



## Communication

## Hydrogen adsorption in Pt catalyst/MOF-5 materials

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## ABSTRACT

Hydrogen adsorption properties of well-known MOF-5 were studied at near ambient temperature and hydrogen pressures up to 120 bar. Pristine material was doped with Pt catalysts supported on activated carbon (AC) using two previously described procedures: physical mixture of a catalyst with MOF-5 and “bridging” procedure (MOF-5 and catalyst particles connected via carbon bridges) MOF-5. The maximum hydrogen adsorption measured on doped MOF-5 was 0.43 wt.%. These values are on the same level or even less than for catalyst free MOF-5 material. Therefore, doping of MOF-5 material with Pt catalyst has not resulted in increase of hydrogen storage value. Hydrogen adsorption for the samples with added catalyst showed correlation with BET surface area, exhibited isotherms typical for physisorption and no features which could be assigned to spillover effect.

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## 1. Introduction

The problem of hydrogen storage is the main obstacle to commercial application of hydrogen powered vehicles [1,2]. One possible solution is to use light-weight solids which could reversibly adsorb hydrogen at near ambient temperatures. 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, research in this field had suffered some major drawbacks 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.% [3–6]. Hydrogen clathrate THF/hydrates have been reported to exhibit 4 wt.% of hydrogen just below room temperature [7], the number proved to be overestimation by about 10× according to recent publications [8,9]. First report of hydrogen adsorption in metal–organic framework materials (MOF) (~1 wt.% for MOF-5 at 20 bar H<sub>2</sub> pressure) [10] also proved to be erroneous. At least 5× smaller value of hydrogen adsorption has being found at the same conditions according to later studies [11,12]. Measurements of hydrogen adsorption are seemingly simple, but experience proves that many possible technical problems may result in overestimation of hydrogen storage values. In fact, US DOE program has recently degraded their targets to 5.5 wt.% reflecting growing skepticism. Therefore, it

is extremely important to verify independently new reports of high hydrogen adsorption in various materials.

Despite early drawbacks, MOF materials are still considered as promising for hydrogen storage applications due to extremely high surface area (e.g. 5994 m<sup>2</sup>/g Langmuir surface area was reported for MOF-177 [13]), almost an infinite number of geometrical and chemical variations for structures of these materials and possibilities for post-synthetic modification [14,15]. MOFs exhibit superior hydrogen adsorption properties at cryogenic temperature (77 K) [13,16]. However, in order to be practically useful a material must adsorb and release H<sub>2</sub> near ambient temperatures. The hydrogen adsorption measured on as-synthesized MOFs usually does not exceed 1 wt.% [15,17]. Introduction of open metal coordination sites [18], catenation (or interpenetration) [19], mixed ligand systems [20] were recently considered as main routes influencing hydrogen adsorption processes.

However, the most promising results were obtained on MOFs using “spillover” effect. The “spillover” effect suggests dissociation of hydrogen on one site (e.g. transition metals such as Pt, Ni, Pd, and Ru), and subsequent migration of atomic hydrogen onto receptor surface. Hydrogen spillover effect have been reported for various carbon materials, some zeolites, and finally for MOF materials [21–30]. As a result of doping with metal clusters the hydrogen adsorption have been reported to increase by factor 1.5–10 in different materials [21–30]. Especially easy method for preparation of samples with pronounced spillover effect has been recently reported by group of Yang [26,27]. 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

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IRMOF-8 and 3.3 for MOF-5 [26]. It should be noted that MOF-5 is one of the most famous and best investigated MOF material due to relatively simple synthesis procedure, certain structure and relatively strong stability of material [11,31–33]. 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 [27]. Those results have been recently confirmed by one more group [28,34,35]. Unusual and very promising feature of reported “spillover” effect is linear high-pressure hydrogen isotherm at pressures at least up to 10 MPa. Another specific feature, slow kinetics of adsorption/desorption, could be considered as an obstacle to hydrogen storage application. Extrapolation of linear isotherms to higher pressure shows that gravimetric DOE target could be achieved already at rather conventional pressure of 140 bar. Later on, Liu et al. reported that the spillover effect could be used to increase the hydrogen adsorption on MIL-101 and MIL-53 materials with H<sub>2</sub> storage values increased by a factor 3 [29].

