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Ball milling and compression effects on hydrogen adsorption by MOF:Pt/carbon mixtures

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ABSTRACT

The effect of ball milling energy on hydrogen adsorption on metal–organic framework:Pt/AC mixtures (HKUST-1:Pt/AC, AC – activated carbon) is reported. Experiments within a wide range of ball milling energies show a decrease of hydrogen adsorption with the increasing energy transferred to the sample. The results correlate well with the decrease of surface area and pore volume. The infrared spectra reveal that the mechanical energy transferred to the sample induces modifications in the metal coordination environment, the most compliant to compression part in the structure of the metal–organic frameworks. A comparison with the results on compressed pellets of the mixture reveals that both the ball milling and compression lead to similar effects, originating in mechanical energy transferred to the sample.

1. Introduction

An efficient on-board hydrogen storage system is the key towards the applications of this clean energy carrier in transportations. The revised DOE targets for 2017 require 0.055 kg H_2 per kg system gravimetric storage capacity and 0.04 kg H_2 per L system volumetric capacity. Hydrogen storage by physisorption has been extensively studied on metal–organic frameworks (MOFs) due to their high surface area and pore volume. At low temperatures they show high sorption capacity, meeting some of the DOE targets [1]. The advantage of physisorption lies in the rather low adsorption heat, very convenient for the thermal management of cryo-adsorption based storage systems [2] in the range 80–160 K [3].

Hydrogen storage systems at ambient temperature are strongly required for applications, but the low adsorption heat (4–10 kJ/mol) of MOFs leads to low storage capacity at 298 K, much below the needs. On the other hand, the current technology of compressed hydrogen at 70 MPa suffers from the low efficiency due to the high cost of compression [2] and safety concerns.

Significant enhancements of hydrogen adsorption at room temperature, up to 3–4 times, were reported for different mixtures of MOF:Pt/AC (AC – activated carbon) [4–10], assigned to the dissociation of hydrogen molecule on the catalyst and migration of H atoms into MOFs pores via the spillover effect. Other authors [11–13] did not succeed to reproduce high enhancements on such ball milled mixtures. It was replied [14] that the transfer of the sample through air is a misstep emphasizing that the key consists in achieving good MOF/catalyst contacts through a proper mixing procedure by grinding or ball milling MOFs with Pt/AC. Increased hydrogen uptake at 298 K by mixtures of copper benzene-tricarboxylate metal–organic framework (also known as HKUST-1) with spillover catalyst were reported, suggesting a hydrogenation process of the carboxylate group at a little higher temperature [15].

Recent experiments on Pd-doped MIL-101 concluded that despite of good contact Pd-MOF pore “hydrogen atoms do not chemisorb on the host framework, which excludes the possibility of hydrogen spillover” [16] and it was shown that the small increase of hydrogen uptake at room temperature is “solely due to Pd hydride formation”. The study of Pt catalytic activity for H_2 dissociation on templated carbon obtained from sucrose concludes that the negligible enhancement obtained “suggests no connection between the spillover effect and a feasible hydrogen storage enhancement” [17]. Other authors [18] reported high pressure (18 MPa) spillover enhanced excess H_2 uptake of Pt, Pd-doped activated carbon of high surface area, pointing out that the pore volume is a key factor for total hydrogen storage. However, the paper does not report sample volumes measured with helium because the total hydrogen uptake calculations reported are based on the pore volume obtained from N_2 adsorption isotherms and it can be inferred that the same value was used in the calculations of excess adsorption. Experimental data on 10 MOFs [19] show that the pore volume from nitrogen or argon adsorption are generally different from that which can be calculated [20,21] from crystal density and skeletal density measured with helium. A Round Robin

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test involving 12 laboratories showed that accurate sample volumes measured with helium are required for reliable calculation of excess uptake [22].

Pt-loaded graphene oxide/HKUST-1 hybrid composites, prepared by in-situ synthesis, were reported to adsorb nearly twofold hydrogen as compared to HKUST-1 at 298 K and 8 MPa, assigning the increase to the spillover effect [23]. The hydrogen adsorption isotherms of HKUST-1 alone to at 77 K are in agreement with literature data but at 298 K the results are very different [19,20,24]. At 298 K and high pressure, using a high resolution magnetic suspension balance, the authors do not supply details of calculations. The gravimetric method is very sensitive to the corrections required by the buoyancy effect of all the components [22,25]. However, there is no mention about evaluating these corrections and the accurate volume of the samples, by measurements in helium.

The survey of many carbon and MOF adsorbents shows that excess hydrogen adsorption depends linearly on surface area (Chahine's rule) and micropore volume (<2 nm) at cryogenic conditions [26,27]. However, the excess adsorption at high pressures (35 MPa), beyond the linear Henry's law region of adsorption isotherm, no such trend was observed and the surface coverage (excess uptake normalized to the surface area) correlates with the volume of micropore smaller than 0.8 nm, also normalized to surface area [28].

