(31.2%)·Zr(68.8%)

(1) The 1st phase is found to be divided into two sub-phases;

- **1a phase**; with rapid absorption/adsorption and high heat output.
  - Probably occurring in the near-surface region
  - Oxygen incorporation is necessary for this phase to appear.
  - η_D value is larger than η_H., several times in some cases.
- **1b phase**; with a lower heat output nearly equal to the bulk value.

(2) The 1a phase is observed only in #1 and #3 runs.

(3) The **as-received** sample has very large 1^{st}-phase parameters;
(specific output energy $E_{1D(H)}$, the loading ratio D(H)/Pd, and the hydridation energy $Q_{D(H)}$).
Forced **reduction** of the sample has given the significantly smaller 1^{st}-phase parameters
Forced **oxidization** of the sample has substantially recovered the large values of the 1^{st}-phase parameters

Summary of the runs at R.T. (continued)

PP: 99.5%-pure 100-nmϕ Pd **and** **PB: 99.9%-pure 300-mesh Pd-black**

(1) The effects similar to those for PZ are observed less prominently;
- the existence of the 1a and 1b phases, and
- increased absorption parameters by oxygen incorporation.

PS: Nano-porous-silica-included Pd nanoparticles

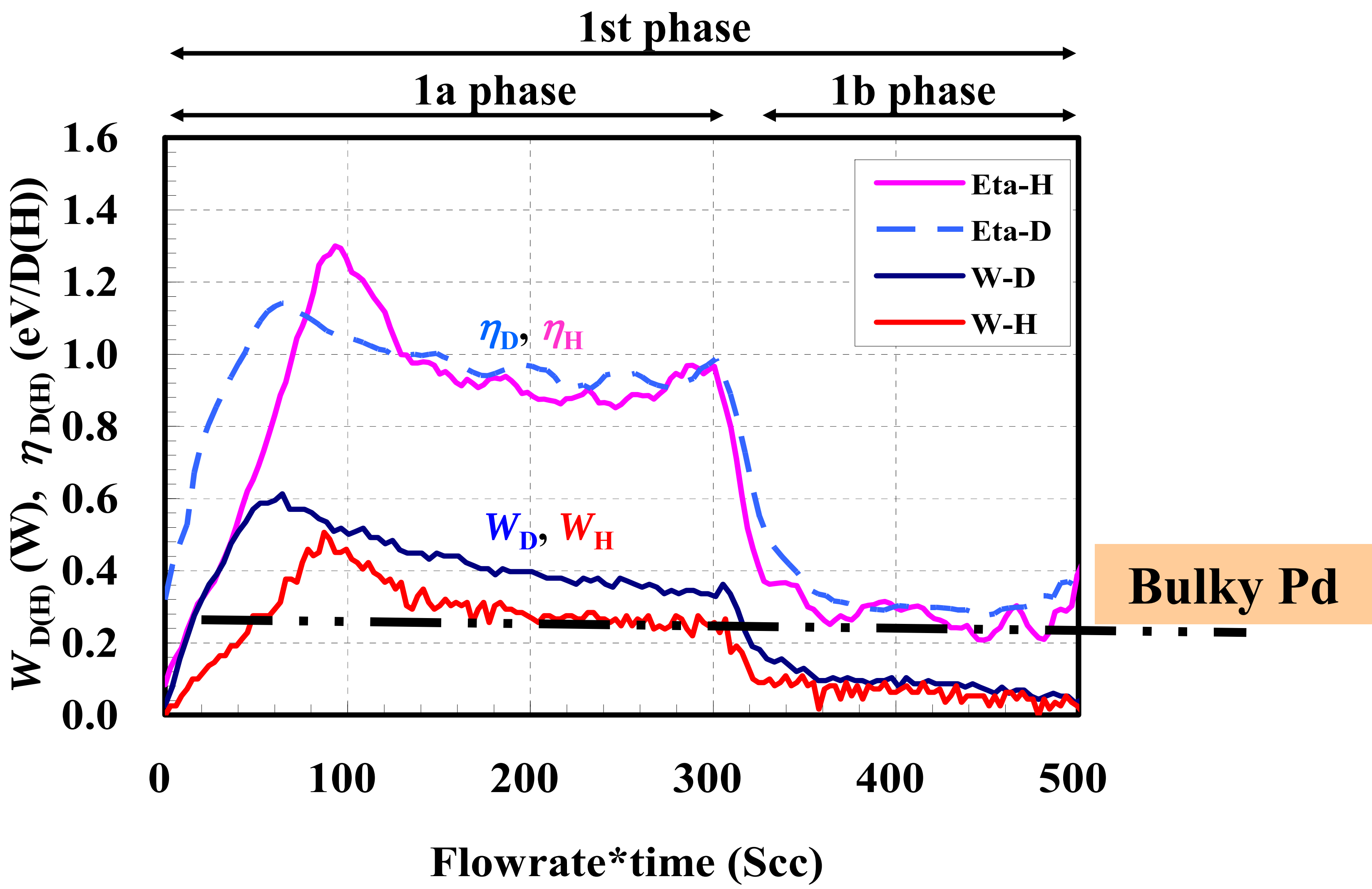
(1) can avoid clumping-together to enable multiple use with more excellent characteristics of Pd nanoparticles.

(2) The as-received samples showed very large loading ratio D(H)/Pd reaching 3.5 and absorption energy E_1 exceeding 2.5 eV/atom-Pd. These are much larger than other Pd nano-particle samples ever used.

(3) The similar effects of the sample treatment in the recycled use are observed: Forced oxidization recovers large values of D(H)/Pd exceeding 2.2 and E_1 exceeding 1.3 eV/atom-Pd.

(4) It is inferred that contribution of the oxygen pickup reaction to D(H)/Pd and E_1 is small. This means that both D(H)/Pd and $Q_{D(H)}$ are rather large compared with bulky Pd samples.

PS samples (nano-porous-silica-included Pd) show even larger capacity for sorption and improved repeatability.



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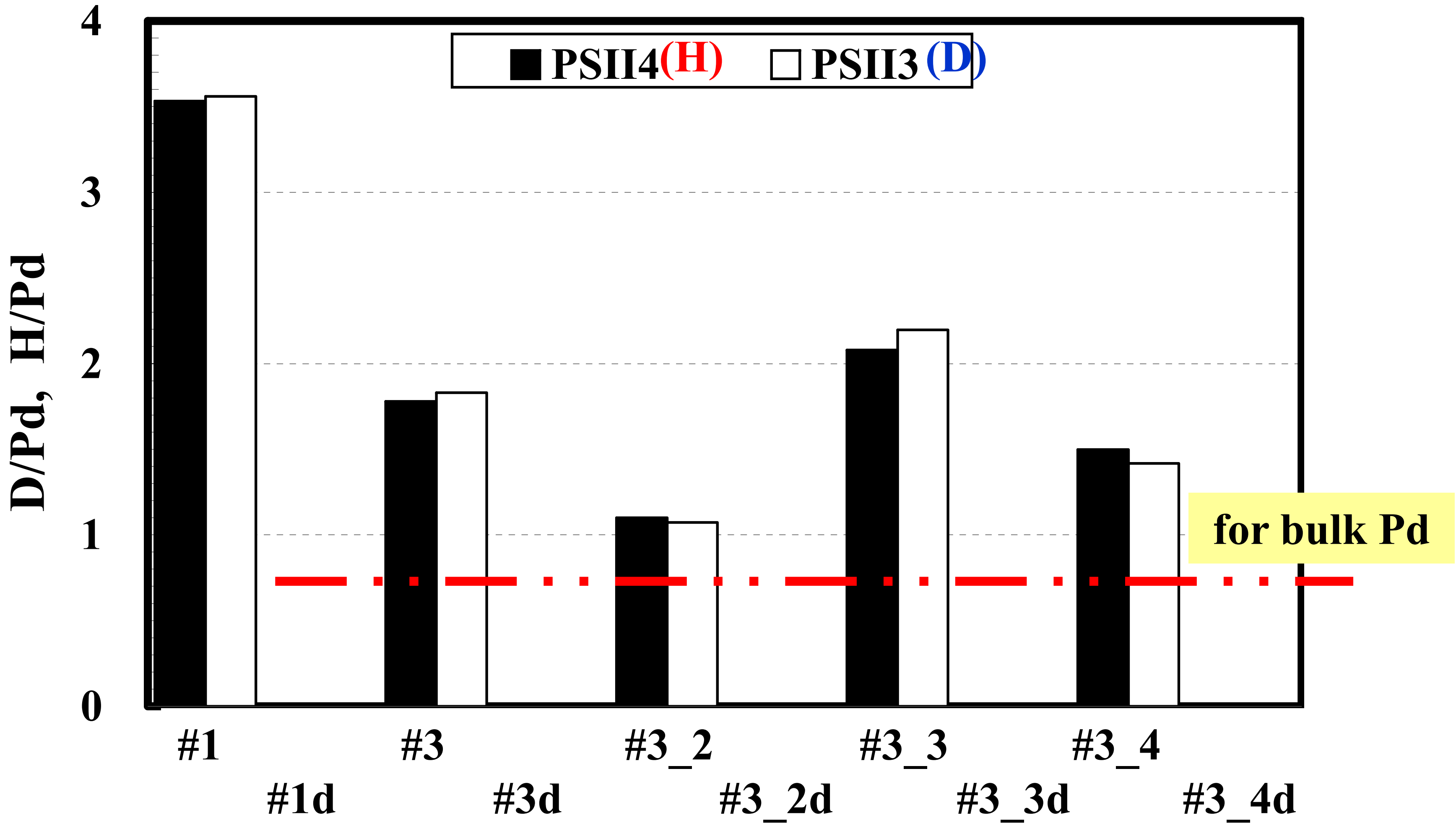

