

# HYDROGENATION AND PROPERTIES OF Pd-Mg-C AND Pd-Al-C NANODISPERSION SYSTEMS

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## Introduction

In 60<sup>th</sup> of past century materials and technologies were found allowing hydrogen accumulation in quantities necessary for transportation problems solution. The main barrier on the way of the energy-saturated materials usage was their stability only at cryogenic temperatures. The most perspective materials are Al and Mg. Thus, the problem reduced to problem of synthesis materials which would be stable at normal conditions. We see the solution of this problem at the way of synthesis and investigation of nanodispersed many-shell systems of “core-shell” type or onion type. Core is the most energy saturated part of the structure, and the main function of shells is to isolate the core from environment.

## Results and discussion

The estimates of hydrogen sorption and desorption barriers by large and small metallic (Al,Fe,Mg) and bimetallic clusters (Al covered by Fe, Fe covered by Al, Mg covered by Pd) by quantum-chemical calculations by VASP package were carried out [1].

For small clusters less than 8 Å in diameter the results were obtained:

1. Hydrogen position on the cluster surface was the most favorable for all accounted clusters, with binding energy 3-4 eV per hydrogen atom.

2. Hydrogen transition from surface inside to Mg cluster occurred without barrier. In other clusters the transition needed barrier overcoming.

3. Hydrogen atom desorption from Al and Fe-Al cluster needed to overcome barrier of 1-3 eV.

After inclusion of H<sub>2</sub> molecule into Al<sub>13</sub> cluster its geometry optimization lead to extrusion of hydrogen onto the cluster surface. After coverage of Al<sub>13</sub> by thirty hydrogens, its structure had changed, and became close to hexagonal structure of aluminum hydride AlH<sub>3</sub>.

After geometry optimization of Al<sub>13</sub>Fe<sub>20</sub> cluster (Al covered by Fe) with few hydrogen atoms in different positions, mixing occurred: iron became

the cluster core, aluminum extruded to the cluster surface, and all hydrogen atoms bonded to iron.

After geometry optimization of small spherical Mg cluster covered by Pd (Mg<sub>18</sub>Pd<sub>17</sub>), mixing of Mg and Pd atoms occurred.

To study the process of H and H<sub>2</sub> sorption by large Mg particles, the model structure Mg<sub>64</sub> was constructed as infinite plane of 4 layers. Hydrogen sorption was compared with the same structure covered by one palladium layer Mg<sub>64</sub>Pd<sub>16</sub>.

The calculation of the energy of the system during H<sub>2</sub> approaching had shown that there is a potential well at the metal surface: 0.1 eV for Mg and 0.2 for Pd. Therefore, at same temperature hydrogen concentration on the Pd surface will be higher than on the Mg surface.

Whereas, it is known from experiment that hydrogen dissociates to atoms on the Pd surface, it is practically to carry out the calculations with hydrogen atoms inside material, not molecules. Inside the Mg crystal lattice hydrogen bonded in atomic phase, not molecular. It was verified by calculations in VASP package on the example of Mg<sub>16</sub> cell. The energy gain was about 4 eV.

Then hydrogen atom translation barriers through the metal layers were estimated. The energy of the system was calculated at hydrogen atom moving normally to metal surface. Infiltration of H atom into pure magnesium through the first layer needed 0.92 eV barrier overcoming. At once, infiltration through the Pd layer needed 0.62 eV barrier, and 0.85 eV through the following Mg layer. Thus, coating Mg by Pd lowered the energy barrier of hydrogen atoms infiltration through the metal surface by 0.3 eV.

At the next stage the molecular dynamics calculations were carried out for free intercalation of hydrogen molecule into magnesium covered by palladium Mg<sub>64</sub>Pd<sub>16</sub> at 300 K, without fixing the trajectory. The initial kinetic energy of hydrogen molecule was 3.24 eV (velocity 0.25 Å/fs). Barrier of H atoms infiltration into surface layer amounted 1.7 eV. The graph of energy of the system at different H<sub>2</sub> positions is shown in Fig.1. The first 30 steps correspond to H<sub>2</sub> vibrations at free moving

to surface. The 40<sup>th</sup> step is the oncoming to surface. The potential well at the 50<sup>th</sup> step is the beginning of hydrogen dissociation to atoms, one of them is above the Pd layer and one is below the layer. The following energy variation corresponds to the situation when one hydrogen atom oscillate in Pd layer and another is moving through Mg layers by along the trajectory close to straight line.

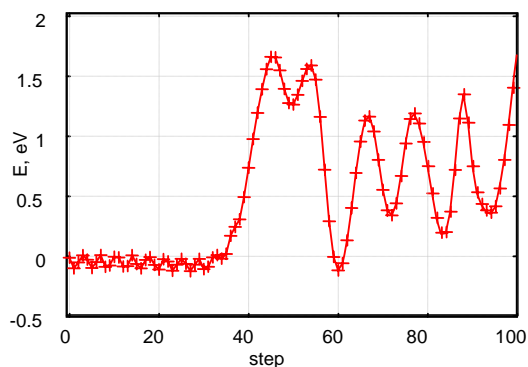


Fig.1. Energy of hydrogen molecule intercalation into magnesium covered by palladium.

We had investigated experimentally three samples: sample A with contents C 45.2 %, Mg 3.8 %, Pd 0.64 %; sample B with contents: C 46.3 %, Mg 3.3 %, Pd 0.25 %; and sample C - nanodispersed carbon with fractal structure, carbon nanotubes with contents of Ni 9.5 %.

Specific surface area of the samples was determined by the BET method by nitrogen adsorption at 77K at  $P/P_0 = 0.2$  with appliance of specific surface area analyzer "Sorbotometr-M": sample A – 143 m<sup>2</sup>/g, B – 189 m<sup>2</sup>/g, C – 91 m<sup>2</sup>/g.

The estimation of hydrogen sorption capacity was made at liquid nitrogen temperature (77K). The samples was placed in measurement cell and carried out preparation at vacuum at 275°C during

90 min. After the treatment the cell with sample was cooled to room temperature, pumped up by hydrogen at 6.5 MPa pressure, and placed into vessel with liquid nitrogen. In this stage the sample was conditioned at 77 K during 30 min. Desorption was carried out in non-isothermic regime (rate of temperature growth 5°C/min) to the final temperature 275°C.

Hydrogen sorption capacity amounted: sample A – 0.6%wt, B – 0.4%wt, C – 1.3%wt. Then the samples investigated for hydrogen sorption, were investigated by PES. But it was impossible for the A and B samples because they heated by X-rays and emitted gas (presumably hydrogen) even at long-time pumpdown at vacuum.

## Conclusions

Theoretical estimations had shown that nanodispersed particles based on Pd, Fe, Mg, and Al are perspective materials in hydrogen accumulation. Also carbon can be good stabilizer. Despite of ternary systems calculations are much more complicated it is necessary to carry them out. Simultaneously with computer modeling, it is also necessary to carry out direct synthesis and investigation of ternary systems. Because the heating up to 275°C was insufficient for complete desorption, and, hence, for determination of full quantity of stored hydrogen, we plan treat samples at temperatures up to 600°C.

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## References

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