In this study we attempted to reproduce hydrogen spillover effect on catalyst/MOF-5 materials obtained according to procedures described by Li and Yang [26,27]. Despite seemingly similar structural properties of prepared samples, the spillover effect was not observed, while the highest hydrogen adsorption of ~0.53 wt.% was observed at studied conditions for pure unmodified carbon supported Pt catalyst. This result is in agreement with our previous unsuccessful attempts to reproduce spillover effect in carbon materials doped by Ni nanoparticles [36].

## 2. Experimental section

Two sets of MOF-5 (MOF-5\_a and MOF-5\_b) were successfully prepared following a slightly modified procedure given in literature [11,32]. 2.4 g of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O, 98%, Sigma–Aldrich) and 0.668 g of terephthalic acid (H<sub>2</sub>BDC, 98%, Sigma–Aldrich) were dissolved in 80 ml of *N,N*-dimethylformamide (DMF, ≥99.8%, A.C.S. reagent, Sigma–Aldrich) under mild stirring. 4.4 ml of triethylamine (TEA, ≥99%, Sigma–Aldrich) was slowly added to the solution under agitation. After 2 h of stirring the solution was filtered off, washed three times with DMF, and put in the oven maintained at 105 °C under atmospheric conditions. In order to accelerate drying process, vacuum was applied to MOF-5\_a for ca. 3 min after it was kept in the oven for 15 h. MOF-5\_b was dried in the oven for 20 h. For the spillover experiments, doped (a physical mixture of MOF-5 and catalyst) and modified (MOF-5 and catalyst particles connected by carbon bridges) samples were synthesized.

MOF-5\_a and platinum 5 wt.% on activated carbon (Sigma–Aldrich) powders were ground together using agate mortar for 1 h (weight ratio 9:1). A doped sample based on MOF-5\_b and platinum 10 wt.% on matrix activated carbon support (Sigma–Aldrich) was produced using the same technique. Carbon bridges between MOF-5 and the catalyst were built using a heating protocol similar to one reported by Li and Yang [27]. The ternary physical mixture of sucrose (A.C.S. reagent, Sigma–Aldrich), Pt/AC catalyst, and MOF-5 (the weight ratio 1:1:8) was first heated to 200 °C with a ramp of 1 °C/min and kept for 3 h in helium atmosphere (the melting point of sucrose is 186 °C). During the first step sucrose is supposed to melt thoroughly and to fill spaces between catalyst particles and MOF-5. Then the temperature was increased to 300 °C, and held for 12 h. After the bridging process was completed, samples were cooled down to room temperature with a ramp of 1 °C/min. Two modified samples based on MOF-5\_a, sucrose, 5 wt.% Pt/AC (or MOF-5\_b, sucrose, 10 wt.% Pt/AC) were synthesized.

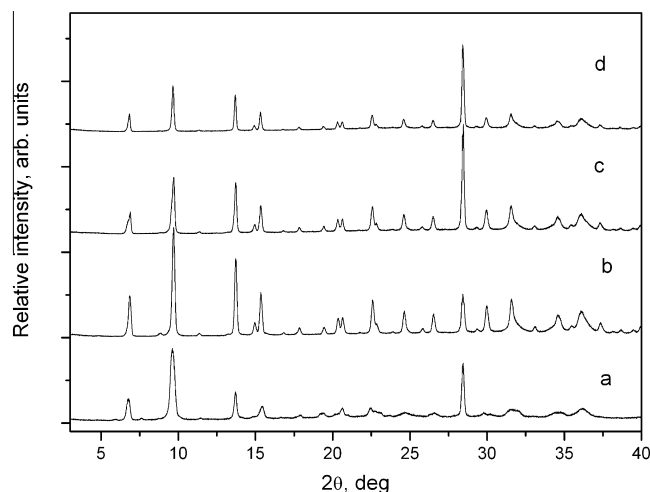
Hydrogen adsorption was measured by gravimetric method using magnetic suspension balance from Rubotherm at hydrogen

pressure up to 120 bar and *T* = 15 °C. Details of Rubotherm system used for our measurements of hydrogen adsorption can be found elsewhere [12,37]. Prior to hydrogen adsorption measurements some samples were degassed at 120 °C with some tests of degassing at 200 °C in vacuum (results of measurements appeared to be almost the same for both degassing temperatures). Quantachrome NOVA 1200 gas sorption analyzer was used to evaluate BET surface area and the total pore volume of studied samples. Structural stability of samples upon hydrogen adsorption measurements and bridging processes was controlled using powder X-ray diffraction (Siemens D5000 diffractometer with CuKα radiation). Completeness of the sucrose carbonization processes was verified using a Perkin–Elmer Spectrum BX FT-IR system.