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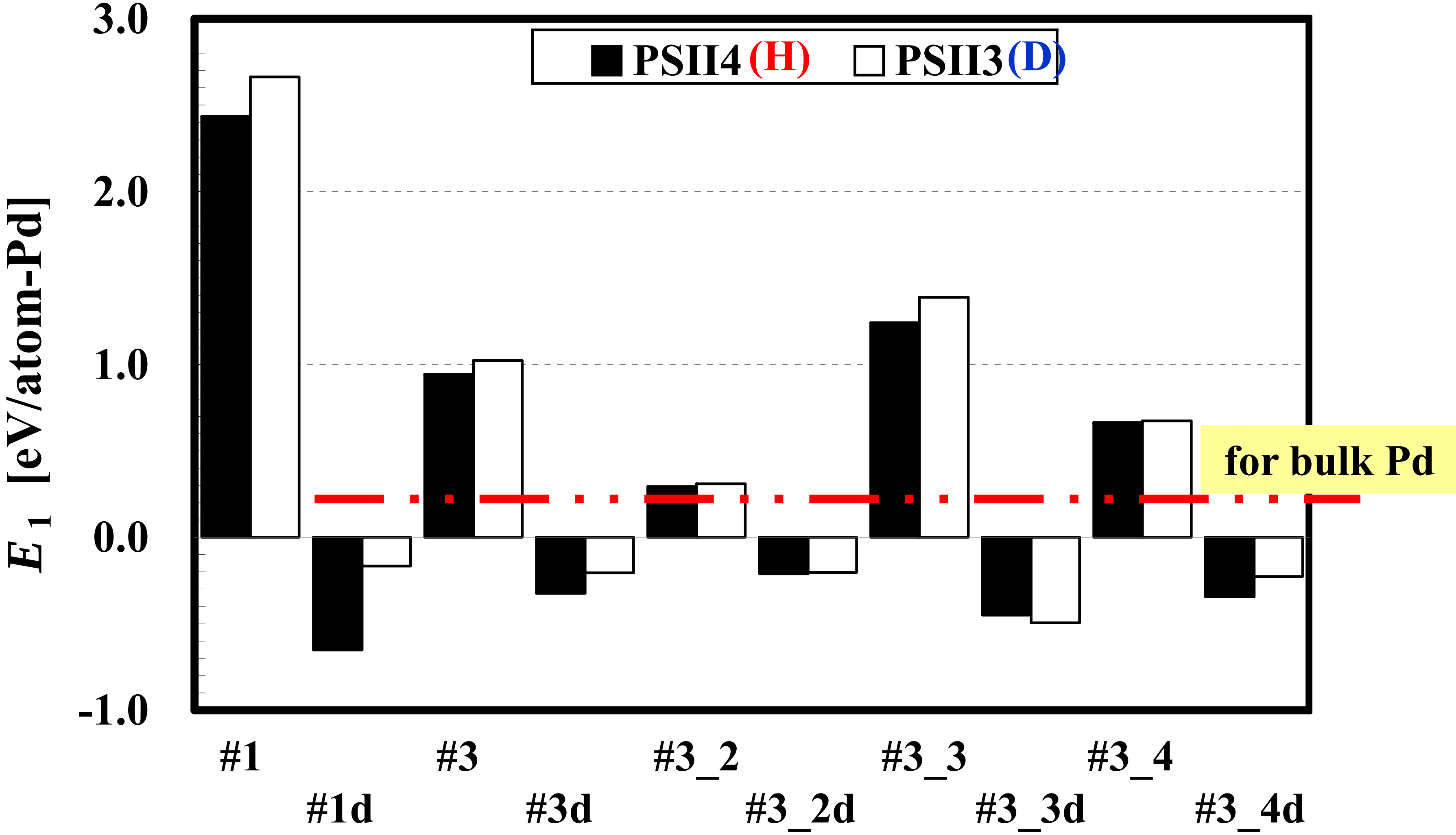

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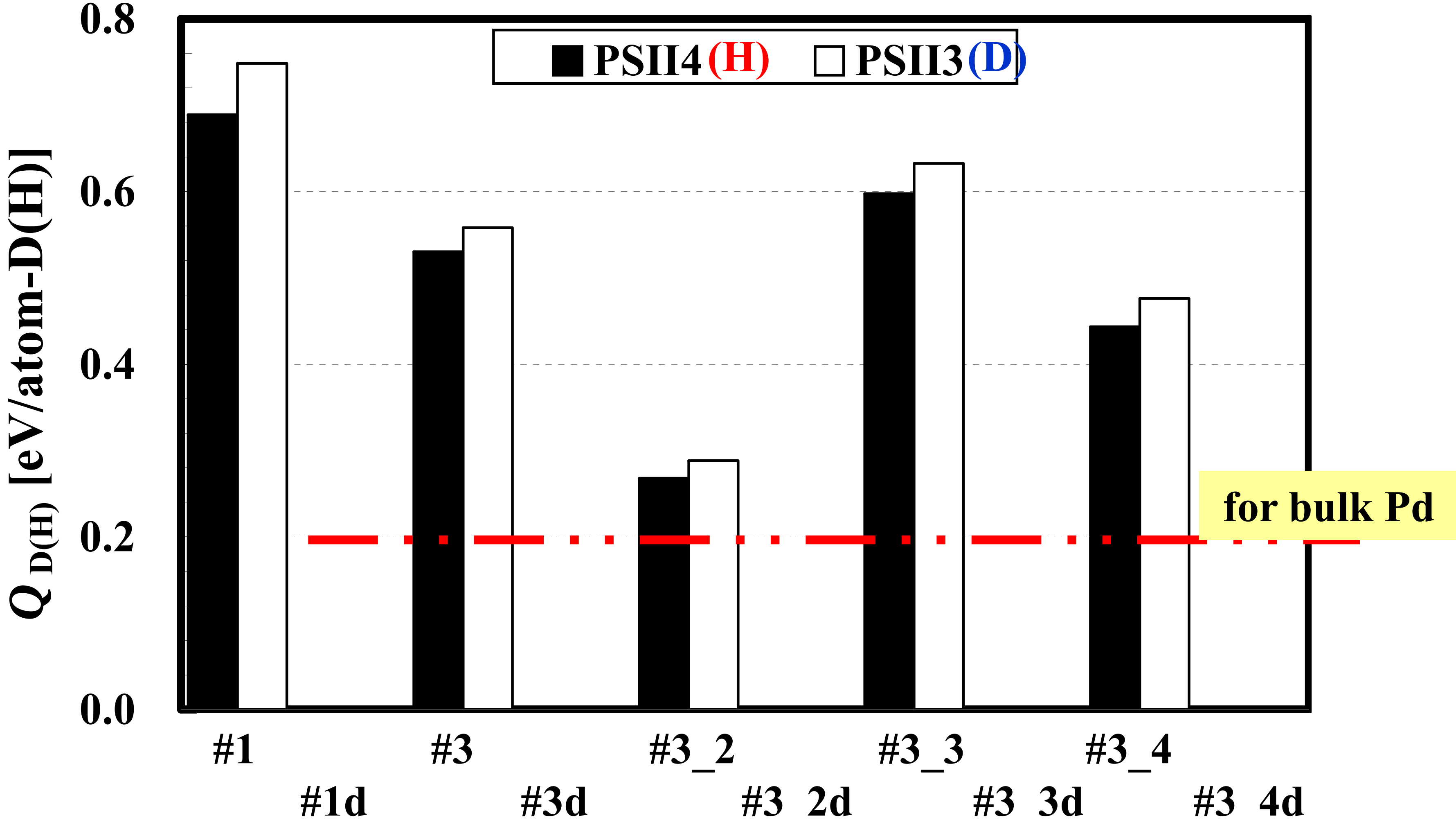


$$\mathrm{PdO}_x + (x + y/2)\cdot \mathrm{D_2(H_2)} \rightarrow x\cdot \mathrm{D_2O(H_2O)} + \mathrm{PdD}_y(\mathrm{PdH}_y)$$
$$+x\cdot Q_{\mathrm{R}} \qquad +y\cdot Q_{\mathrm{D(H)}}$$

Specific output energy $E_{\mathrm{1D(H)}} = xQ_{\mathrm{RD(H)}} + yQ_{\mathrm{D(H)}}$ [eV/atom-Pd]

Summary of the runs at R.T. (continued)

PNZ2B: 2-nmϕ [Pd(4%)Ni(29%)]Zr67%

(1) Differently from the Pd-based samples (PP, PB, PNZ and PS), both forced oxidization and deoxidization substantially recover the large values of the 1st-phase parameters.

(2) Condensation of $D(H)_2O$ is prominent in the initial stage. Water formation does, however, not contribute so much to the hydrogen isotope consumption nor the output energy.

(3) The loading ratio of D(H)/Pd·Ni exceeds 3, which indicates that hydrogen isotopes are absorbed by not only Pd but also Ni. Since Ni does not absorb hydrogen isotopes at room temperature, Pd is acting as a catalyst.

