

# ÅFORSK – Ångpanneföreningens Forskningsstiftelse Report for 2008/2009.

**Title: Hydrogen storage for new environmentally clean car engines.**

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## **Abstract.**

None of existing materials satisfy to parameters required for efficient hydrogen storage on-board of hydrogen-driven vehicles. One of the most promising types of materials for hydrogen storage application is Metal Organic Framework Materials (MOF's). Hundreds of MOF's are synthesized every year in various laboratories; systematic study of their hydrogen adsorption properties is rather important. Search for new MOF's and for methods to modify their structure for increased adsorption is one of the main priorities of our research. One of the methods reported in literature is doping MOF's with catalytic metal particles which according to some studies results in 5-8 fold increase of hydrogen adsorption by so called "spillover mechanism". Spillover suggests dissociation of molecular hydrogen on metal particles and migration of atomic hydrogen to carbon and then to MOF material. Within current project we studied hydrogen storage parameters of MOF-5 material doped by metal catalyst according to published methods. However we did not observed any signs of "spillover effect" in our experiments. Similar results are simultaneously published by one more group which is co-authored worlds known expert in physisorption of hydrogen by high surface area materials. There is ongoing discussion on possible reasons for contradictory results from different groups. At the same time the research activity is focused also on synthesis of new hydrogen storage materials based on carbon. New methods for synthesis of nanocarbons using various organic precursors and fullerenes are developed. Finally, hydrogenation/dehydrogenation of fullerenes aimed on reversible hydrogen chemisorption and release is studied.

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**1. Introduction**

## 1.1. Overview of progress in 2008/2009

During the past year the hydrogen storage project was running well. Research work performed in the frame of project resulted in two new papers published [1,2] and one more paper cited as submitted in 2008/2009 report was published (all with acknowledgements to Ångpanneföreningens Forskningsstiftelse). The result which will possibly attract a lot of attention from scientific community [1] is related to so called “spillover effect” in MOF materials doped with metal catalyst particles. The paper was published in August 2010 with Editorial note from Chief Editor of journal, response from authors of original report of “spillover effect” Prof. R.T. Yang and remarks from world known expert in physisorption of hydrogen Prof. M.Hirscher. See details in next sections.

At the same time we continued to work with synthesis of new carbon materials using large organic molecules as precursors and with hydrogenation/dehydrogenation of fullerenes. Some interesting results are obtained and will be published during the end of 2010 or in 2011. I also actively worked with scientific networking and established some new active collaborations. The project workforce in 2008/2009 included two researchers: Alexandr Talyzin as project leader and PhD student Sergey Luzan. In this report I omitted general introduction to the field of hydrogen storage, it can be found in previous reports (2008/2009).

### **Publications:**

- 1) Serhiy M. Luzan, A.V. Talyzin, Hydrogen adsorption in Pt catalyst/MOF-5 materials, *Microporous and Mesoporous Materials* 135 (2010) 201–205
- 2) Martin NM, Luzan SM, Talyzin AV, ”High-temperature reactions of C60 with polycyclic aromatic hydrocarbons “Source: *Chem. Phys.* 368 , 49, 2010
- 3) S.M. Luzan, H. Jung, H. Chun, A. V. Talyzin, “Hydrogen storage in Co-and Zn-based metal-organic frameworks at ambient temperature, *Int. Journal of Hydr. Energy* 34 , 9754, 2009

## 1.2. Background.

Main problem which hinders development of hydrogen driven vehicles is hydrogen storage. There is **no available technology** to store sufficient amounts of hydrogen in reasonably small volume. The problem can be solved through the development of new hydrogen adsorption materials. A number of materials are currently explored for possible hydrogen storage applications but none of them, so far, meets target requirements.