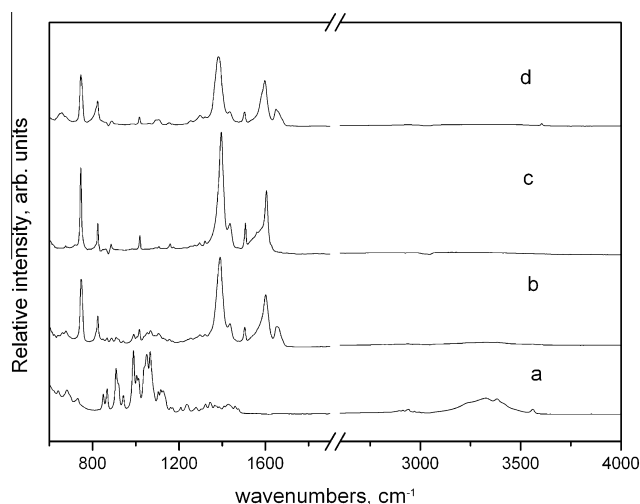
## 3. Results and discussion

Based on the results of X-ray diffraction and IR spectroscopy we conclude that sucrose was completely carbonized supposedly forming carbon bridges between MOF-5 and Pt/AC catalyst particles (both for MOF-5\_a and MOF-5\_b). New “bridged” materials retained the same crystal structure as untreated MOF-5. Values of BET surface area (MOF-5\_a: 832 m<sup>2</sup>/g; MOF-5\_b: 908 m<sup>2</sup>/g) and pore size (main peak in distribution of pore size at 12 Å), were in a reasonable agreement with previously published results. X-ray diffraction patterns shown in Fig. 1 (see also [Supplementary material](#)) for as-synthesized MOF-5\_a and MOF-5\_b were indexed in Fm-3m structure (*a* = 25.8 Å) in a good agreement with previously published results [11]. No degradation of materials was observed after full cycle of hydrogen adsorption measurements. The carbonization temperature of sucrose used in the present study to build carbon bridges between Pt catalyst and MOF-5 was chosen within the thermal stability range of MOF-5 [38].

IR spectra of as-synthesized MOF-5\_a and MOF-5\_b were in good agreement with previously published results [26,38], see Fig. 2 and [Supplementary material](#). Spectrum of mixed MOF-5\_a/5 wt.% Pt/AC/sucrose sample before bridging reaction shows distinct peaks from both pristine MOF-5 and sucrose. After bridging reaction the peaks attributed to sucrose disappeared and the IR spectrum of MOF-5\_a bridged with 5 wt.% Pt/AC was identical to the IR spectrum of pristine MOF-5\_a recorded after hydrogen adsorption measurements. A broad asymmetric peak at ~1660 cm<sup>-1</sup> which was also present on the IR spectrum of pristine



**Fig. 1.** X-ray diffraction patterns of: (a) as-synthesized MOF-5\_a; (b) MOF-5\_a after hydrogen adsorption measurements; (c) MOF-5\_a mixed with 5 wt.% Pt/AC (after hydrogen adsorption measurement); (d) MOF-5\_a bridged with 5 wt.% Pt/AC (after hydrogen adsorption measurement).



**Fig. 2.** IR spectra of: (a) sucrose; (b) mixture of sucrose, MOF-5\_a, 5 wt.% Pt/AC catalyst before bridging process; (c) mixture of sucrose, MOF-5\_a, 5 wt.% Pt/AC catalyst after bridging process; (d) pristine MOF-5\_a material.

MOF-5\_a before degassing could be attributed to the overlap of the bending band of water and the C=O band of DMF [39]. This peak was absent in IR spectra of catalyst free MOF-5\_a after hydrogen adsorption measurements and MOF-5\_a bridged with 5 wt.% Pt/AC. Moreover, the intensity of two other peaks at 1061 and 1094  $\text{cm}^{-1}$  attributed to DMF significantly decreased [38]. Therefore, DMF solvent molecules were mostly removed from pores of MOF-5\_a during the degassing process prior hydrogen adsorption measurements or during the bridge building process. Similar results were also obtained for MOF-5\_b with 10 wt.% Pt/AC (see [Supplementary material](#)).