(4) The 1a/1b sub-phase transition is not apparent.

(5) The ratio of η_D/η_H is a little larger than 1.0.

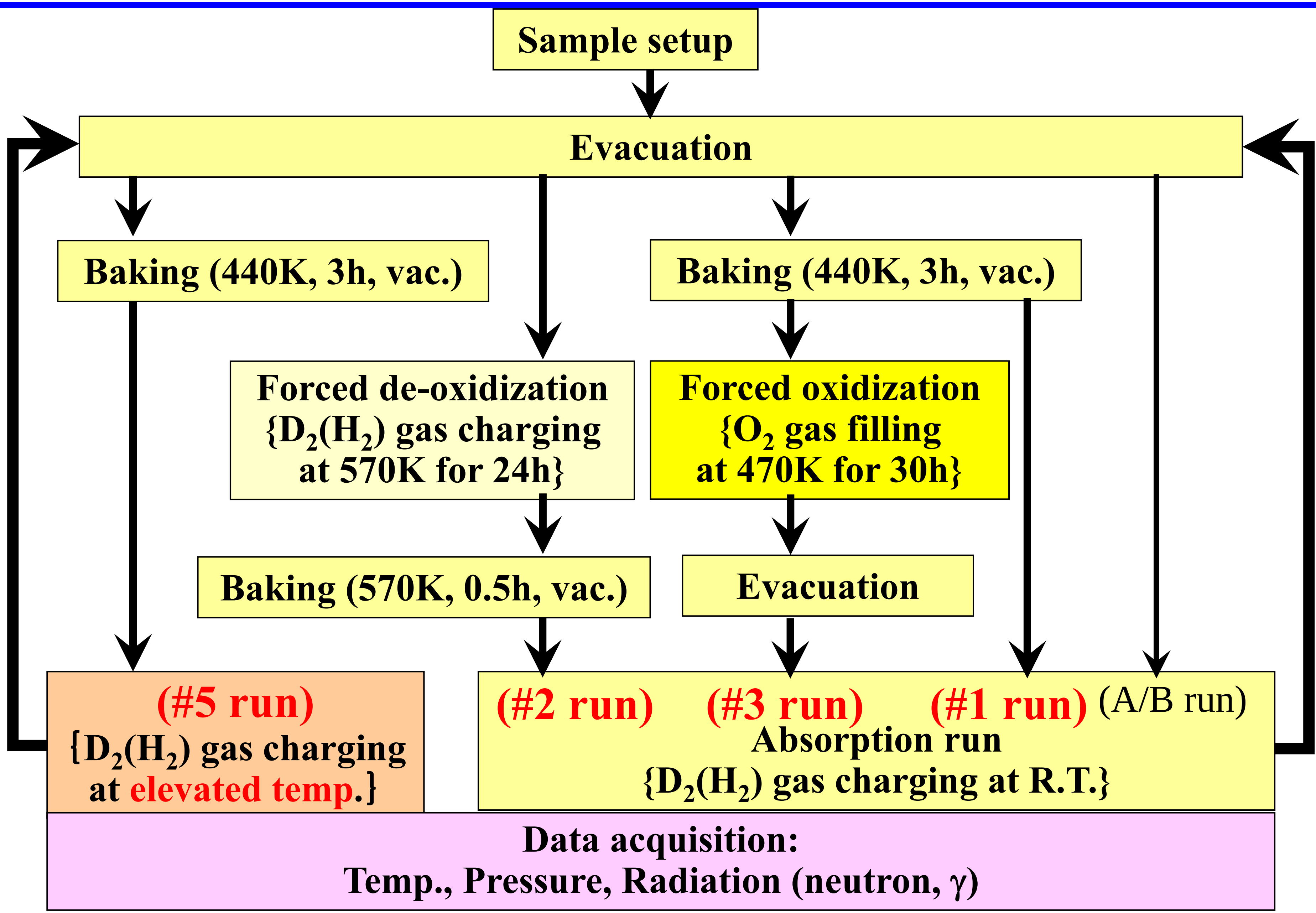
Nuclear diagnostics - Summary

- Gamma rays; NaI Scintillation Detector
- Neutrons; ^{3}He Doseratemeter
- High energy charged particles; Silicon Surface Barrier Detector,
  Ion Implanted Silicon Detector
- X-rays; Si-PIN Detector

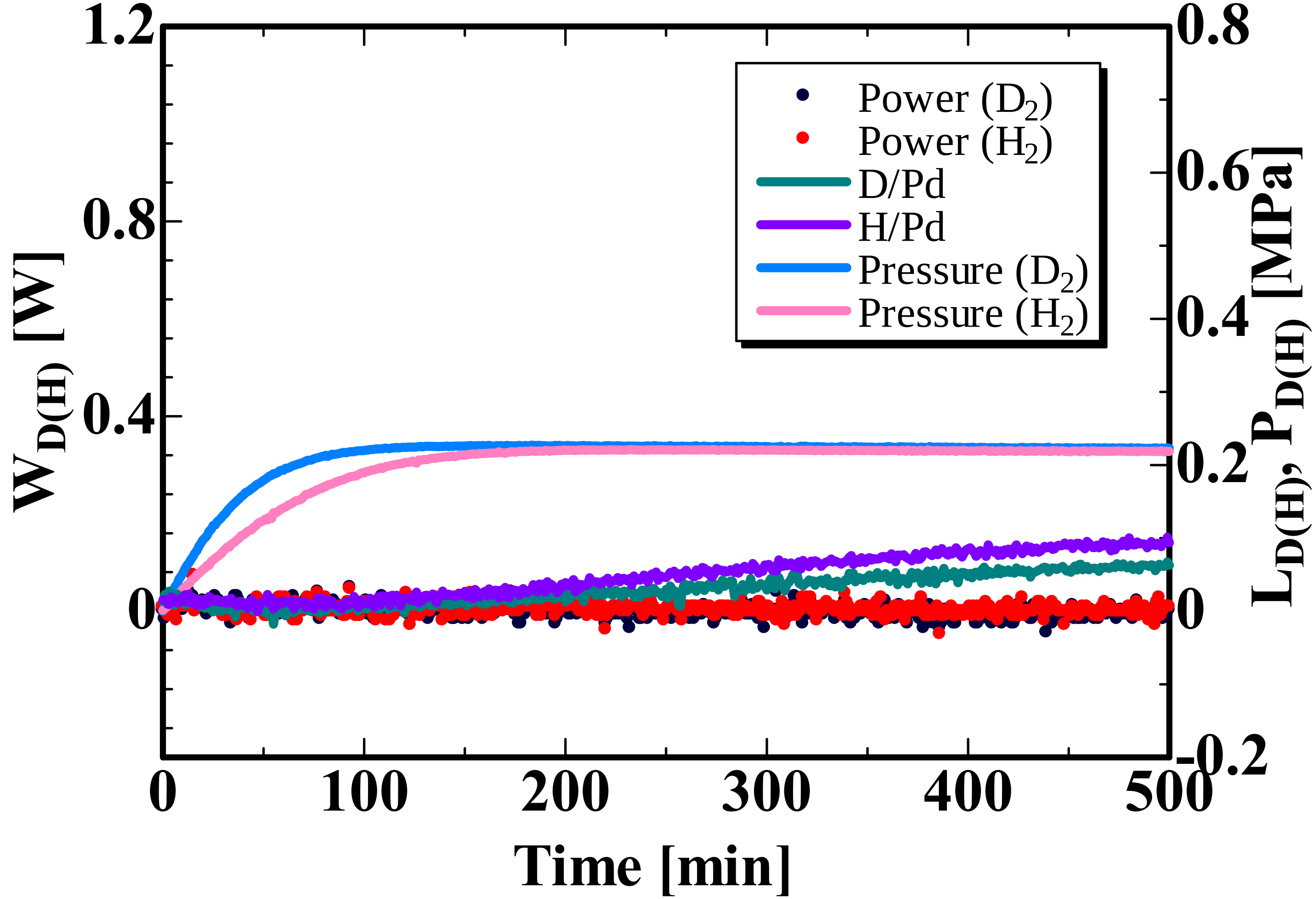
No reliable indication of nuclear reaction products up to now.

[5] J. Condensed Matter Nucl. Sci. 5 (2011) 48-57.

