

MOF-5 및 마이크로다공성 카본의 수소 저장 성능: Pt 첨가 및 하이브리드화의 영향

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Hydrogen Storage Capacities of MOF-5 and Microporous Carbon: Effects of Pt Loading and Hybridization

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ABSTRACT

최근 수소 저장물질로서 금속-유기 골격체(metal-organic frameworks; MOFs)가 주목을 받고 있으나 상온에서의 수소 저장성능이 낮은 문제점을 가지고 있어 이를 개선하기 위한 노력들이 필요하다. 본 연구에서는 MOF-5 및 제올라이트 Y로부터 합성된 마이크로다공성 카본을 합성하여 상온 및 약 80 bar에서 수소 저장성능을 측정하였으며, 그 결과 이들의 수소 저장성능은 각각 0.77 및 0.59 wt%였다. 이에 두 물질의 수소 저장성능을 향상시키기 위하여 5 wt% 백금을 각각의 물질에 담지시켜 백금이 없는 물질에 비하여 1.21 내지 1.25배의 개선 효과를 얻을 수 있었다. 한편 수소 spillover 현상을 활용하기 위하여 MOF-5 및 Pt/마이크로다공성 카본을 sucrose와 함께 탄화시킨 결과, 최종 하이브리드 물질이 상온 및 약 82 bar에서 0.93 wt%의 수소 저장성능을 보였으며, 이는 백금에 의하여 흡착된 수소 원자가 MOF-5 및 마이크로다공성 카본으로 이동하여 저장되는 것으로 해석된다.

KEY WORDS : MOF-5(금속-유기 골격체-5), Microporous carbon(마이크로다공성 카본), Hydrogen storage(수소저장), Spillover(스필오버), Hybrid material(하이브리드 물질).

1. Introduction

Hydrogen has been considered as an ideal energy for replacing fossil fuel to relieve the global environmental issues because it is nonpolluting and forms water as a harmless

by-product during its use. In comparison with H₂ production technology well developed so far, an effective and cheap H₂ storage system is indeed required for the future use of hydrogen as a pollution-free energy carrier. The current available technologies for hydrogen storage include physical storage via compression or

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liquefaction, chemical storage in irreversible hydrogen carriers, reversible metal hydrides, and porous adsorbents. Chemical storage generally needs conversion process which makes the system more complicated. Storage by metal hydrides has the advantage of low pressure, but the storage system is heavy and additional heating is needed for hydrogen release. Hydrogen storage by porous adsorbents represents a potential strategy for effective and relatively safe hydrogen storage. Porous materials can store considerable quantities of hydrogen at low temperature due to their light weight, high surface areas and ability to physisorb molecular hydrogen.

High-surface-area carbon is one of solid materials that could potentially store significant amounts of hydrogen. The advantages of carbon for hydrogen storage are a well-defined surface with low density and chemical inertness. Carbon materials adsorb hydrogen at extremely low temperatures. Adding metals to the system will significantly increase the hydrogen uptake.

Another solid material that can be used for hydrogen storage is metal-organic frameworks (MOFs). In recent years, MOFs have received a great deal of attention as a new class of porous materials, showing extremely high surface areas (up to 4500 m²/g) and specific micropore volumes. Moreover, such MOFs have exhibited promising gas-storage capacities for hydrogen, carbon dioxide and hydrocarbons, combined with high chemical inertness and thermally robust behavior. However, MOFs have shown low hydrogen storage capacity at room temperature.