Nitrogen sorption isotherms of all studied materials appeared to have Type I character with H4 hysteresis loop (according to IUPAC classification). Therefore, adsorption branches of isotherms were used for the analysis. Such isotherms are usually obtained on materials with a wide range of narrow slit-like nanopores. Pores size distribution analysis of the nitrogen sorption isotherm of MOF-5\_a showed one strong peak for the pore diameter 12 Å. This value is in a good agreement with results published by Yaghi et al. [40]. In contrast to MOF-5\_a, MOF-5\_b besides the main peak located at 12 Å had a wide distribution of low-intensity peaks in the range of 30–140 Å which may represent cavities formed between grains of MOF-5\_b during synthesis. This agreed well with a fact that MOF-5\_b had bigger total pore volume of 0.44  $\text{cm}^3$  (against 0.37  $\text{cm}^3$  for MOF-5\_a) while micropore volume calculated by t-thickness method was the same for both MOFs. According to previously published reports the surface area and pore volume of MOFs are strongly affected by synthesis conditions (e.g. heating or cooling ratio, synthesis temperature, addition of triethylamine) [34,41]. The BET (or Langmuir) surface area and total pore volume of 5 wt.% Pt/AC were almost two times higher compared to 10 wt.% Pt/AC (see [Table 1](#)). Decrease of BET surface area and pore volume in bridged MOFs was observed in agreement with previous reports and was attributed to the blockage of some micropores by carbon bridges [27].

Hydrogen adsorption measurements are summarized in [Fig. 3](#) and [Table 1](#). Pristine unmodified MOF-5\_b adsorbed 0.47 wt.% of hydrogen at 15 °C and 120 bar, this value is in rather good agreement with the literature data. However, all Pt-doped samples failed to show any increase in hydrogen adsorption capacity compared to reference sample, thus not revealing spillover effect. In fact, highest adsorption was found for pristine 5 wt.% Pt/AC catalyst at 15 °C and 120 bar of hydrogen pressure (0.53 wt.%). No

**Table 1**

Hydrogen/nitrogen adsorption data for samples of pristine MOF-5 samples, Pt catalysts and MOF/Pt samples synthesized by “mixing” and “bridging”.  $\text{H}_2$  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.

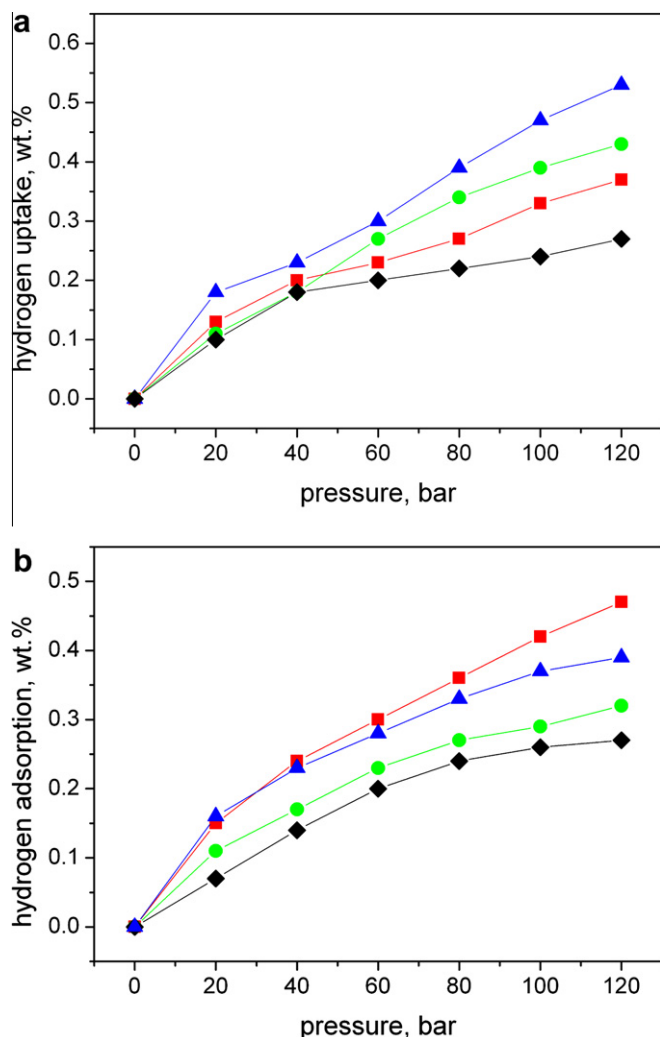
	BET ( $\text{m}^2/\text{g}$ )	Langm. ( $\text{m}^2/\text{g}$ )	Micropore volume ( $\text{cm}^3/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	$\text{H}_2$ uptake (wt.%)
MOF-5_a	832	862	0.31	0.37	0.38
MOF-5_b	908	943	0.31	0.44	0.47
MOF-5_a Pt 5 wt.% “mixed”	759	789	0.29	0.37	0.43
MOF-5_b Pt 10 wt.% “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