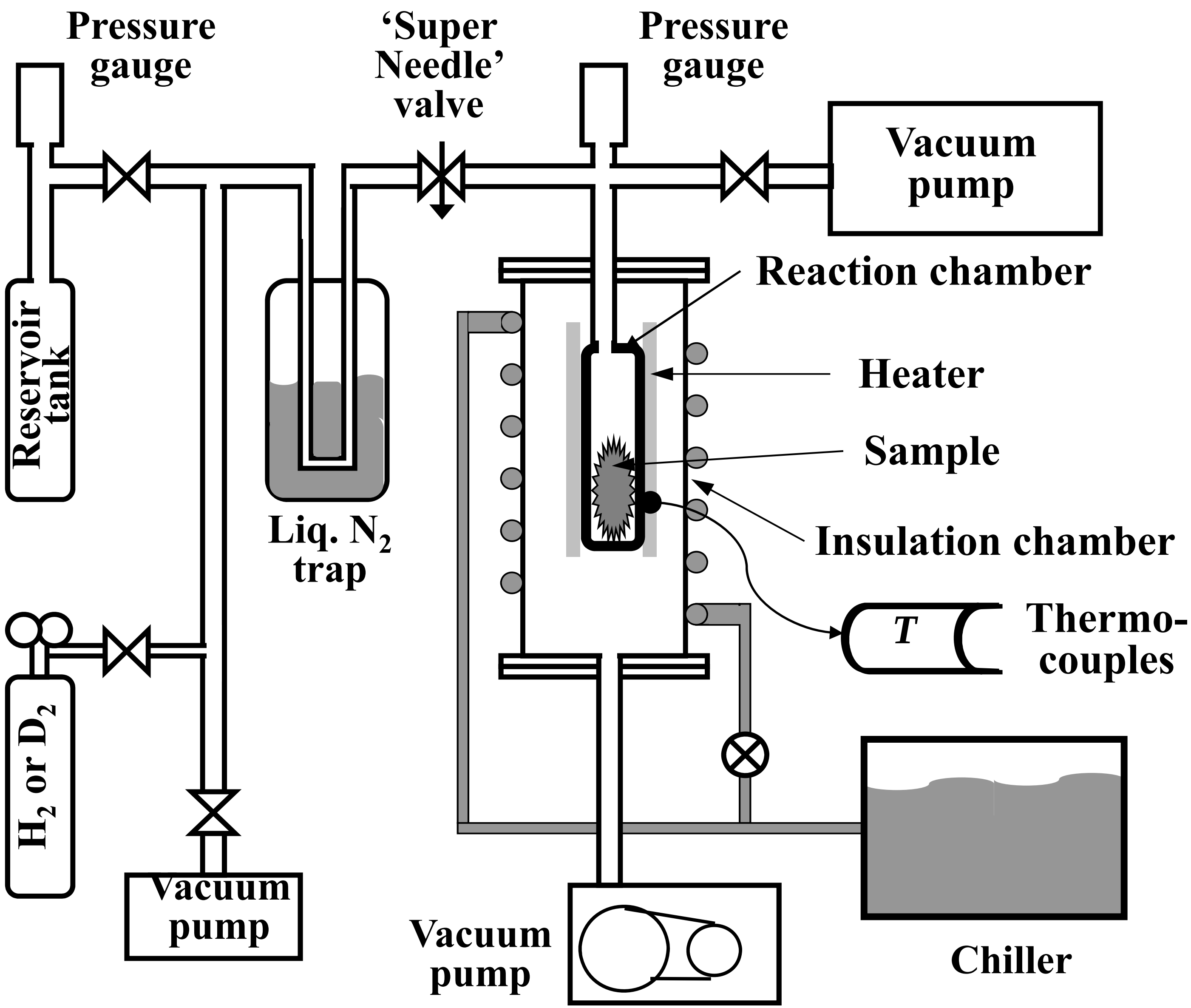
Experimental procedure



CNZI samples (Cu : 8%, Ni : 35%, Zr : 57%) absorb little amount of D(H) with very little heat output at R.T.



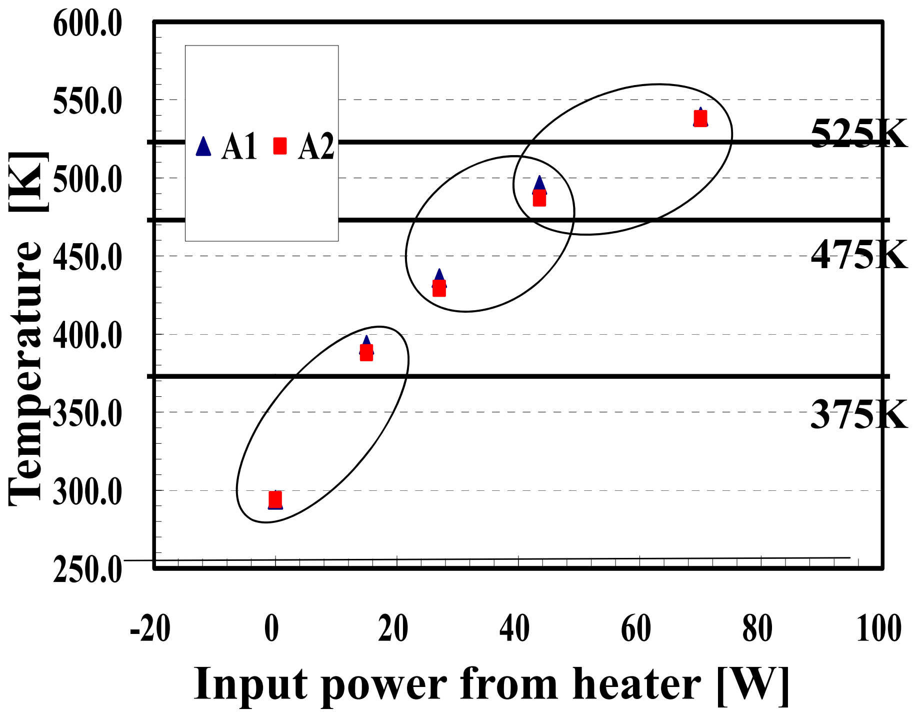
Arrangement for absorption runs using CNZI samples



Calibration

- Relation between the temperature of the reaction chamber and the heater input power.
- The differential $\Delta T/\Delta W$ is the slope of the line connecting the neighboring points, and is used to evaluated the output power.

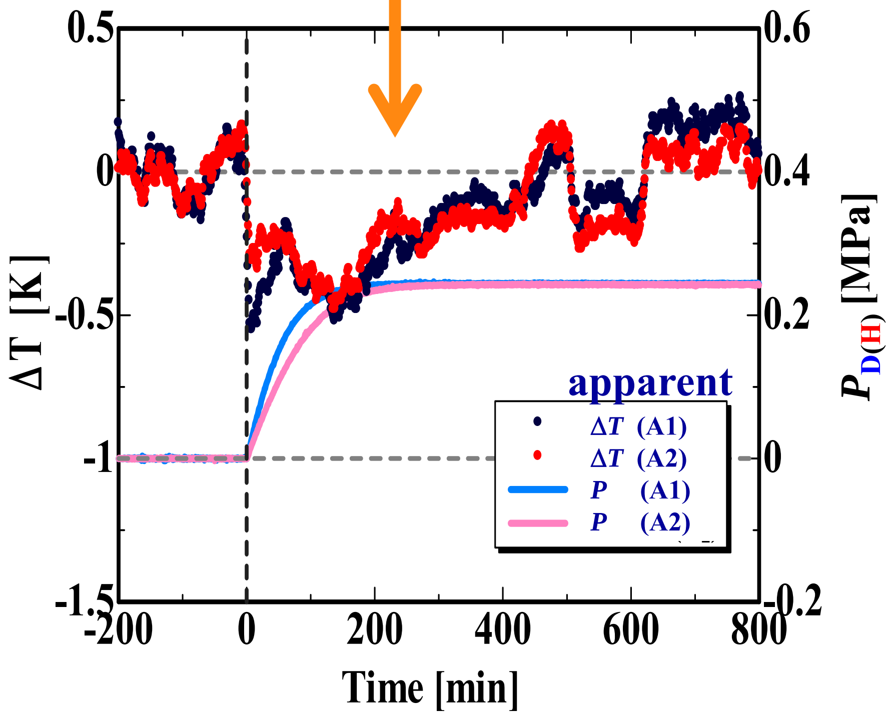
Input Power [W]	T [K]		$\Delta T/\Delta W$	
	A1	A2	A1	A2
0	294.2	294.2		
15	393.3	388.2	6.61	6.27
27	435.9	429.3	3.55	3.43
43.5	480.7	472.1	2.72	2.59
70	524.5	523.2	1.65	1.93
105	564.4	565.5	0.99	0.99

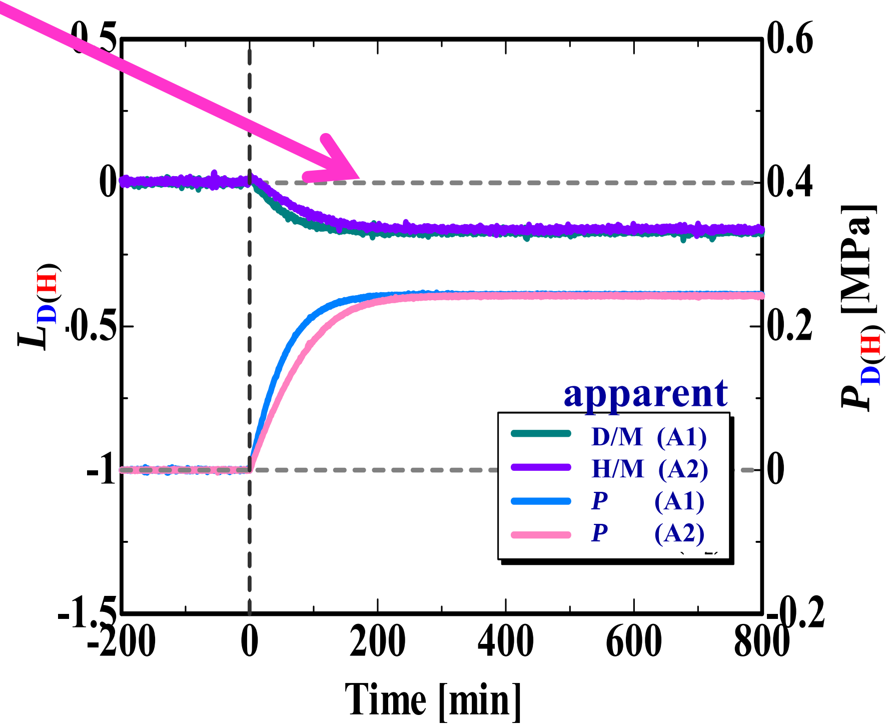


Blank runs for CNZI samples (Cu : 8%, Ni : 35%, Zr : 57%)