It has been recently reported that the hydrogen storage capacity in MOFs and carbon materials can be increased by loading noble metal and/or combining these two materials

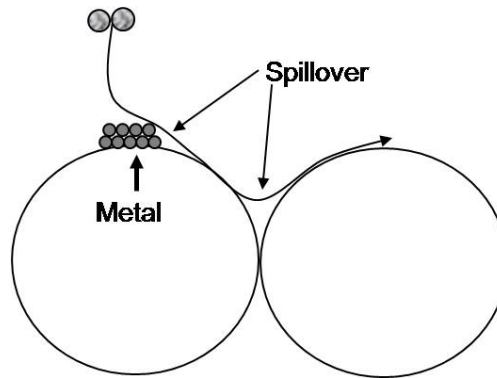


Fig. 1 Spillover process from a metal surface to a support; and then onto another surface in contact with the support⁴⁾

using physical bridges to increase the contacts and facilitate secondary spillover¹⁻³⁾. Spillover was found to be involved in many surface reactions and transport phenomena, schematically depicted in Fig. 1. The concept of secondary spillover in hydrogen storage materials consisting of a metal and a support can be used to increase the storage capacity. Therefore, that the hydrogen storage capacities by combining MOF with metal supported on carbon as the matrix is promising.

In this study, we report the synthesis of MOF-5 and carbon, and their application for hydrogen storage at room temperature. In more detail, the hydrogen storage capacities on MOF-5, Pt/MOF-5, microporous carbon (MC), Pt/MC and a hybrid material with 5 wt% Pt/MC and MOF-5 were observed.

2. Experimental

2.1 Synthesis of MOF-5

Crystals of MOF-5 were synthesized using terephthalic acid and zinc nitrate, and diethylformamide as the organic solvent, following the literature method⁵⁾.

2.2 Synthesis of microporous carbon using zeolite Y as a hard template

The microporous carbon (MC) was prepared by using zeolite Y as a template⁶⁾. Dry zeolite-Y (Na-form) was impregnated with furfuryl alcohol (FA), yielding FA/zeolite composite. FA was polymerized in the zeolite channels by heating the composite at 150 °C under N₂ flow. The obtained polyfurfuryl alcohol (PFA)/zeolite composite was treated at 700 °C to carbonize the polymer in the zeolite channels and then propylene gas (2.0% in N₂) was introduced for 4 h, resulting in pyrolytic carbon deposition in the channels. The prepared zeolite/carbon composite was then subjected to propylene-CVD with further heat-treatment at 900 °C for 3 h under N₂ flow to fill carbon into the zeolite channels as much as possible. After the propylene-CVD step, the zeolite template was removed by aqueous HF and HCl solution, finally producing microporous carbon as an insoluble fraction.

2.3 Pt loading on MOF-5 and carbon

2.3.1 Pt loading on MOF-5

The loading of platinum on MOF-5 was carried out via incipient wetness impregnation of a platinum precursor (Pt(acac)₂, acac = acetylacetonate) dissolved in chloroform²⁾. Then the Pt(acac)₂/MOF-5 was reduced using 20% hydrogen flow, yielding Pt/MOF-5.

2.3.2 Pt loading on MC

For doping 5 wt% platinum onto MC, a literature method⁷⁾ is followed. Pt was doped by liquid-phase impregnation augmented by ultrasonication. H₂PtCl₆ was used as the platinum source and dissolved in acetone to

facilitate impregnation. After the H₂ reduction process, Pt/MC was finally obtained.

2.4 Hybridization of bridges samples

Carbon bridges between the carbon and MOF-5 were produced by carbonization of sucrose introduced into the physical mixture of two components. The MOF-5/sucrose/MC weight ratio was 8:1:1, based on the complete carbonization of the precursor. The mixture was ground together, and then subjected to the heat treatment as described in the previous paper⁸⁾.

2.5 Characterization

Power X-ray diffraction (XRD) pattern was recorded on a Rigaku D/MAX-2500 diffractometer at 30 kV and 100 mA for Cu K α (λ = 0.1453 nm). Brunauer-Emmett-Teller (BET) isotherms were measured on a Micromeritics ASAP 2010 sorptometer using N₂ adsorption at 77 K. The field emission scanning electron microscopy (FE-SEM) images of the materials were obtained on a Hitachi S-4100 analytical electron microscope. The thermogravimetric analysis (TGA) was performed using a TA Instruments 2050 TGA V5.4A. The FT-IR spectrum was obtained on a Thermo Mattson Infinity Gold FTIR 60 AR.