difference was observed upon increase of Pt load in carbon supported catalyst from 5 to 10 wt.%. The hydrogen adsorption recorded for 10 wt.% Pt/AC catalyst was even lower: 0.39 wt.% at the same  $P$ – $T$  conditions (see [Fig. 3](#), [Table 1](#)). It is well-known that hydrogen adsorption in MOF materials depends on specific surface area and pore volume of the adsorbent [12,17,42].

Slight variations of hydrogen adsorption observed on our samples are also well correlated with BET surface area and total pore volume (see [Fig. 4](#)). Small difference in adsorption values was observed even for pristine catalyst free samples of MOF-5 (possibly due to somewhat different microstructure or defects); variation in adsorption values of catalyst added samples is on the same level. Increase of degassing temperature from 120 to 200 °C (tested for “bridged” sample) resulted in slight increase of  $\text{H}_2$  adsorption but typical for “spillover” slow kinetic failed to appear (see [Supplementary material](#)). That is in strong disagreement with data reported by Li and Yang who achieved the enhancement factor of 3.3 by simple mixing 5 wt.% Pt/AC with MOF-5 [26] and by factor 8 in carbon bridged MOF-5 samples compared to unmodified MOF-5 [27]. Two features typical for reported spillover adsorption, slow kinetics of adsorption (tens of minutes) and linear pressure dependence of adsorption values, also were not observed in our experiments, see [Figs. 3 and 5](#).

Hydrogen adsorption measured in our samples was reversible, and the maximum was achieved in few minutes after pressure stabilization. It proves that observed hydrogen adsorption was solely due to physisorption. Surprisingly, no evidence of hydrogen spillover effect in MOFs was found in our experiments despite seemingly similar structural properties of studied samples and synthesis routines. Results reported here disagree with initial reports of significant hydrogen adsorption enhancement due to addition of noble metal catalysts by Yang group [26,27]. These results were confirmed so far by only one more recent study by Tsao et al. [34]. This is seemingly independent verification while one more paper [35] combines results from both groups involved in Refs. [26,27,35,43]. The reason for disagreement is not clear at the moment. However it should be noted that the same group by Yang had earlier also reported high hydrogen adsorption in metal doped MWNT (4 wt.%) which remain to be unconfirmed to the date [44]. The reports of spillover effect in other carbon materials (activated carbons [45]) doped with metal catalyst also have not been reproduced in the most recent studies [46,47].

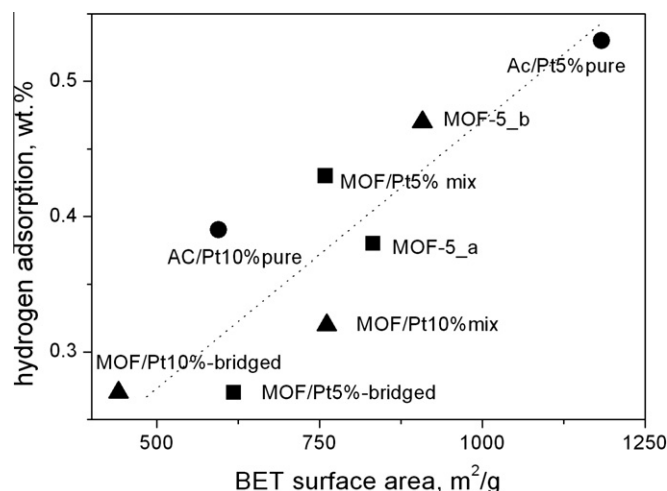
Group of Yang had recently proposed theoretical model which was supposed to explain observed experimental results for spillover effect in MOF [48]. However, this model was subjected to