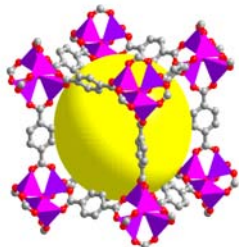
None of existing hydrogen storage materials satisfies all these requirements. Therefore, novel types of materials need to be found for application as hydrogen storage. The work in this direction was stimulated during past decade by US DOE program which set target values (4.5 wt.% by 2007, 6 wt.% by 2010, and 9 wt.% by 2015) cited widely by international community. However, US DOE program has recently degraded their targets to 5.5 wt.% which emphasizes the difficulty of our task. Measurements of hydrogen

adsorption are seemingly simple, but experience proves that many possible technical problems may result in overestimation of hydrogen storage values. Research in this field had suffered some major drawbacks during last decade when several big claims positioned to satisfy DOE targets proved later to be incorrect. For example, hydrogen adsorption by nanostructured carbon materials (e.g. carbon nanotubes, carbon nanofibres) at ambient temperature proved to be on the level of 1–1.5 wt.% down from initially reported 7–70 wt.%. Hydrogen clathrate THF/hydrates have been reported to exhibit 4 wt.% of hydrogen just below room temperature, the number proved to be overestimation by about 10 times according to recent publications. First report of hydrogen adsorption in metal–organic framework materials (MOF) (~1 wt.% for MOF-5 at 20 bar H<sub>2</sub> pressure) also proved to be erroneous. At least 5 fold smaller value of hydrogen adsorption has being found at the same conditions according to later studies. Therefore, it is extremely important to verify independently new reports of high hydrogen adsorption in various materials.

## 2 Hydrogen storage in MOF materials: spillover effect.

### 2.1 Reports of high hydrogen storage capacity, review.

a) **Metal Organic Framework materials (MOF)** Group of O.M.Yaghi, [4] proposed significant advantage compared to known carbon materials. These advantages can be formulated as following: *well defined crystal structure, interconnected pore structure through all the volume of material, possibility for variation of pore size.*



**Figure 1. MOF-5 structure.** [1] Samples of this material was synthesized and tested for hydrogen adsorption within current project as a reference.

The structure shown in the Figure 1 is for most common MOF-5 material. Hydrogen adsorption properties of this material have been studied in many papers and it was used in our previous paper [3] as a reference material to verify that our measurements of hydrogen storage capacity are in agreement with literature. However at ambient conditions the hydrogen adsorption in this material is not sufficiently high. The hydrogen adsorption in this material is directly correlated to surface area with approximately 0.5 Wt% per 1000 m<sup>2</sup>/g and highest surface area on the level of ~ 2500 m<sup>2</sup>/g. Therefore, attempts to increase hydrogen adsorption by modification of structure or by using catalysts have been taken. The most spectacular reports in this direction were published in 2006 by Prof. R.T Yang group in two high profile papers [5, 6]. Using a simple mechanical mixture of 5 wt.% Pt/AC catalyst with IRMOF-8 or MOF-5 to cause the spillover, they reported that the storage capacity was increased up to 1.8 wt.% for IRMOF-8 or up to 1.6 wt.% for MOF-5 at 298 K and 10 MPa. This represented an increment by factor 3.1 for IRMOF-8 and 3.3 for MOF-5 [5]. By using “bridging” procedure, the hydrogen adsorption have been further increased up to 4 wt.% for IRMOF-8 or up to 3 wt.% for MOF-5 at the same conditions [6]. Moreover, new high profile paper was published in 2009 [7] with seemingly independent confirmation of result.

These papers suggested that hydrogen dissociates on metal particles (which is known from catalysis) and then migrates in atomic state on support materials (carbon or MOF's) to provide higher adsorption capacity. It should be noted that hydrogen adsorption isotherm was not saturated at 100 bar and capacity seemed to increase linearly with increase of pressure. Having 3 Wt% already at 100 Bar H<sub>2</sub> pressure the DOE target value (5.5 Wt%) can be achieved already at easily available pressures of 200Bar. Some of our measurements have been performed previously at 180 Bar hydrogen. Therefore, we had the ability not only to verify the "spillover effect" but also to check if linear pressure dependence of hydrogen adsorption vs pressure extends into higher pressures and possibly to achieve DOE targets if it does so. I contacted Prof R.T. Yang and proposed to make measurements on their samples. Unfortunately our proposal was not accepted and we tried to make experiments using own samples following published procedures for doping MOF-5 with catalyst particles. To our surprise the experiments have not revealed any signs of spillover effect. See results below.

