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Abnormally high heat generation by transition metals interacting with hydrogen and oxygen molecules

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Abstract Abnormally high heats, exceeding 2000 kJ/mol (20 eV) per molecule of O_2, are generated by interaction of the oxygen with the hydrogen absorbed on palladium, gold and nickel particles at 25 °C to 220 °C. The highest heats were observed when the metals were treated with micromole quantities of argon, prior to absorption of hydrogen, as well as its interactions with metal particles reaching nanometer size. In the latter case the heat evolutions due to the interactions with hydrogen were approaching 5000 kJ/mol. The interactions with oxygen in inert gas environments, such as that of argon, yielded higher heat evolutions than those given by pure O_2 pulses injected into nitrogen carrier gas.

The results revealed an important role of argon in increasing the intensity of atomic hydrogen-oxygen reactions to a level several times higher than the heat of water formation from molecular hydrogen and oxygen.

Keywords Flowmicrocalorimetry · Heats of adsorption · Hydrogen absorption · Oxygen absorption · Hydrogen and oxygen absorption on palladium · Gold and nickel

1 Introduction

Recent flow microcalormetric work has shown that exposures of gold to hydrogen led to its dissociation and chemisorption of the resulting H atoms. The process was found to be strongly exothermic, especially when the exposures occurred in inert gases, such as He, Ar and nitrogen and intensified with decreasing size of the metal particles (Groszek et al. 2010). The absorbed H atoms could be slowly desorbed by any of the inert gases flowing through the metal powders, but importantly, the H atoms being displaced by the inert gases during the desorption process, interacted exceptionally strongly with small doses of molecular oxygen, producing abnormally high evolution of heat. This heat was much higher than that evolved during interactions of oxygen pulses with the chemisorbed hydrogen on metals immersed in hydrogen flows prior to its desorption by the inert carrier gases. (The term 'abnormally' high heat' means the heat that exceeds the heat of formation of water vapour from 1 molecule of oxygen and two molecules of hydrogen at room temperature.)

The high activity of the freshly displaced chemisorbed hydrogen from the metals by the inert carrier gases was also reported by Ceyer (2001) and Dus and Nowicka (1995), who found that hydrogenation activities of hydrogen strongly bound by Ni and Pd were much lower than the hydrogen freshly desorbed from the metals. The work reported recently by the author on the heats of interactions of hydrogen with the particles of pure Au and Pd powders and gold catalysts, confirms the Ceyer's conclusions.

A number of other transition metals, such as molybdenum, iron, platinum and cobalt, also absorb hydrogen, which reacts strongly with oxygen, but this is not recorded in this paper. Here I report work carried out with the precious metals and a pure nickel powder, aiming to evaluate the heat of their interaction with hydrogen and the effect of these interactions on the heat evolution produced during the subsequent interactions of the metals with oxygen. The effect of treatments of the metals with argon on their interactions with hydrogen and the following heat of interaction with oxygen was also investigated.