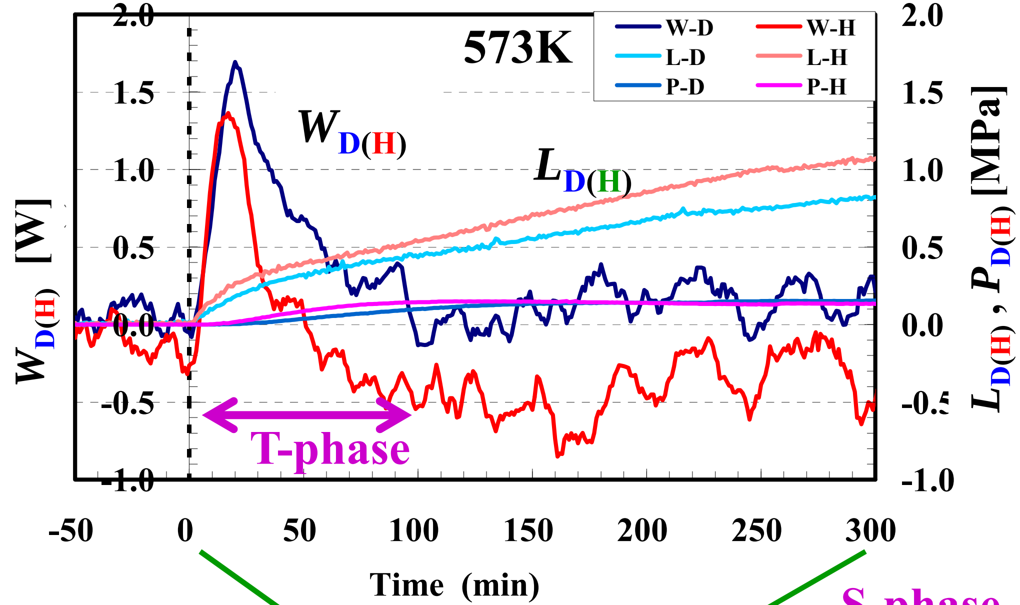
introducing He gas is necessary to correct for

- apparent temperature drop due to the introduction of the cool gas, and
- apparent negative absorption due to pressure increase by heating.

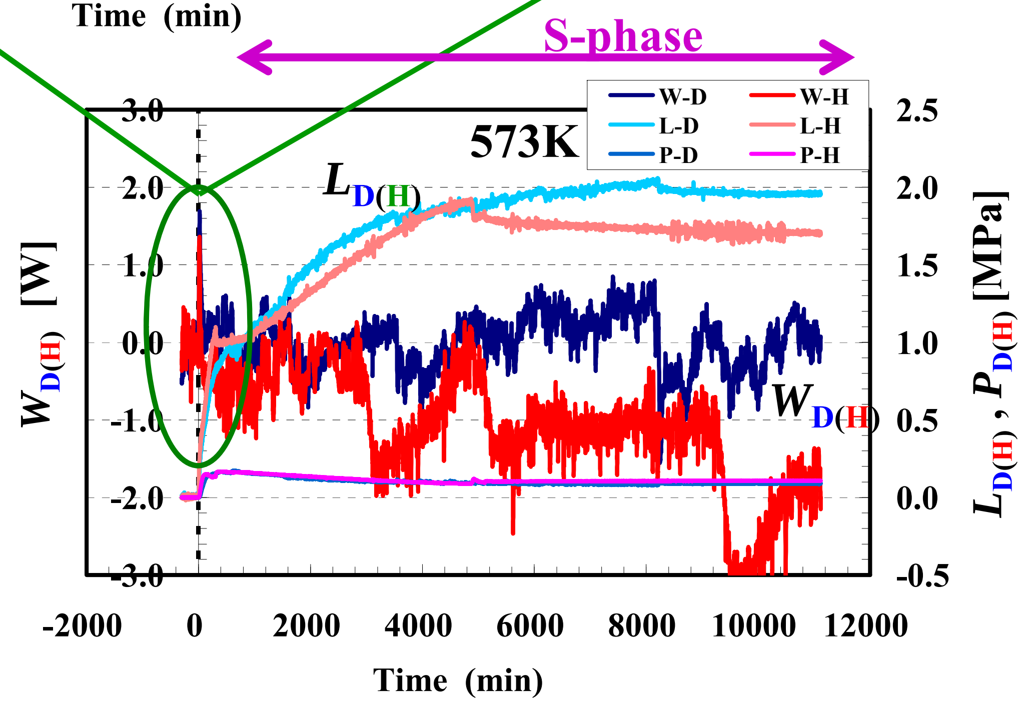




H(D)-CNZI3(4)#5_573K



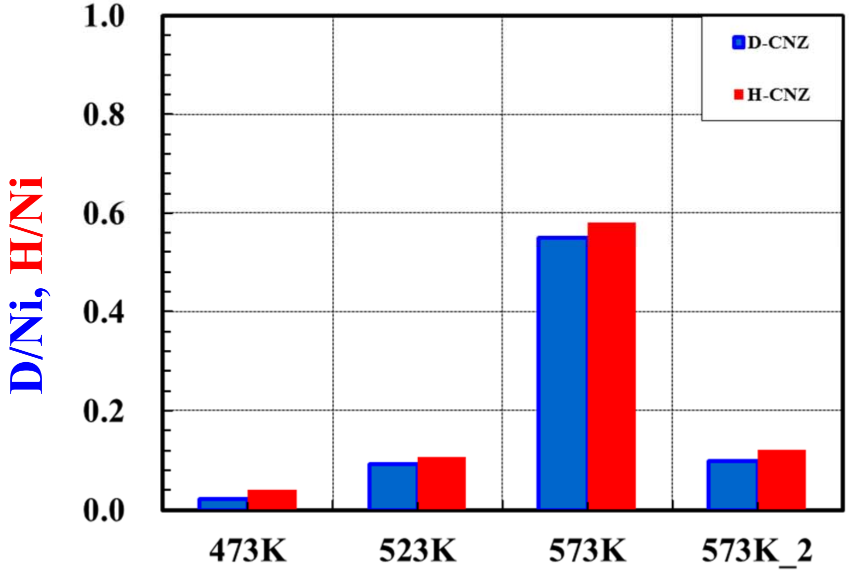
D(H)-CNZI3(4)#5_573K;
W_{in} = 69W

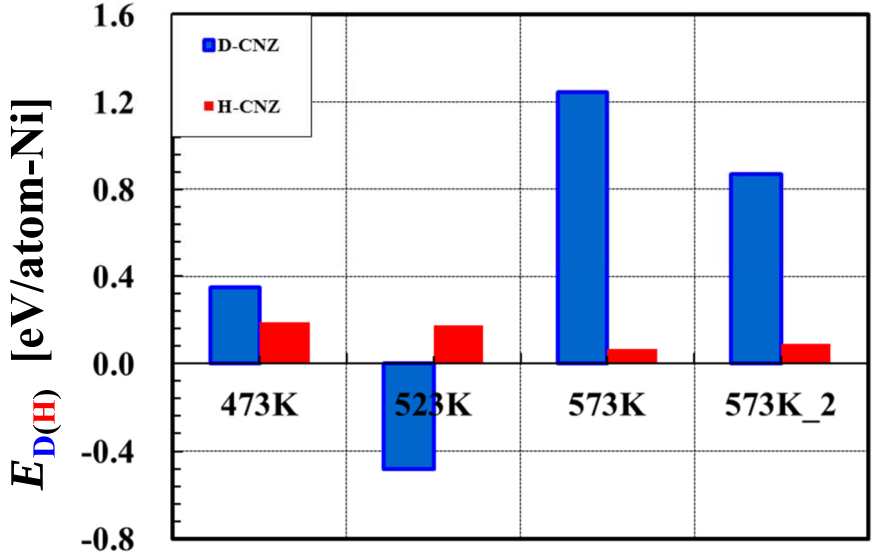


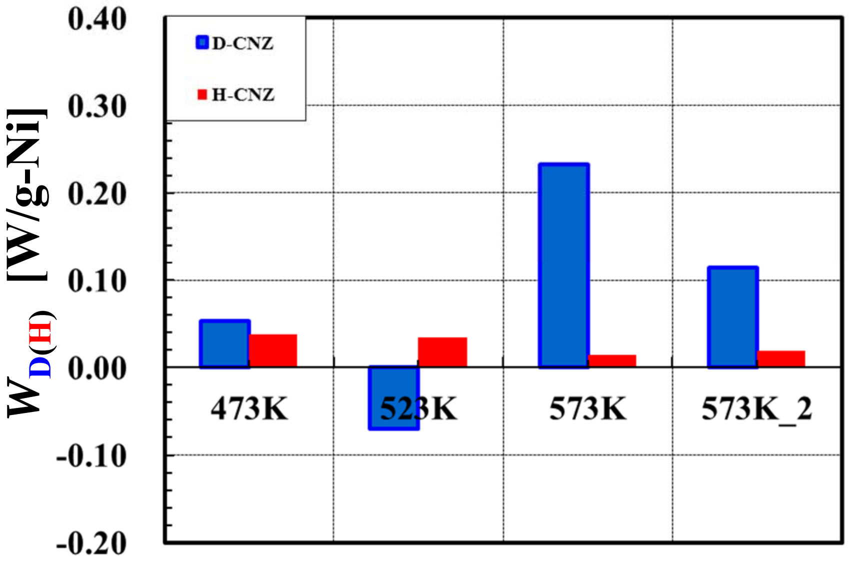
T-phase parameters of H(D)-CNZI3(4)#5_***K Runs