[4] N.L. Rosi, M. Eddaoudi, D.T. Vodak, J. Eckert, M. O'Keeffe, O.M. Yaghi, *Science* 300

[5] Y.W. Li, R.T. Yang, *J. Am. Chem. Soc.* 128 (2006) 726.

[6] Y. Li, R.T. Yang, *J. Am. Chem. Soc.* 128 (2006) 8136.

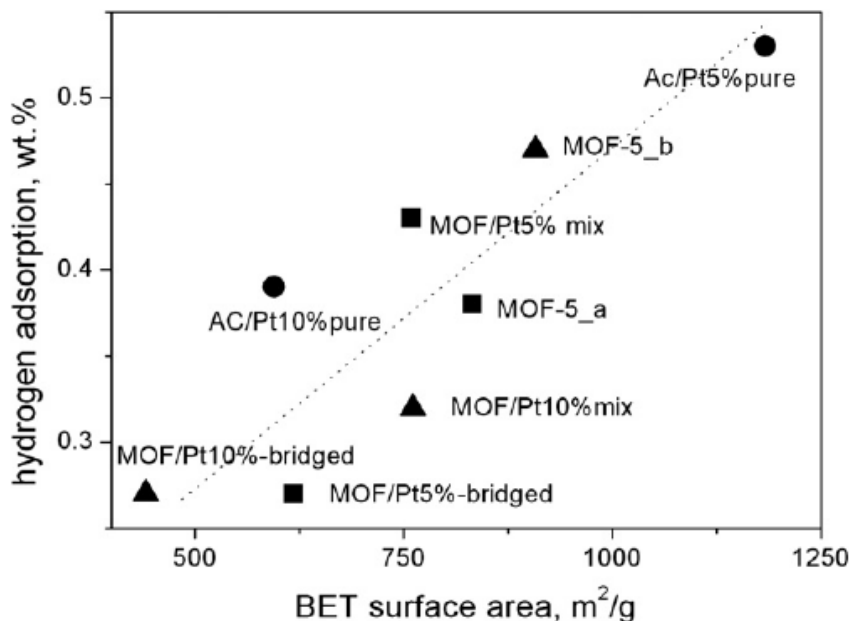
[7] C.-S. Tsao, M.-S. Yu, C.-Y. Wang, P.-Y. Liao, H.-L. Chen, U.-S. Jeng, Y.-R. Tzeng, T.-Y. Chung, H.-C. Wu, *J. Am. Chem. Soc.* 131 (2009) 1404.

## **2.2. Brief description of research and obtained results.**

Two sets of MOF-5 (MOF-5\_a and MOF-5\_b) were successfully prepared following a procedure (slightly modified) given in literature. These samples were doped by Pt catalyst also following two methods reported in literature [5,6]: using grinding of powders mixture and by "bridging" which is achieved by carbonization of sucrose. Characterization of samples on different stages of synthesis (pristine MOF's, doped MOF's and some on samples after H<sub>2</sub> tests) was performed using XRD and IR spectroscopy, hydrogen adsorption measured using gravimetric system and BET surface area measured using own analyzer. The results are summarize din the table 1.

	BET (m <sup>2</sup> /g)	Langm. (m <sup>2</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Pore volume (cm <sup>3</sup> /g)	H <sub>2</sub> uptake (wt.%)
MOF-5_a	832	862	0.31	0.37	0.38
MOF-5_b	908	943	0.31	0.44	0.47
MOF-5_a Pt 5 wt.% "mixed"	759	789	0.29	0.37	0.43
MOF-5_b Pt 10 wt.% "mixed"	761	802	0.29	0.33	0.32
MOF-5_a Pt 5 wt.% "bridged"	618	652	0.23	0.31	0.27
MOF-5_b Pt 10 wt.% "bridged"	441	451	0.16	0.18	0.27
Pt 5 wt.% on AC	1183	1267	0.48	0.97	0.53
Pt 10 wt.% on AC	595	612	0.24	0.45	0.39
MOF-5 [26]	1021	1355	0.39	0.68	0.4
MOF-5 [26] Pt 5 wt.% "mixed"	n/a	n/a	n/a	n/a	~1.6
MOF-5 [27] Pt 5 wt.% "bridged"	890	n/a	n/a	0.61	3.0

**Table 1** Hydrogen adsorption Hydrogen/nitrogen adsorption data for samples of pristine MOF-5 samples, Pt catalysts and MOF/Pt samples synthesized by "mixing" and "bridging". H<sub>2</sub> uptake is for 120 bar and 15 °C. The data are compared to values reported previously [26,27]. "n/a" stands for not available in the reference.