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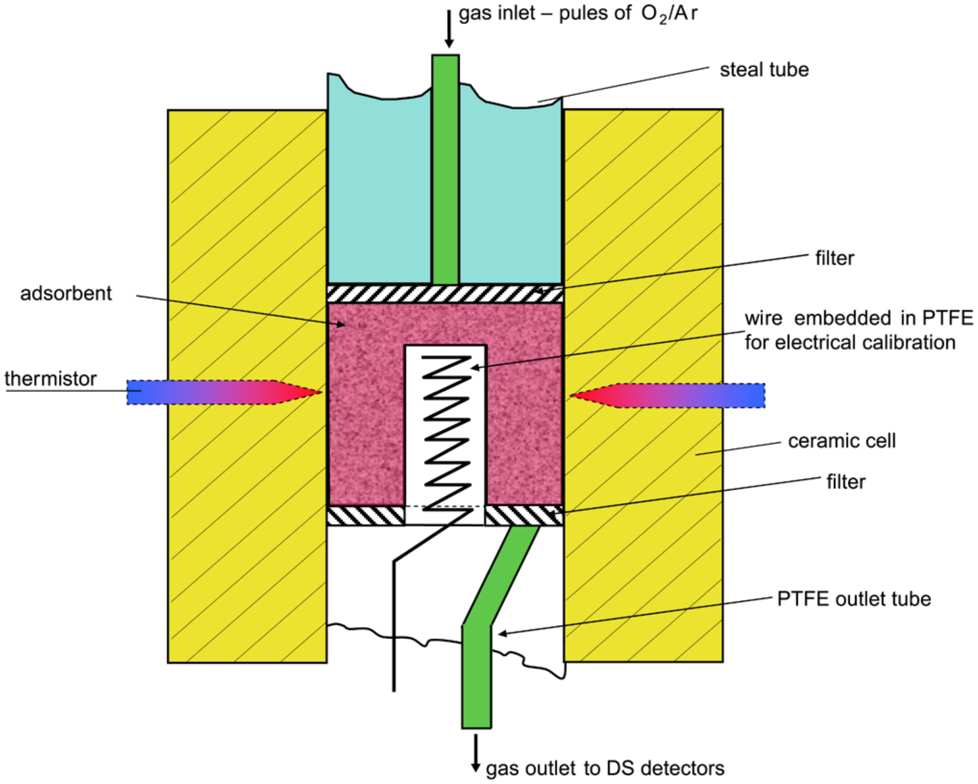
Fig. 1 Schematic representation of FMC cell



2 Experimental

Heat evolutions produced by the interactions of metal powders with hydrogen and oxygen were determined in Microscal flow-through microcalorimeter (FMC), model 4112, described previously (Groszek 1998). A sketch of the calorimetric system used in this work is shown in Fig. 1.

For irreversible interactions the inert gas effluent passing through a downstream detector (DSD), such as a thermal conductivity detector (TC), does not indicate the presence of the reactant, which is totally absorbed by the metal sample. Otherwise the detector indicates the presence of the reactants in the effluent in the form of peaks, the shape of which indicated the rate of their desorption by the carrier gas. Thus the amounts of the reactants taking part in the interaction are estimated from the response of the appropriate DSD detectors indicating complete or partial uptake of reactants by the metal samples. The heat effects were calibrated *in situ* by an electrical coil surrounded by the metal powder. The areas of the electrically produced heat peaks were proportional to the amounts of heat evolutions caused by the interactions of the reacting gases and the adsorbents residing in the calorimetric cell.

The carrier gases had a purity of 99.999 %, supplied by Sigma-Aldrich. For all experiments the carrier gas flows were set at 1 cc/min and the heat interactions determined isothermally at constant temperatures ranging from 25 °C to 220 °C.

3 Results and discussion

3.1 Interactions with palladium

Integral heats of interaction of hydrogen with the palladium powders were determined at room temperatures by exchanging the flow of nitrogen carrier, used for purging a Pd sample placed in FMC for 20 hours, by the flow of pure hydrogen lasting 1–2 hours until the cessation of heat evolution accompanying the absorption process. The integral heats obtained in this way agreed broadly with the values reported in the literature (20 kJ/mol corresponding to hydrogen uptake of 2.3–2.7 mmol per gram of Pd (Flanagan and Oates 1991)). A return to nitrogen flow produced slow desorption of the absorbed hydrogen.

There are some important differences in this respect depending on the nature of carrier gases involved in the desorption of the absorbed hydrogen and its reactivity with oxygen during the desorption process. This is illustrated by the results shown in Tables 1, 2 and 3, listing the molar heats of the interaction of oxygen with the desorbed hydrogen carried out in the atmospheres of argon, helium and nitrogen.