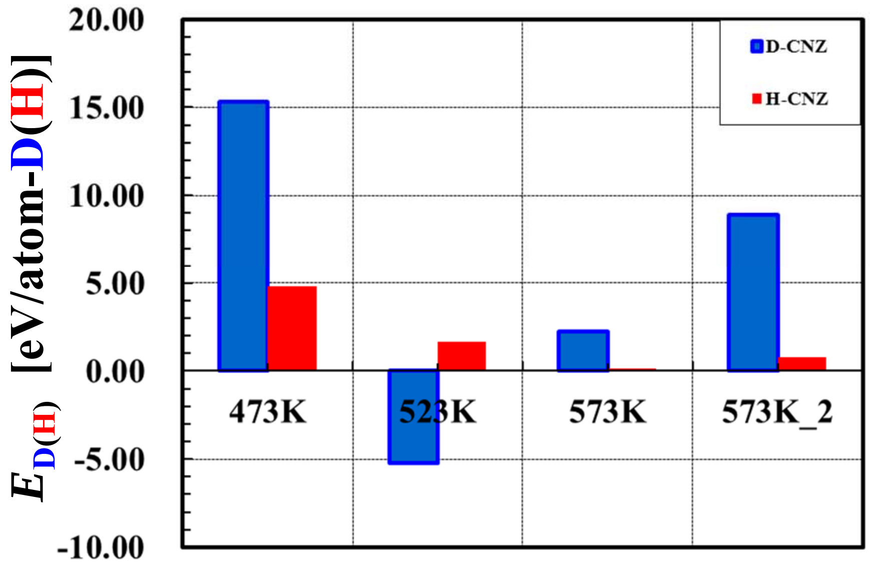
	A1	A1	A1	A1	A1	A1	
	KJ	KJ/g-Ni	KJ/g-Ni/h	W/g-Ni	eV/atom-M	H/M	time(min)
473K	0.58	0.29	0.14	0.04	0.19	0.04	125
523K	0.53	0.27	0.12	0.03	0.18	0.11	130
573K	0.21	0.10	0.05	0.01	0.07	0.58	116
573K_2	0.28	0.14	0.07	0.02	0.09	0.12	123
	A2	A2	A2	A2	A2	A2	
	KJ	KJ/g-Ni	KJ/g-Ni/h	W/g-Ni	eV/atom-M	D/M	time(min)
473K	1.06	0.53	0.19	0.05	0.35	0.02	165
523K	-1.46	-0.73	-0.25	-0.07	-0.48	0.09	175
573K	3.78	1.89	0.84	0.23	1.25	0.55	135
573K_2	2.636	1.32	0.41	0.11	0.87	0.1	193