**Figure 2.** The relationship between hydrogen adsorption and BET surface area of studied materials: Pt catalysts (-●-); as-synthesized, doped, and bridged MOF-5\_a (-■-); as-synthesized, doped, and bridged MOF-5\_b (-▲-).

The results shown in the table show that no increase of hydrogen adsorption was observed for samples doped with Pt catalyst. At the same time, other features of hydrogen adsorption reported for spillover effect were also not found. As it can be seen

from Figure 2 the hydrogen adsorption correlated with surface area (it was not correlated according to ref [7]), linear increase of adsorption was not observed and very slow kinetics (up to 70 hours in ref [7]!) was also not observed. Hydrogen storage capacity was saturated at each pressure step within 3 minutes after exposure to the gas and isotherm was clearly not linear with dependence of H<sub>2</sub> adsorption approaching saturation at 120 bar.

The results were complete surprise for us as we expected to find at least some influence of catalyst on hydrogen adsorption by MOF's and to continue work on optimization of its parameters. Our experiments prove that simple formula proposed by Prof. R.T. Yang group: MOF+Pt catalyst=spillover does not work and there must be some additional parameters which are crucial for spillover effect. Alternatively, it could be that measurements of hydrogen adsorption performed by this group were erroneous. This, however, is somewhat difficult to suggest since there was independent confirmation of their report [7] and we had to believe that three high profile papers published in high ranked JACS journal are wrong. One should note though that careful examination showed that these groups were financed from the same program and collaborated in one more paper which means they are not 100% independent and could possibly use the same methods or even equipment to make their measurements of hydrogen adsorption. On other hand, careful examination of literature showed that "spillover" effect "was reported by the same group also for other materials: activated carbons and carbon nanotubes. Unfortunately, most recent studies performed on these materials (some published in 2010) have not confirmed these reports (see our paper for details). Moreover, at the moment of manuscript preparation we discovered conference presentation title which obviously was related to our research. I contacted the main author of this presentation-worlds known expert in the field of hydrogen storage, Prof. Hirscher and he informed me that they also attempted to reproduce MOF /Pt catalyst with results the same as in our experiments. With this information we decided to proceed with publication of our data which appeared to be very difficult: in first two submissions (JACS and Int.J.Hydr. Energy) we received one completely positive reviewer report and second completely negative (from authors of original claims as it become clear). Finally paper was accepted in Microporous and Mesoporous Materials with personal involvement of their Chief Editor. As a result the latest issue of this journal published our paper [1], response from Prof. R.T Yang group [8] and Remarks by Prof. Hirscher [9] prefaced by Editorial Note in the beginning of the issue. It makes it quite unusual story which will hopefully attract attention with broader scientific community and make more people involved in our research and with more independent studies to come. In any case, we raised some very important questions which must be addressed. New discoveries become ones only if anyone can reproduce results. If some parameters are not described in the original paper or the measurements were erroneous we will see only when more studied will be published. At the same time, results very similar to ours were published on line by Prof. M.Hirscher group [10] just one month before our publication.

[8] Yingwei Li, Lifeng Wang, Ralph T. Yang, Response to "hydrogen adsorption in Pt catalyst/MOF-5 materials" by Luzan and Talyzin, Microporous and Mesoporous Materials 135 (2010) Pages 206-208

[9] Michael Hirscher Remarks about spillover and hydrogen adsorption – Comments on the contributions of A.V. Talyzin and R.T. Yang, *Microporous and Mesoporous Materials* 135 (2010) Pages 209-210

[10] R. Campesi, F. Cuevas, M. Latroche, M. Hirscher, “Hydrogen spillover measurements of unbridged and bridged metal-organic frameworks-revisited”, *Phys. Chem. Chem. Phys.*, 2010, published on line as advance article.