The results in this series of experiments were obtained on a 0.251 g sample of Pd powder treated with a dose of 20 micromoles of hydrogen (2.8 % of total H_2 absorption at 25 °C) injected into the flow of carrier gas. It was estimated from the response of the TC detector, that about 10 micromoles of the injected H_2 was absorbed before the start

Table 1 Influence of inert carrier gases on heats of interaction of oxygen with 0.251 g palladium powder containing chemisorbed hydrogen at 25 °C—argon carrier

Treatment of Pd	Heat evolution mJ	Molar heat of reaction kJ/mol O_2	Increase over heat of water formation
Interactions in *argon* carrier gas			
0.45 µmol O/Ar	1706	3791	×7.8
0.45 µmol O/Ar	1488	3306	×6.8
0.45 µmol O/Ar	1413	3140	×6.5

Table 2 Influence of inert carrier gases on heats of interaction of oxygen with 0.251 g palladium powder containing chemisorbed hydrogen at 25 °C—helium carrier

Treatment of Pd	Heat evolution mJ	Molar heat of reaction kJ/mol O_2	Increase over heat of water formation
Interactions in *helium* carrier gas			
0.45 µmol pure O	606	1347	×2.8
0.45 µmol pure O	619	1376	×2.8
0.45 µmol pure O	544	1209	×2.5

Table 3 Influence of inert carrier gases on heats of interaction of oxygen with 0.251 g palladium powder containing chemisorbed hydrogen at 25 °C—nitrogen carrier

Treatment of Pd	Heat evolution mJ	Molar heat of reaction kJ/mol O_2	Increase over heat of water formation
Interactions in *nitrogen* carrier gas			
0.45 µmol pure O	666	1480	×3.1
0.45 µmol pure O	675	1500	×3.1
0.45 µmol pure O	530	1400	×2.9

of its desorption by the carrier gas. The heat of absorption of this dose of H_2 from the argon carrier was estimated to be 91 kJ/mol. Similar heats of absorption of the H_2 doses were obtained for nitrogen and helium carriers. Following the start of desorption of hydrogen by argon, injection of 3 consecutive 0.45 micromole pulses of oxygen, in the form of 1 % mixture in argon, produced the highest heat evolutions exceeding the heat of water formation by factors ranging from 6.5 to 7.8. However the same injections of pure oxygen produced much lower heat evolutions, but still exceeding the heat of formation of water by factors ranging from 2.8 to 3.1. It is clear that the gaseous environment, in which the interaction of hydrogen and oxygen took place, had a strong influence on the magnitude of heat generation. Similarly lower heat generations were obtained when the gas carriers, in which the interactions occurred, on the same sample of Pd, were nitrogen and helium.

The environment in which the interaction of O_2 takes place contains primarily a carrier gas desorbing gradually diminishing amounts of hydrogen. It is estimated that the concentration of activated hydrogen in the carrier gas, before the arrival of the 0.45 µmol of O_2 pulses, was about 0.5 %–1.0 % vol. The interaction of this freshly desorbed hydrogen with the oxygen pulses produced the high heat evolutions observed in this work. However it is believed that the pulses of oxygen injected into the carrier gas passing through the metal sample containing absorbed hydrogen atoms, dissociates the oxygen molecules, which then combine with the freshly desorbed active hydrogen, contributing to the production of the observed intense evolution of heat. An example of such a process is illustrated in Fig. 2 showing heat evolution peak occurring when a 10 micromole pulse of hydrogen reacts with a 60 mg catalyst containing 5 % Pd deposited on active carbon generating a heat effect of 602 mJ (60.2 kJ/mol), followed by the desorption with nitrogen carrier for 13 minutes and then exposed to a 0.45 micromole pulse of oxygen mixed with argon. The heat evolution in this case was 3173 kJ/mol of oxygen, exceeding the heat of water formation by a factor of 6.5. It should be noted that the heat of interaction with 10 micromoles of hydrogen was much smaller than that produced by the subsequent interaction of the catalyst with as little as 0.45 micromoles of oxygen.