T-phase parameters of H(D)-CNZI3(4)#5_***K Runs

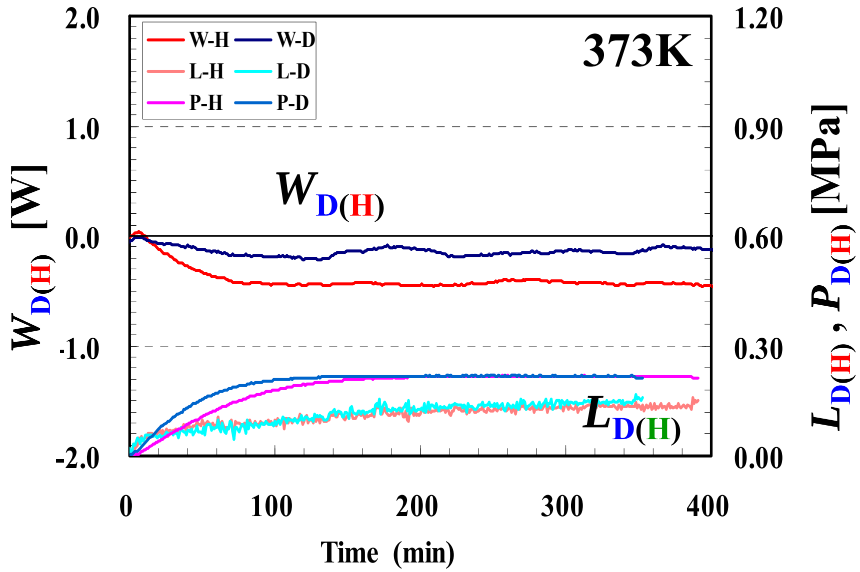




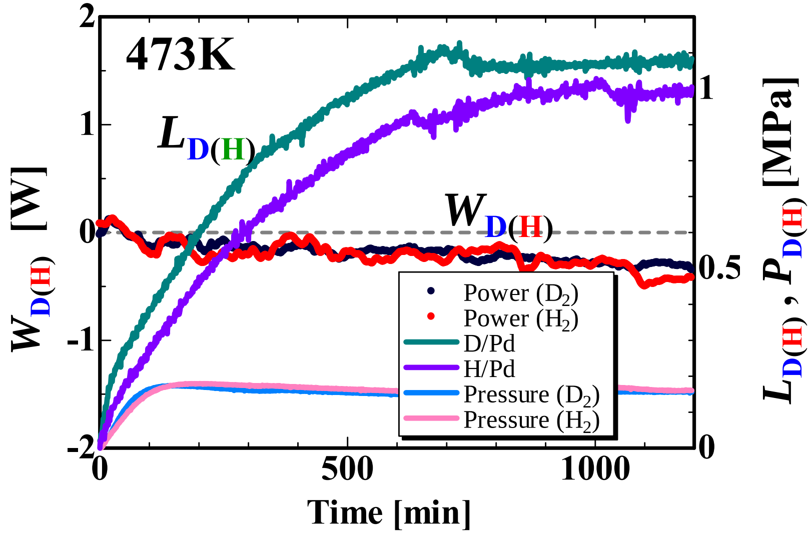




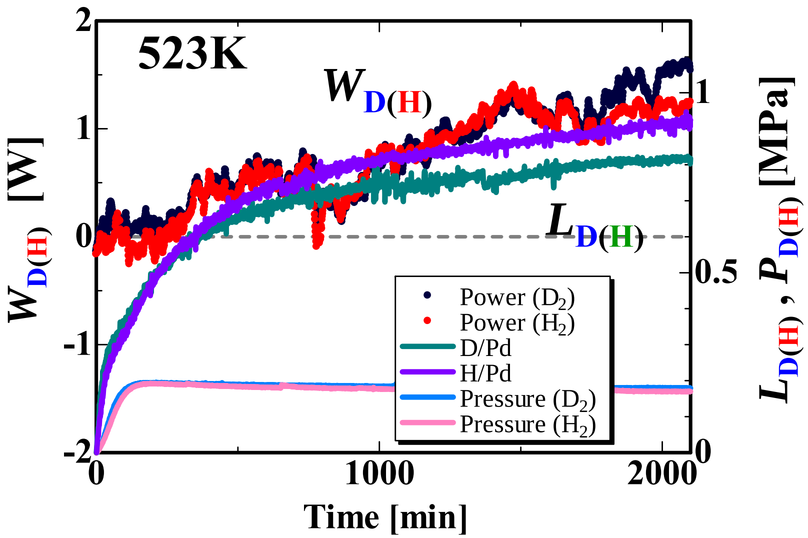
D(H)-CNZI1(2)#5_***K Runs



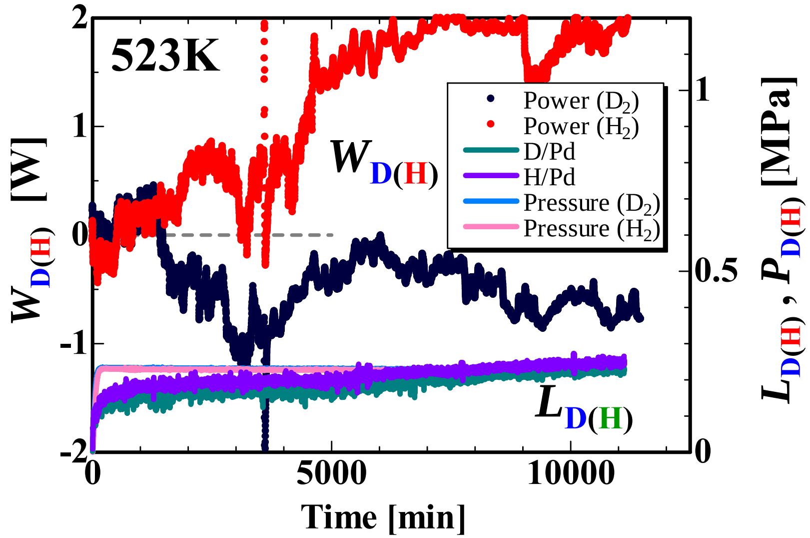
D(H)-CNZI1(2)#5_373K; W_{in} = 13W



D(H)-CNZI1(2)#5_473K; W_{in} = 42W

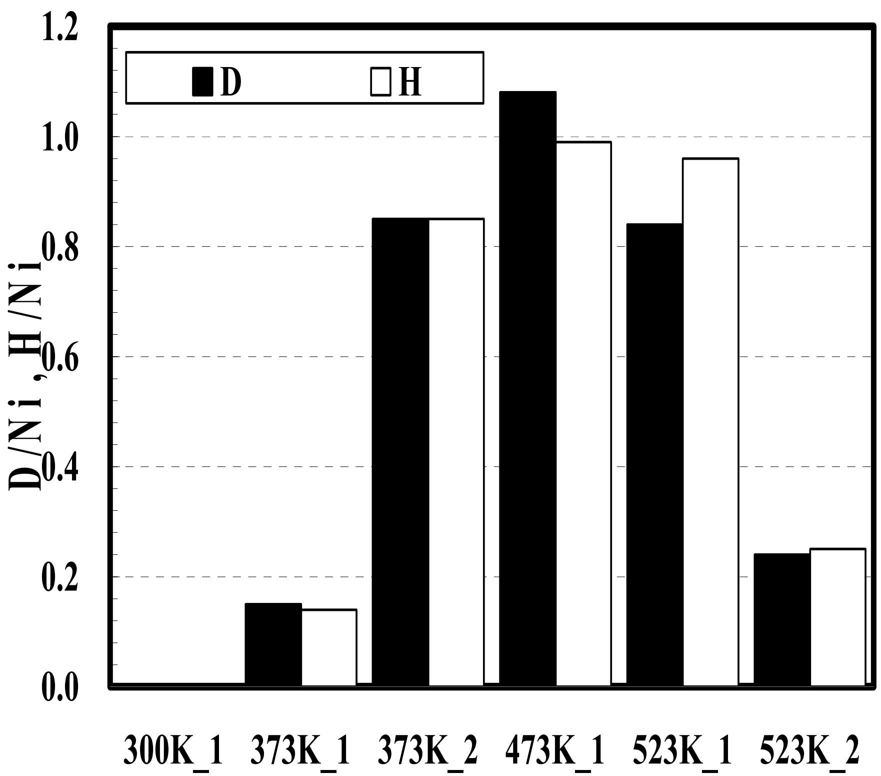


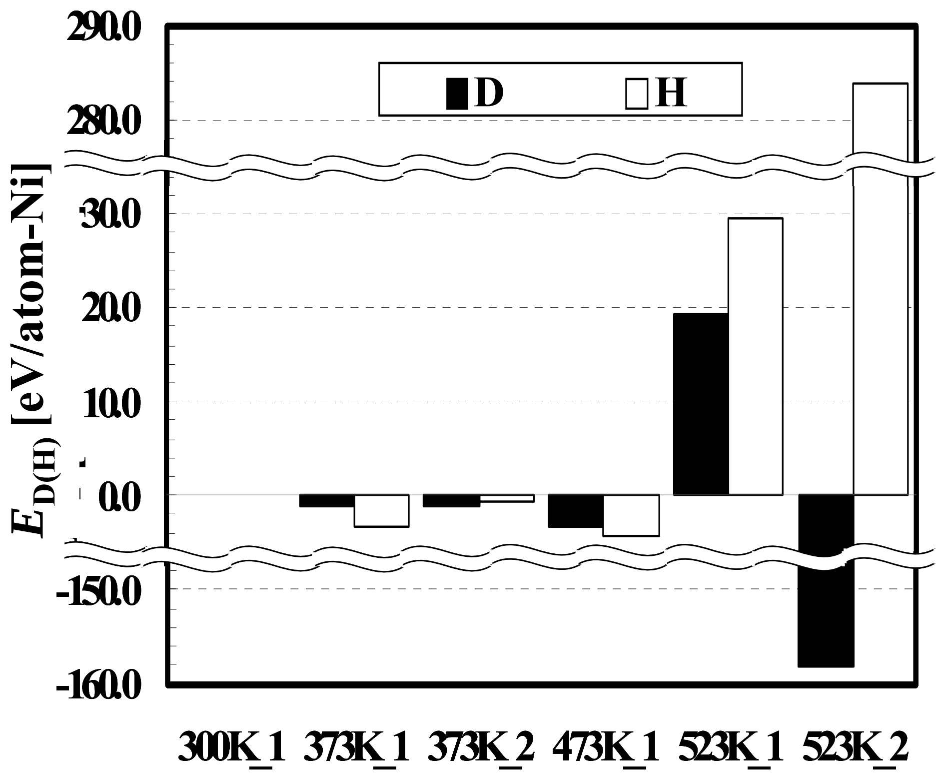
D(H)-CNZI1(2)#5_523K; W_{in} = 69W



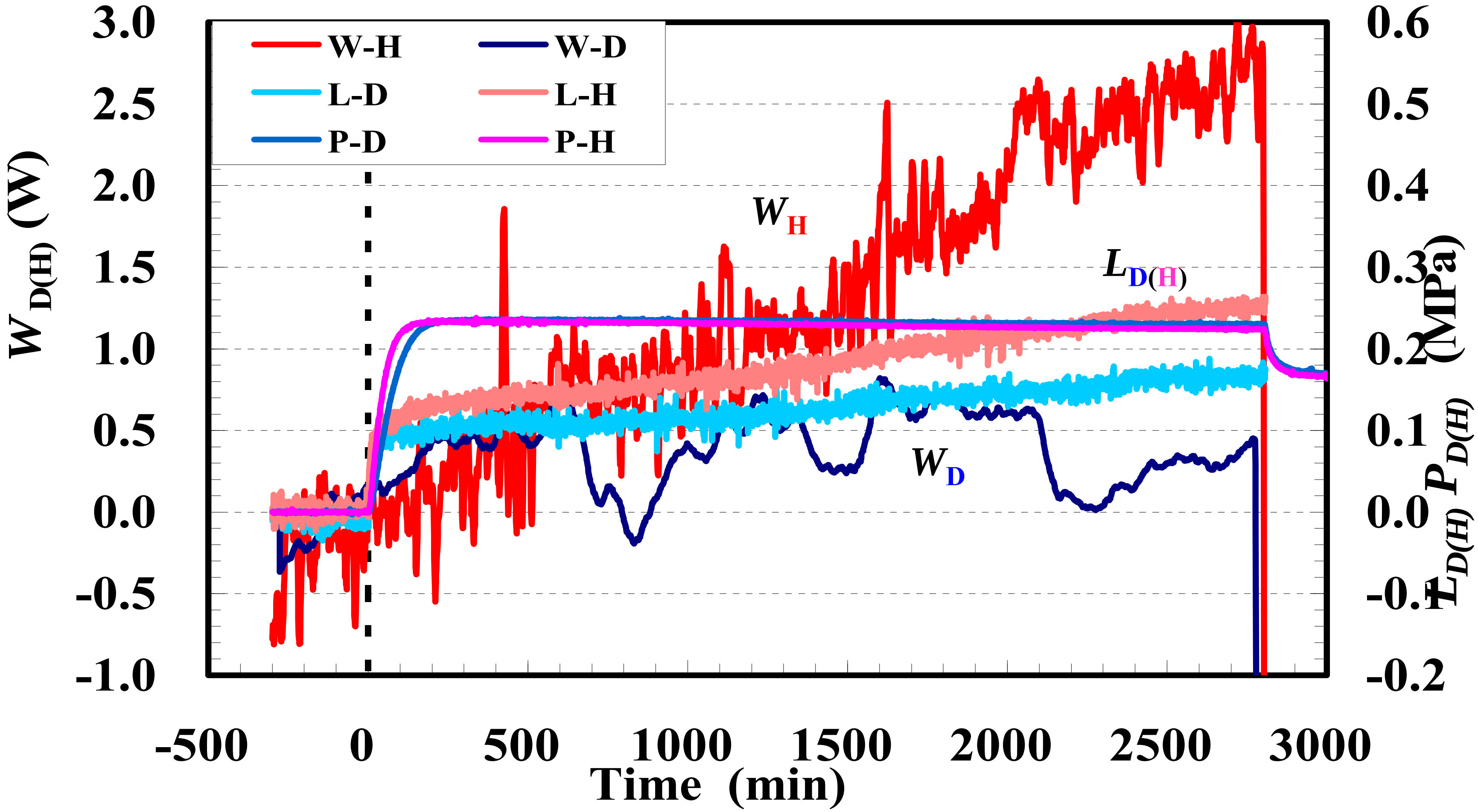
D(H)-CNZI1(2)#5_523K_2; W_{in} = 69W

S-phase parameters in the D(H)-CNZI1(2)#5_***K Runs





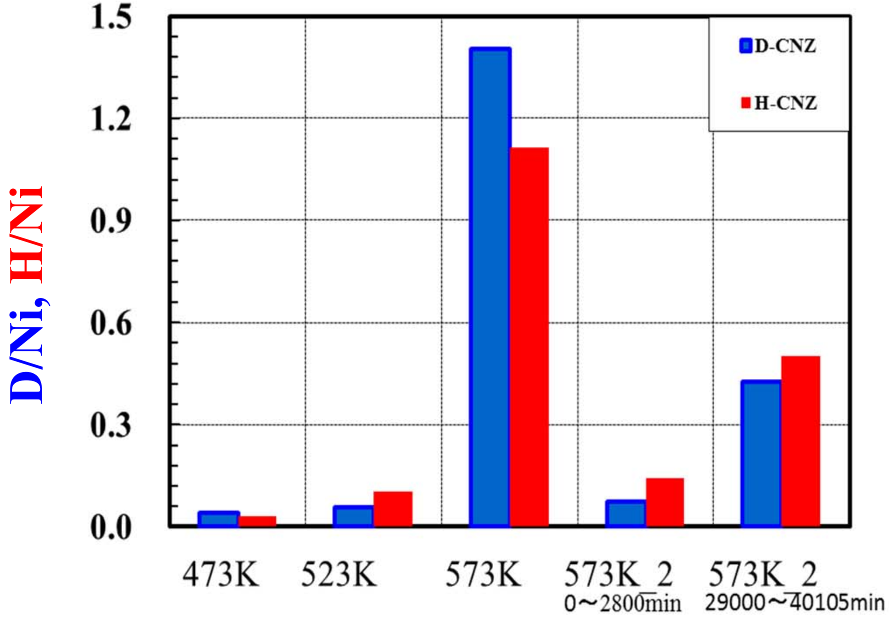
H(D)-CNZI3(4)#5_573K_2

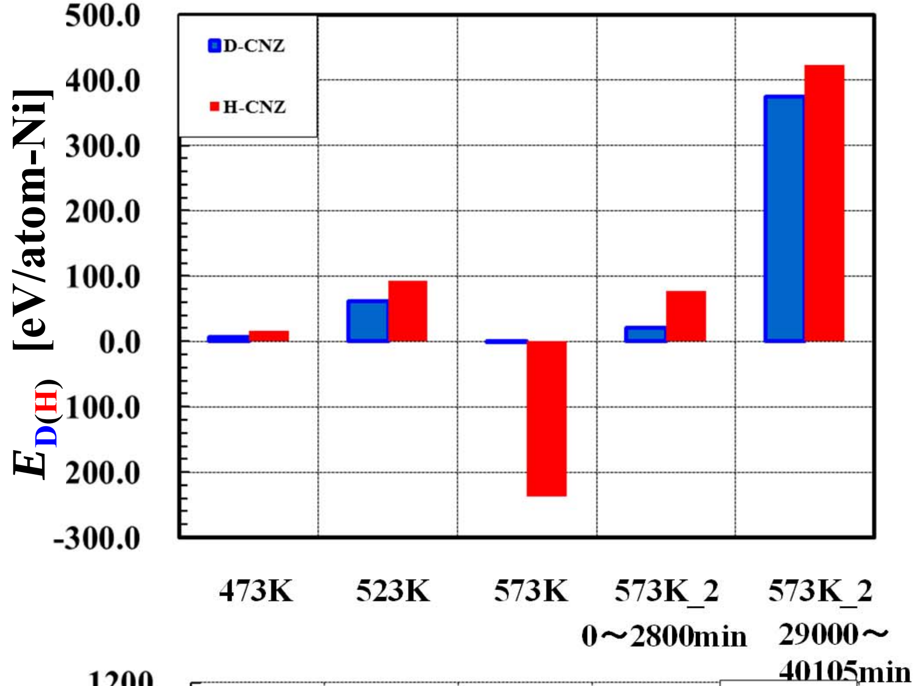


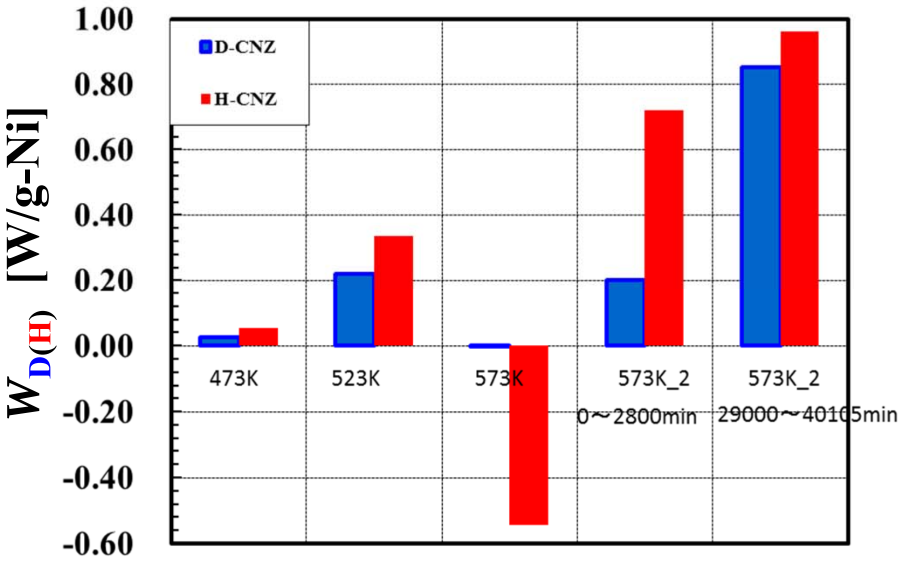
S-phase parameters of H(D)-CNZI3(4)#5_***K Runs

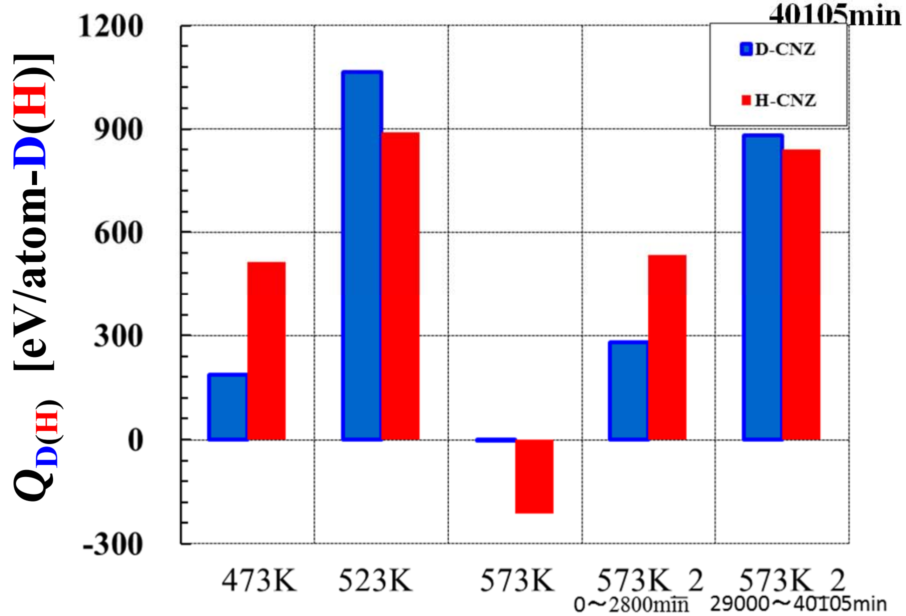
	A1	A1	A1	A1	A1	A1	
	KJ	KJ/g-Ni	KJ/g-Ni/h	W/g-Ni	eV/atom-M	H/M	time(min)
473K	46.98	23.50	0.20	0.06	15.50	0.03	7105
523K	283.27	141.68	1.20	0.33	93.47	0.10	7070
573K	-717.47	-358.84	-1.96	-0.54	-236.74	1.11	11004
573K_2	231.37	115.72	2.59	0.72	76.34	0.14	2677
573K_2 (29000～40105)	1280.44	640.41	3.46	0.96	422.50	0.50	11104