2.6 H₂ adsorption measurement

The hydrogen adsorption measurement was performed using a static volumetric method⁹⁾. Prior to the hydrogen adsorption measurement, all adsorbents were treated in vacuum oven at 200 °C for 12 h to eliminate physisorbed and/or trapped molecules. The adsorption equilibrium state was considered to occur when the temperature and pressure of the cells were

constant. The amount adsorbed was calculated using a mass balance derived from the generalized equation of state obtained before and after adsorption equilibrium.

3. Results and Discussion

3.1 H₂ adsorption on MOF-5

MOF-5 consists of four ZnO₄ tetrahedra sharing an oxygen atom in the center of an octahedral Zn₄O(CO₂)₆ subunit¹⁰. Each metal-carboxylate cluster is connected by benzene groups to its nearest neighbours in a cubic porous framework. MOF-5 was prepared of zinc nitrate tetrahydrate with terephthalic acid in diethylformamide (DEF). The product was washed with N,N'-dimethylformamide (DMF) to remove unreacted materials. A solvent exchange between DMF and chloroform was then performed.

Figure 2 shows the XRD patterns of as-synthesized and solvent-free MOF-5, indicating that the crystalline structure remains intact after the solvent removal and the sharp peak represents high crystallinity of MOF-5. The solvent-free MOF-5 was then characterized by FT-IR, TGA, SEM and BET analyses. As shown in Fig. 3a, all the solvent was completely removed from the MOF-5 framework due to negligible peak at 2941 and 2870 cm⁻¹ characteristic of DEF. In addition, the TGA curve of MOF-5 upon heating in N₂ revealed that MOF-5 is thermally stable up to 400 °C (Fig. 3b). The morphology and N₂ physisorption isotherm of MOF-5 were investigated by SEM and BET analyses. As shown in Fig. 3c, MOF-5 crystals were typically cubic-shaped with the size of approximately 500 nm. It is presented in Fig. 3d that the N₂ adsorption isotherm follows a

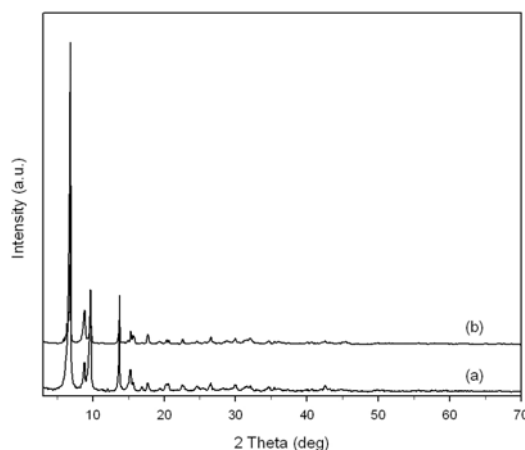


Fig. 2 XRD patterns of (a) as-synthesized MOF-5 and (b) solvent-free MOF-5

Type I isotherm according to the IUPAC classification, indicative of the microporous material. The BET and Langmuir surface areas of MOF-5 were 2970 and 3064 m²/g, respectively.

The hydrogen adsorption measurement was performed using a static volumetric method. In detail, the hydrogen uptake at 298 K was measured by introducing H₂ gas into the cell chamber containing the solid sample and subsequently monitoring the pressure change with H₂ dose increasing. As shown in Fig. 4, MOF-5 showed a substantial H₂ uptake which increased linearly with the pressure, meaning that hydrogen monolayer is formed on the surface of MOF-5. At 93 bar and 298 K. H₂ uptake of MOF-5 prepared in this study was about 0.77 wt%.