3.2 Interactions with metallic gold and gold catalysts

Similar results were obtained with a metallic gold powder having a surface area of 0.27 m^2/g, but in this case the gold sample activated with several doses of argon produced relatively high heats of H_2 absorption comparable to those observed during the interaction of Pd with H_2, but with a much lower H_2 uptake (Groszek et al. 2010). More recently hydrogen adsorption studies on the same sample of gold were carried out at 125 °C The heat of absorption of hydrogen at this temperature in the atmosphere of nitrogen was found to be 462 mJ evolved in 50 minutes, with the estimated H_2 uptake of 9.3 micromoles, the molar heat of the interaction being 49.7 kJ/mol.

Further work was carried out at 125 °C with 1%Au/TiO_2 catalyst kindly supplied by Prof. M. Scurrell. Two pulses of oxygen into nitrogen carrying desorbed hydrogen, produced heat effects equivalent to heat generation of 862 kJ/mol and 811 kJ/mol. Exposure of this catalyst for 60 minutes to pure hydrogen flow at 125 °C produced heat evolution of 2405 mJ. On exposure to a 20 micromole of hydrogen, the heat evolution was 120 kJ/mol. Subsequent pulses of oxygen injected into nitrogen flow displacing the chemisorbed hydrogen produced heat effects ranging from 1493 kJ/mol

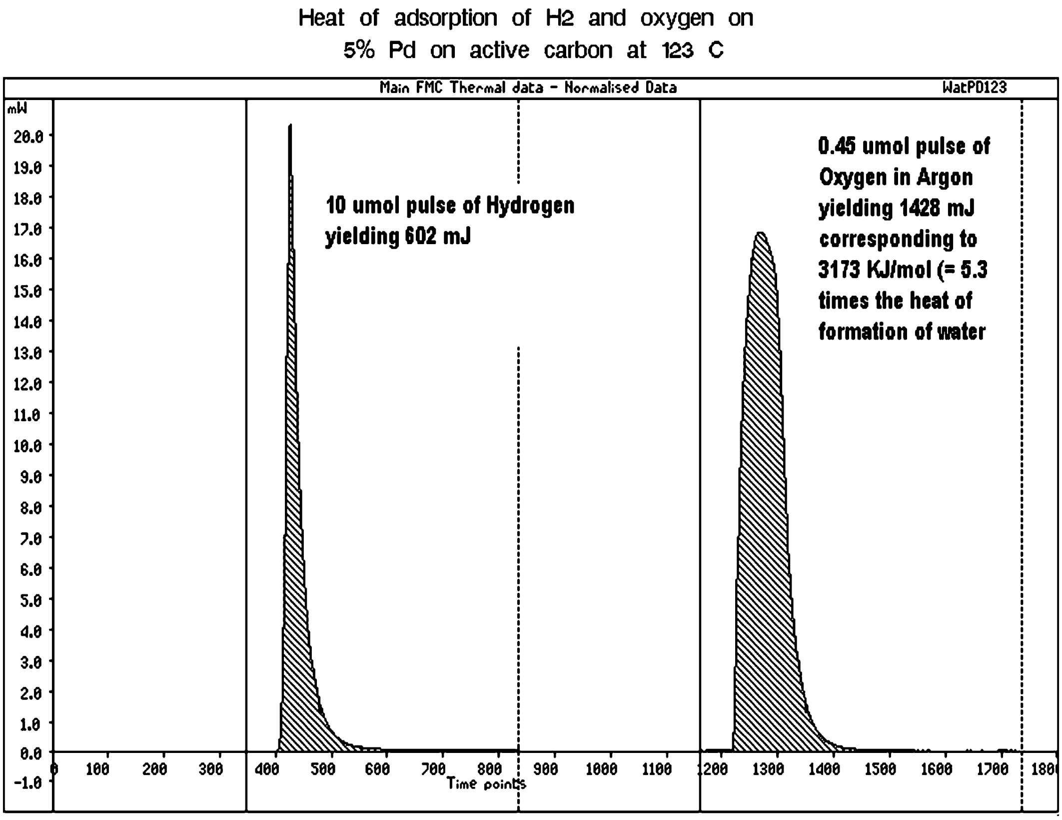


Fig. 2 Heats of adsorption of hydrogen and oxygen on 5 % Pd on active carbon at 123 °C

to 1798 kJ/mol being greater than the heat of water formation by factors 3.1 and 3.7 respectively (Groszek and Lalik 2011).