### **3. Synthesis of new carbon materials and nanocarbons from large polycyclic aromatic hydrocarbons (PAH's).**

Last year we made set of experiments with high temperature treatments of  $C_{60}$  mixed with various PAH molecules. These experiments revealed among other results one curious bi-reaction: dimerization of coronene into dicoronylene. This reaction appeared to be reported about 50 years ago but seem to be little know to scientific community outside of narrow range of specialists in PAH field. Currently we are making experiments with heat treatment of coronene at various temperatures in attempts to make larger polycyclic hydrocarbons and in the final goal to make carbon material which would consist of small graphene islands. A set of samples was synthesized and characterized by XRD, IR spectroscopy and NEXAFS. For the last method we established collaboration with Prof. Ellen Moons from University of Karstad and the data were recorded during her session at MAXLAB synchrotron in Lund. To record TEM data we also established collaboration with Uppsala University, Prof. Klaus Leifer. In the current state I prefer to wait until the analysis of results is done before making detail reports. Hopefully the work will be completed by the end of year and some paper submitted.

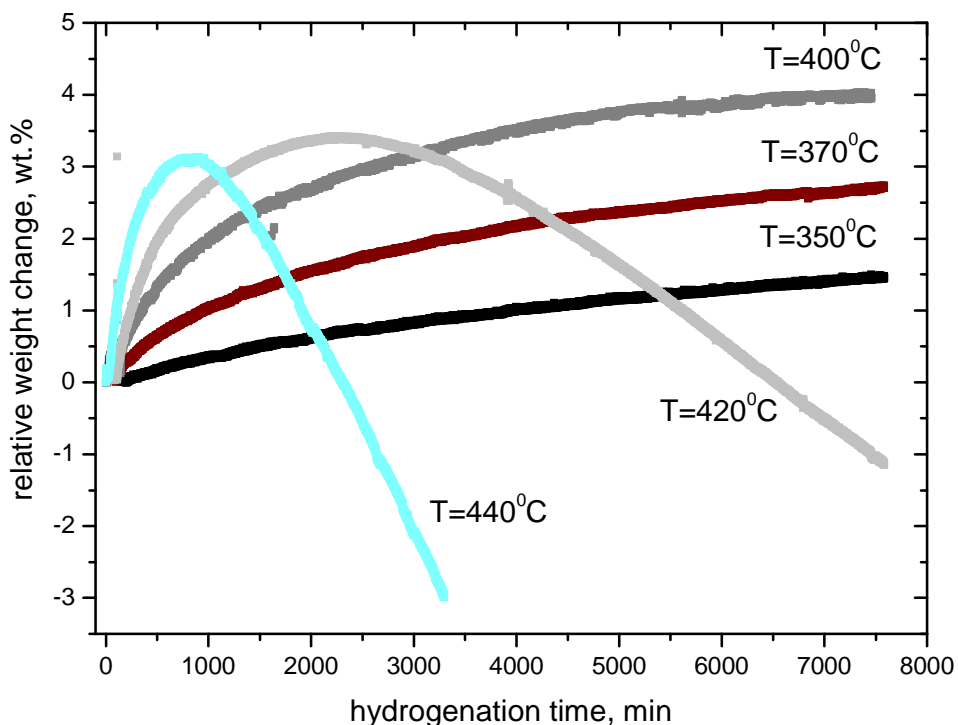
### **4. Fullerenes hydrogenation.**

Highly reduced fullerenes are able to store large amounts of hydrogen, e.g.  $C_{60}H_{36}$ , contains about 5% by weight of hydrogen, which is close to the target of 5.5% for on-board transport storage systems. The volumetric hydrogen density of  $C_{60}H_{36}$  is about 329 g L<sup>-1</sup>, much higher than the DOE specification of 45 g L<sup>-1</sup>. The main obstacles to the application of hydrofullerenes for hydrogen storage are the relatively high temperatures of hydrogenation and dehydrogenation and the partial collapse of the fullerene cage structure during thermal dehydrogenation. However, this results are typically observed was very complicated mixtures of fullerenes while many hydrogenated species  $C_{60}H_x$  with various X were never isolate din pure state and their properties are unknown. Despite my extensive experience with hydrogenation of fullerenes a lot of questions are need to be answered and potential of this material for hydrogen storage is clarified. This research is part of my fundamental interests and overlaps with hydrogen storage field which make sit especially interesting.