	A2	A2	A2	A2	A2	A2	
	KJ	KJ/g-Ni	KJ/g-Ni/h	W/g-Ni	eV/atom-M	D/M	time(min)
473K	22.34	11.17	0.09	0.03	7.37	0.04	7065
523K	184.22	92.14	0.79	0.22	60.79	0.06	7025
573K	-1.41	-0.71	0.00	0.00	-0.47	1.40	10985
573K_2	62.39	31.20	0.72	0.20	20.59	0.07	2607
573K_2 (29000～40105)	1136.54	568.43	3.07	0.85	375.02	0.43	11104

S-phase parameters of H(D)-CNZI3(4)#5_***K Runs









Summary of the CNZI runs at elevated temperature

CNZI: [Cu(8%)Ni(35%)]Zr(57%)

(1) Absorption of both D and H is possible at *T* > 370 K, and the loading ratio D/Ni (H/Ni) > 1 at *T* > 470 K.

(2) The endothermic tendency in the S-phase is observed both in D and H runs below 470 K.

(3) Above 500 K, while some runs remain endothermic, most runs show the exothermic tendency with a specific output energy reaching 400 eV/atom-Ni at an averaged power of 1 W/g-Ni.

(4) However, no conclusive evidence for the excess heat has been obtained at present.

(5) If this turns out to be a true exothermic phenomenon, it is suggested strongly that a nuclear process participates in the phenomenon.

(6) Calorimetry with increased amount of the powder at higher temperatures is in preparation.