Additional work was carried out on the gold catalyst prepared by H.H. Kung et al. containing 7 % Au/Rutile catalyst (Yang et al. 2005). Exposure of this catalyst to hydrogen revealed a delayed hydrogen uptake associated with high heat evolution confirming the microcalorimetric results shown in the above paper. Sequential pulses of H_2 injected into argon carrier passing through 0.1 g sample of the catalyst at 25 °C produced gradually increasing heat evolutions reaching a value of 1740 kJ/mol of H_2, when its uptake rose to 30.5 micromoles and then dropped to 355 kJ/mol for the H_2 uptake of 39.8 micromoles. The heat values after the first injection produced heat evolutions considerably higher than the heat of water vapour formation exceeding the latter heat by a factor of 7.2. The hydrogen absorption by the catalyst at 125 °C also produced high heat evolutions associated with relatively low hydrogen uptake. The integral heat of H absorption in this case was 603 kJ/mol for the H_2 uptake of 25.5 micromoles. Desorption of hydrogen by nitrogen carrier gas was, however, still taking place at 25 °C and at 125 °C. The following interactions of oxygen pulses with the desorbed hydrogen produced considerably higher heat evolutions than those observed for the 1 % $AuTiO_2$ described above. This is shown in Fig. 3 by two 0.45 micromole pulses of O_2 interacting at 127 °C with hydrogen, producing heat effects of 4569 kJ/mol and 4776 kJ/mol of O_2, exceeding the heat of water formation by factors 9.4 and 9.9 respectively.

3.3 Interactions with nickel

Nickel is another transition metal well known for its affinity for hydrogen, which is widely used in hydrogenation treatment. More recently there have been several publications reporting generation of abnormally high heat by hydrogen interactions with fine Ni particles. The work in this area was recently reviewed by Focardi et al. (1998) and Celani (2012). The results obtained in this work indicate and confirm that significant hydrogen absorption takes place on pure nickel powders starting at about 150 °C. At 180 °C the heat evolution following the chemisorption of H_2 in the environment of nitrogen flow produces heat evolution of 14,879 mJ on 0.337 g of the Ni powder associated with the uptake of 395 micromoles of hydrogen during 2500 seconds. The molar heat of hydrogen adsorption in this process is therefore 39.7 kJ/mol. On switching the flow of N_2 to hydrogen and exposing the sample of Ni to 0.45 micromoles of O_2 (1 cc