On the other hand, platinum metal was loaded into MOF-5 to enhance the hydrogen uptake. As a result, Pt/MOF-5 showed H₂ uptake of 0.99 wt% at 97 bar and 298 K (Fig. 4), which is higher than that of pure MOF-5. Therefore, it is considered that the doping of platinum into MOF-5 enable hydrogen molecules to adsorb

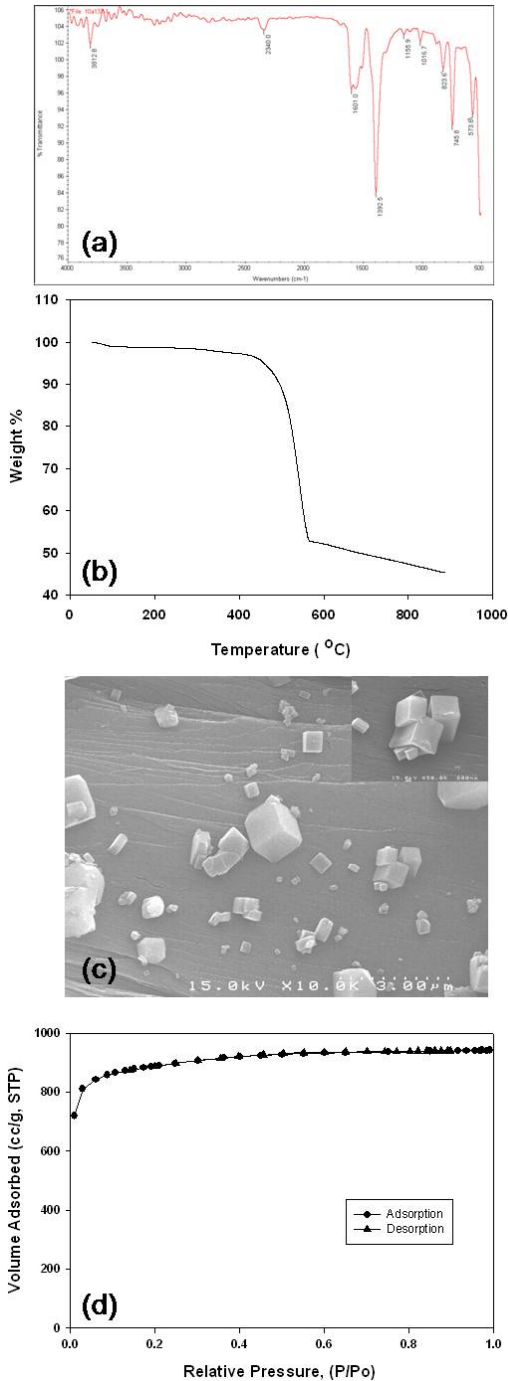


Fig. 3 Characteristics of MOF-5. (a) FT-IR spectrum, (b) TG curve, (c) SEM image and (d) N₂ physisorption isotherm

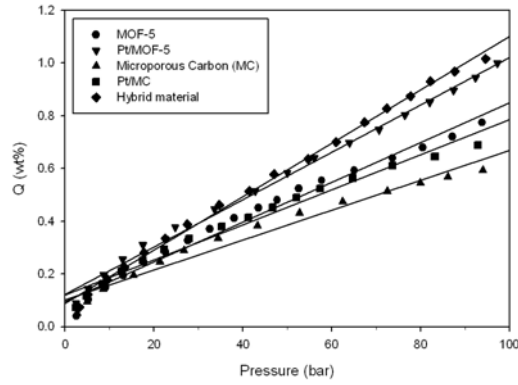


Fig. 4 Hydrogen adsorption capacities of MOF-5, Pt/MOF-5, MC, Pt/MC and hybrid material at 298 K

dissociatively and spill over effectively to the outed and inner surface of MOF-5.

3.2 H₂ adsorption on carbon

An microporous carbon that preserves the structural regularity of zeolite Y has been prepared by carbonization technique using zeolite Y as a template. It is well known that zeolite Y consists of a tetrahedral network structure of sodalite units which results in a large cavity with a diameter 1.2 nm. Each supercage is connected to four other supercages by an opening with a diameter 0.7 nm.