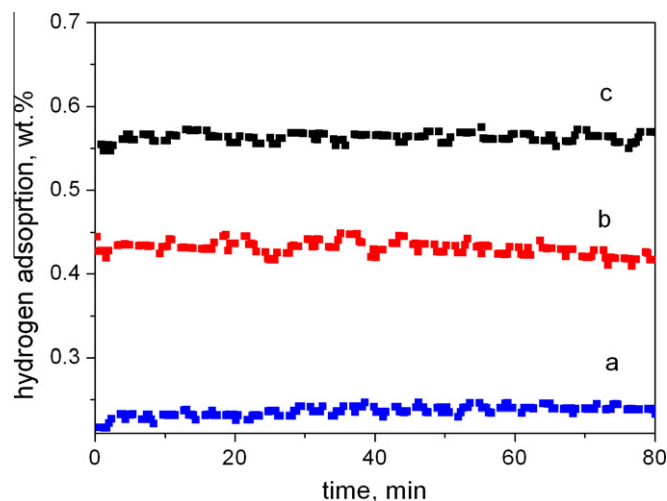
**Fig. 3.** Hydrogen adsorption isotherm measured on: (a) MOF-5\_a (—■—), MOF-5\_a mixed with 5 wt.% Pt/AC (—●—), MOF-5\_a bridged with 5 wt.% Pt/AC (—◆—), 5 wt.% Pt/AC (—▲—); (b) MOF-5\_b (—■—), MOF-5\_b mixed with 10 wt.% Pt/AC (—●—), MOF-5\_b bridged with 10 wt.% Pt/AC (—◆—), 10 wt.% Pt/AC (—▲—). The wt.% values are calculated for whole samples (including mass of catalyst).

strong criticism [49], which was rebutted largely with reference to experimental data reported previously in Refs. [26,27] which are in our turn are not confirmed in our experiments. It is interesting to note that spillover mechanism obviously does not work in our experiments also for pristine Pt catalyst supported on activated carbon. Hydrogen adsorption measured on catalyst material (0.53 wt.%) corresponds to measured surface area (BET 1183 m<sup>2</sup>/g) and is on the same level as for activated carbons without Pt [50]. Possibility of hydrogen migration from metal catalyst to carbon at ambient temperature was found energetically unfavorable in most recent theoretical studies [51]. If hydrogen cannot migrate from Pt to carbon in the catalyst, it is even more unlikely to migrate farther on MOF material. While we do not subject here to doubts spillover mechanism of hydrogen adsorption in principle, the methods proposed in papers by Yang group (e.g. simple mechanical mixture of Pt catalyst and MOF powders) seem to be not efficient to provide spillover.

It looks rather unlikely that absence of spillover effect in our experiments is due to small variations in synthesis conditions (e.g. we have not used H<sub>2</sub>O<sub>2</sub> addition in the synthesis procedure). The final product of synthesis was in both synthesis procedures the same MOF-5 with very similar structural properties. It should



**Fig. 4.** 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 (—▲—).



**Fig. 5.** Hydrogen adsorption measured as a function of time: (a) MOF-5\_a bridged with 5 wt.% Pt/AC at 15 °C and 100 bar; (b) MOF-5\_a mixed with 5 wt.% Pt/AC at 15 °C and 135 bar; (c) 5 wt.% Pt/AC at 15 °C and 135 bar.

be noted the addition of H<sub>2</sub>O<sub>2</sub> in process of synthesis had resulted in dramatic structural changes according to data of Huang et al. [52]; the final structure was tetragonal (compared to fcc structure of MOF-5) and remains to be unknown to the date. Our own attempts to synthesize MOF-5 using synthesis procedure with added H<sub>2</sub>O<sub>2</sub> have failed to yield desirable product. It is unclear why the samples used for spillover experiments in the study by Li and Yang [26] (see [Supplementary material](#)) exhibited XRD patterns typical for usual MOF-5 fcc structure despite using H<sub>2</sub>O<sub>2</sub> addition.

In conclusion, two sets of MOF-5 with reasonable values of specific surface area and pore volume were synthesized; successful synthesis was confirmed by XRD and IR spectroscopy. These two sets were mixed and bridged with Pt catalysts (5 and 10 wt.%) supported on activated carbon following previously described in literature procedures. The successful bridging was confirmed by IR spectroscopy. The hydrogen adsorption measured on catalyst doped and “bridged” MOF-5 was on the same level or even less than for pristine catalyst free MOF-5. The hydrogen adsorption was found to be in a good agreement with BET surface area and total pore volume of samples, analysis of hydrogen adsorption data



proved that physisorption is responsible for hydrogen adsorption. No evidence of hydrogen spillover effect described previously on seemingly the same kind of samples was found for any of studied materials. At the moment of paper submission we found that results similar to those obtained in our study were recently published independently by other group [53].

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.micromeso.2010.07.018](https://doi.org/10.1016/j.micromeso.2010.07.018).

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