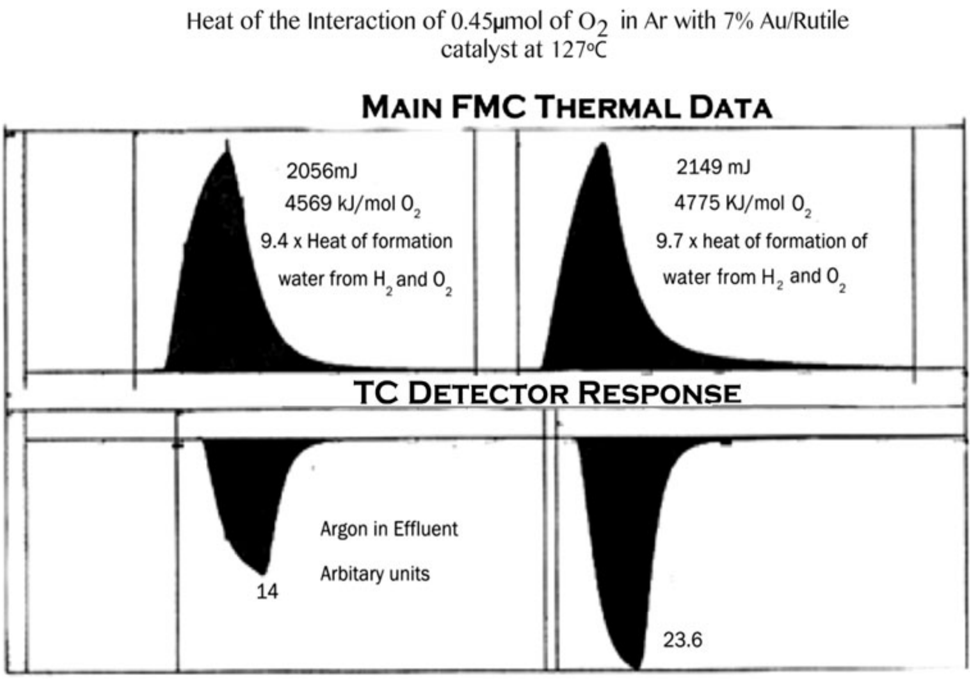


Fig. 3 Heats of the interaction of 0.45 micromoles of oxygen with 7 % Au/Rutile catalyst at 127 °C

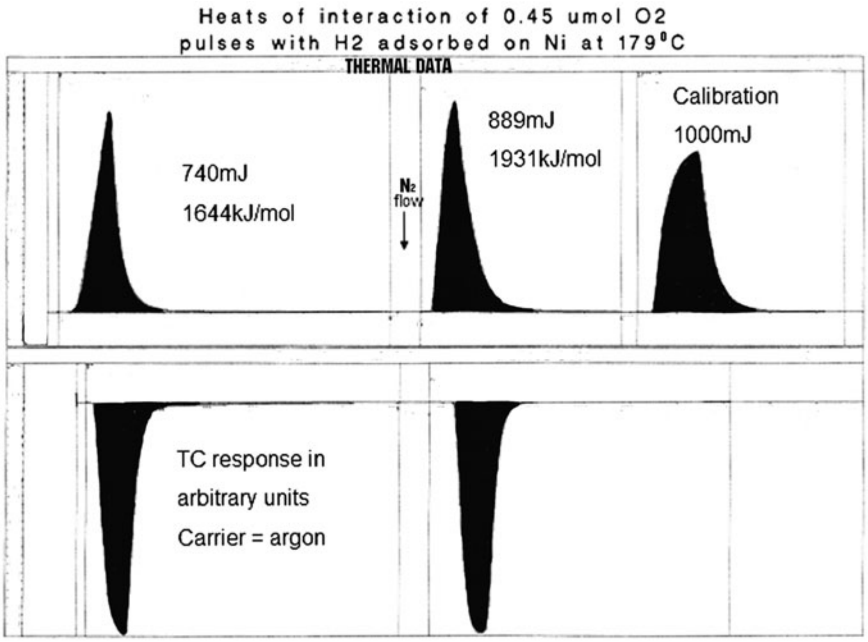


Fig. 4 Heats of interaction of 0.45 micromoles of oxygen with hydrogen adsorbed on Ni powder at 179 °C

1 % O_2 in Ar) a sharp heat evolution of 740 mJ takes place corresponding to 1644 kJ/mol of O_2, as shown in Fig. 4. A second 0.45 μmol pulse of O_2 produced even greater heat evolution of 1931 kJ/mol of O_2. However the third pulse produced only a heat effect of 136 kJ/mol indicating that the most active hydrogen atoms have been consumed by interaction with approximately 1 micromole of oxygen. Subsequent treatment of the Ni sample restored its high reactivity with oxygen pulses, which again subsided after consumption of another 1 micromole of oxygen.