In 2010 we synthesized new set of  $C_{60}$  samples hydrogenated at different temperatures and using different periods of time. The samples were characterized by XRD and IR diffraction at Umeå University and by advanced Mass Spectrometry methods at EPFL, Lousanne, Prof. Yury Tsybin laboratory. We also recorded weight change of samples



during hydrogenation reaction which allowed us to study temperature intervals of hydrogenation and reaction kinetics. The data are unique and have never been published before. See Figure 3.



**Figure 3.** Relative weight change of C60 samples in process of hydrogenation for various temperatures.

The Figure 3 demonstrates that hydrogenation goes to saturation level at the temperature interval up to 400°C. For higher temperatures the reaction proceeds with opening of fullerene cage and partial collapse of molecules with formation of gaseous hydrocarbons which result in the weight loss after certain period of time. At lower temperatures (below 400°C) the kinetics is very slow and saturation of reaction was not observed in a reasonable time. It can be noted that the rate of reaction is very likely can be improved quite a lot by using proper catalysts and by more fine grinding of samples.

Mass spectrometric characterization of hydrogenated samples was performed in June 2010 during 2 weeks visit of EPFL in Lausanne, Switzerland (the travel costs were covered by STINT short stipend grant). State of the art equipment allowed to evaluate composition of samples with high precision. In further attempts to prepare pure hydrogenated species from complex mixtures  $C_{60}H_X$  with X up to 52 we performed HPLC separation of dissolved samples using semi-preparative column. Analyzisi of separation products was again performed by mass spectrometry. Some of the samples looks to be promising and were given to Prof. Dan Johnels (Umeå) for NMR

characterization. With some luck we will be able to solve structure of some hydrogenated fullerene species and to determine exact location of hydrogen atoms on the cage.

## 2.5 Hydrogenation of carbon nanotubes.

Carbon nanotubes are considered as one of possible hydrogen storage materials with both physisorption and chemisorption. However it is widely believed that atomic hydrogen is required for hydrogenation of nanotube walls. Atomic hydrogen can be produced e.g. using plasma or hot tungsten wire. However, it is difficult to apply these methods for hydrogenation of bulk samples. Typically only thin films were hydrogenated by these methods. Very few studies are available for high temperature hydrogenation using molecular hydrogen. In collaboration with Dr. Albert Nasibulin (Center for New Materials, Aalto University, Finland), who provided us with samples of short carbon nanotubes, we performed hydrogenation experiments with temperatures 400-500°C and hydrogen pressures 50 Bars. Surprisingly, we were able to detect quite efficient hydrogenation. Characterization of samples was performed using Raman and IR spectroscopy, XPS and NEXAFS. Analysis of data is on the way, possibly it will lead to some high profile publication. We are waiting for some crucial data to come. Detail description of results will be presented in the next year report after publication of the data. The experiments are related to hydrogen storage problem but also of very high fundamental value and could be useful for some electronic applications.

## 5. Conclusions and future outlook.

Investigation of hydrogen storage properties of MOF materials become main priority of project. Some well known MOF materials were successfully synthesized and modified by doping with Pt catalyst with the aim to observe “spillover effect” which provided according to previous reports several times increase in hydrogen storage capacity. However, our experiments have not confirmed this finding and similar observations were recently published by one more independent group. Prof. M. Hirscher valued our contribution in his Remarks [9] in following expression “Science needs this critical input as by Luzin and Talyzin which will initiate the discussion in a wide audience and, finally, should lead to a clarification”.

We plan to search for other methods to modify MOF materials, e.g. by insertion of catalyst nanoparticles directly into pores of MOF structure. Some new reports from 2010 suggest that it is possible to create 3D network of catalyst particles inside of MOF structure using pores as a “template”. It would be very interesting to verify hydrogen storage properties of these materials. Some promising results for synthesis of novel nanocarbon materials are obtained for the part of project which deals with building larger molecules for PAH's (coronene). Hydrogenation of fullerenes and carbon nanotubes also yielded some important results which are expected to be published during next year.

It should be noted that new nanomaterials synthesized by above described methods are interesting not only for hydrogen adsorption studies, but possibly also for other applications and for fundamental research.