Because grinding and ball milling procedures imply rather different mechanical energies to which the material is subjected, the later depending strongly on the ball milling parameters, it is reasonable to assume that the energy during different ball milling conditions can greatly influence not only the intimate contact between the MOF and catalyst, but also the textural characteristics which strongly affects the hydrogen adsorption. In our knowledge, no systematic reports are available for hydrogen adsorption dependence on the ball milling energy of such composites. The purpose of this work is to study the effect of ball milling within a large range of ball milling energies on the characteristics of HKUST-1:Pt/AC mixture and their hydrogen adsorption. It seemed also interesting to compare the effect of ball milling with that of compression, which also transfers mechanical energy to the sample [29].

2. Experimental methods

2.1. Materials

Copper(II) nitrate trihydrate was purchased from Scharlau, benzenetricarboxylic acid from Alfa Aesar and platinum/charcoal activated (10 wt.% Pt) from Merck.

2.2. HKUST-1 synthesis

HKUST-1 was synthesized by a patented microwave assisted procedure [30]. The reaction mixture, obtained by dissolution of copper nitrate trihydrate (3.85 g, 16.1 mmol) and trimesic acid (1.92 g, 9 mmol) in dimethylformamide (25 ml), ethanol (25 ml) and water (25 ml), was loaded in a Teflon pot, adapted to the coaxial geometry of the unimodal treatment precincts of the device for the microwave power treatment. Then, microwave irradiation (360 W, 70 °C, 10 min) was started. After the completion of the process, the mixture was allowed to cool at room temperature and the solvent mixture was decanted off. For activation the as synthesized form of the HKUST-1 was suspended for 6 days in dimethylformamide (DMF). The solvent was replaced by fresh solvent after each 24 h. After that the blue solid was filtrated and dried in oven at 100 °C. Yield: 1.25 g (47%). Finally, HKUST-1 was thermally activated in vacuum for 24 h at 473 K.

2.3. Ball milled composites preparation and hydrogen adsorption measurements

The entire procedure was conceived to allow in situ hydrogen adsorption measurements between successive ball milling steps at increasing energies of a starting mixture HKUST-1 and Pt/AC. These composites differ from each other by the transferred energy during the milling process at the different rates.

For this purpose was designed and built a special vial (pot) for ball milling, made from stainless steel, with inner diameter of 25 mm, endowed with a valve suitable for tight sealing and connecting to the hydrogen sorption measurement device. This vial allows preparing of composites through milling and measurement of their hydrogen adsorption properties without opening it and avoiding in this way any possibility of contamination. Planetary Ball Mill Retsch PM 400 was utilized for ball milling processes.

Hydrogen adsorption measurements of the mixture (without ball milling) were performed at 298 K with high purity hydrogen (99.9999%) using a home-made Sievert's type device with two 5 digits electronic manometers and following the cautions recommended in literature [22,25] using the same protocol described in detail in literature [13]. The volumes of the sample cell (empty and with sample) were calibrated with helium. The hydrogen adsorption for each step was calculated with the hydrogen equation of state [21], with the overall error ±0.01 wt.% H_2.

In these experiments 0.85 g of HKUST-1 and 0.15 g of Pt/AC were introduced, without mixing, within the vial containing 5 stainless steel balls of 8 mm diameter (2.08 g). The sealed vial was connected to the Sievert apparatus, activated for 20 h at 473 K and 2×10^{-5} mbar and hydrogen adsorption measured. After measurements on this un-milled sample (designated BM-0), hydrogen was evacuated, 0.3 MPa helium introduced and the vial was subjected to ball milling for 1 h at a revolution rate of 100 rpm. Than the vial was reconnected to the Sievert's unit and thermally activated in the same conditions as above, not before the helium evacuation, and hydrogen adsorption measured. This composite was designated BM-100. The entire operation made for BM-100 preparation was repeated for two more times with different milling parameters: 250 rpm for 2 h and 400 rpm for 1 h, thus obtaining the composites designated BM-250 and BM-400, respectively.

In order to evaluate the effect of each step, separate ball milling experiments were performed in the same ball milling conditions, extracting samples after each step for XRD, FTIR spectra and nitrogen adsorption for porosity characterization.

2.4. Compressed pellets preparation

Compressed pellets were prepared by uniaxial compression of 0.1–0.12 g powder in a cylindrical die of 10 mm inner diameter with a hydraulic press. The bi-component pellet was prepared from HKUST-1 and Pt/AC manually mixed for homogenization before compaction. The density of pellets was evaluated accurately on the degassed samples, after the adsorption experiments.

2.5. Materials characterization

The powder X-ray diffraction (PXRD) was performed with a Bruker D8 Advanced diffractometer with Cu Kα radiation (40 kV, 40 mA). An aluminum sample holder was used for recording of the diffraction pattern of HKUST-1 pellet (noted CH). FT-IR spectra of the samples were recorded using a Jasco FT/IR 6100 spectrometer. The surface area and pore volume were obtained from nitrogen