A radical increase in the activity of Ni is achieved by increasing its surface area, a fact well known in catalysis. An example of such improvement is a fine dispersion of 1 % Ni on iron nano-flakes described recently by the author (Groszek 2007). In this case a 20 mg dispersion of 1 % Ni/Fe flakes produced several heat effects on interaction with 0.45 μmol pulses of oxygen, exceeding the heat of formation of water vapour by 10 times. Clearly the reduction of particle dimensions and the corresponding increase in surface area exerts a strong influence on the amount of the high heat generation per unit mass of the Ni in the sample. The situation here is similar to what was found for palladium and gold, albeit at a much lower temperature, than that required for the interaction of Ni/Fe particles with hydrogen requiring the temperature exceeding 210 °C .

It is not possible to be certain at present why the heats of the interaction of the freshly desorbed hydrogen from palladium, gold, nickel and probably, several other transition metals, produce heat evolutions on reaction with oxygen, exceeding greatly the heat of water formation. The desorbed hydrogen diluted with the carrier gas may, at least partly, exist in the form of atoms or protons. The oxygen molecules injected into the carrier gas pass through the metal sample containing the residual absorbed hydrogen, which is believed to cause dissociation of the oxygen molecules into atoms, which, in turn, could rapidly interact with the hydrogen atoms desorbed by the inert carrier gases. In this event the reaction between H and O atoms would release much higher heat than that produced by the formation of water from hydrogen and oxygen molecules, which is 242 kJ/mol (Handbook of Chemistry and Physics 1975).

It is important to note that the abnormally high heats of the interaction of oxygen with the metal hydrides examined n this work resulted in its complete absorption with no indication of appearance of water during desorption with nitrogen.

It is obvious that an explanation is required for the exceptionally high heat evolutions occurring during interactions between oxygen and hydrogen activated by exposure to the metals capable of absorbing hydrogen examined in this work, which revealed the production of heat generations exceeding 20 eV reported in this paper. There is a possibility that such high heats could be produced by hydrogen atoms involved in a low energy nuclear process (LNER) proposed by the Widom-Larsen theory and discussed recently at a CERN colloquium at Geneva (Institute of Science in Society 2008). This theory postulates formation of neutrons during interaction of protons with heavy electrons existing within ionised sites on the surface of metal hydrides (plasmons), on which collective high frequency oscillations of the protons and electrons generate locally high electric fields at low temperatures and pressures, leading to creation of low energy neutrons and high evolution of heat. An important feature of this process is elimination of associated production of harmful beta radiation and He isotopes, which are absorbed by the bulk of the metal (Celani 2012).

Further work is undoubtedly required on a detailed composition of the gaseous mixtures resulting from the metal activated hydrogen-oxygen interactions at different temperatures in the presence of different inert gases.

4 Conclusions

Several pure transition metal powders immersed in inert gases absorb hydrogen displacing the inert gases. This is an exothermic process with the amount of heat evolved, in the case of 7 % Au /Rutile catalyst, exceeding; greatly the heat of water formation. The heats are especially high when the size of the metal particles is very small, which is usually the case when the metal particles are supported on high surface area supports, such as alumina, active carbons and titanium oxide. The absorbed hydrogen is slowly desorbed by nitrogen, or, inert gases, interacting very strongly with pulses of molecular oxygen passing through the metal hydride samples. The process of the heat generation is also considerably enhanced by treatments of the metals with argon before they are exposed to hydrogen. The treatments radically increase both the hydrogen uptake as well as its heat of the interaction with oxygen. The exceptionally high heat generation by these interactions, which can reach values as high as 50 eV and are 10 times higher than the heat of water formation, is attributed to the interactions between the highly active state of the adsorbed and desorbed hydrogen atoms created by their interaction with the metals. It is possible that this active state could be explained by the Widom-Larsen theory postulating generation of high heats by a Low Energy Nuclear Reaction (LNER) process involving protons interacting with the metal electrons.

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