Figure 5 depicts the synthetic methodology of carbon starting from zeolite Y. The preparation of microporous carbon was attempted by filling

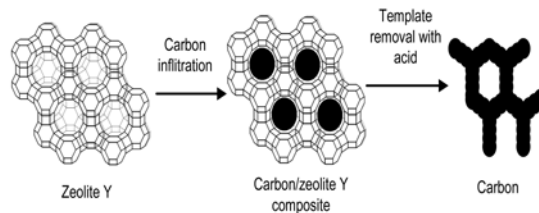


Fig. 5 Schematic of carbon synthesis by zeolite templating

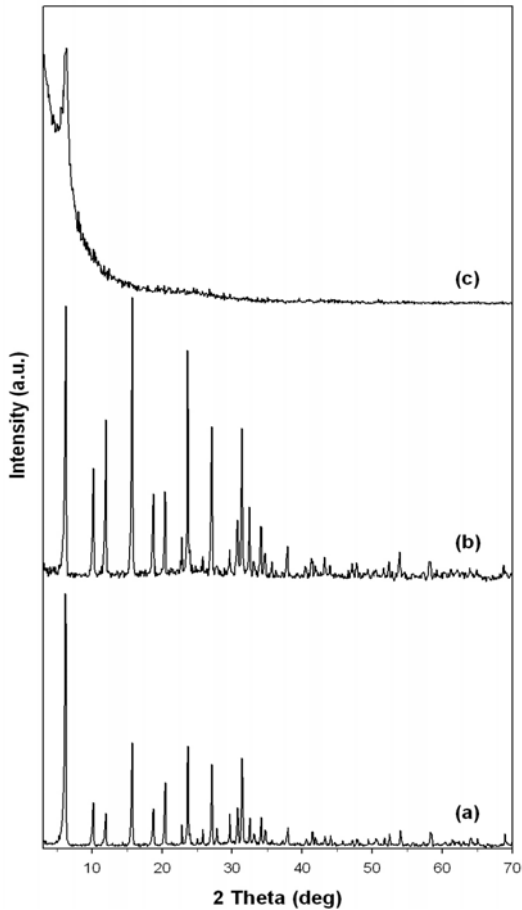


Fig. 6 XRD patterns of (a) zeolite Y, (b) carbon/zeolite Y composite and (c) microporous carbon

as much carbon as possible into the channels of zeolite Y by FA impregnation and propylene CVD, followed by the removal of template through HF and HCl treatment.

Figure 6 shows the XRD patterns of the original zeolite Y, carbon/zeolite Y composite, and microporous carbon. When compared to the XRD patterns of the first two samples (Figs. 6a vs. 6b), the framework of zeolite Y with the strongest 2θ peak of 6.24° was kept intact even upon the carbon filling processes at high temperature. In addition, the XRD pattern of microporous carbon shown in Fig. 6c represents

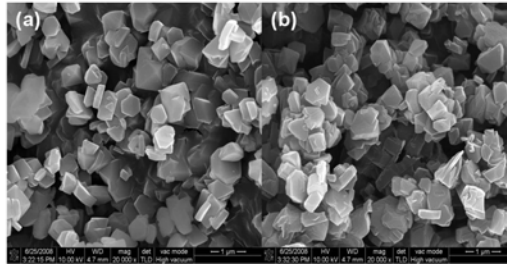


Fig. 7 SEM images of (a) zeolite Y and (b) microporous carbon

a sharp peak at $2\theta = 6.3^\circ$, indicating that the pore structure of carbon resembles that of zeolite Y, as well as a broad peak observed in the 2θ range of $23\text{--}27^\circ$ due to the poor crystallinity of carbon. It was also observed that there is no apparent difference in morphology between zeolite Y and carbon, as shown in Fig. 7. In terms of N_2 physisorption isotherms of zeolite Y and microporous carbon (Fig. 8), both materials follow a Type I isotherm suggesting the development of microporosity. Calculated from these isotherms, the BET surface area is $906\text{ m}^2/\text{g}$ for zeolite Y and $3606\text{ m}^2/\text{g}$ for microporous carbon.

As performed in MOF-5, platinum was doped

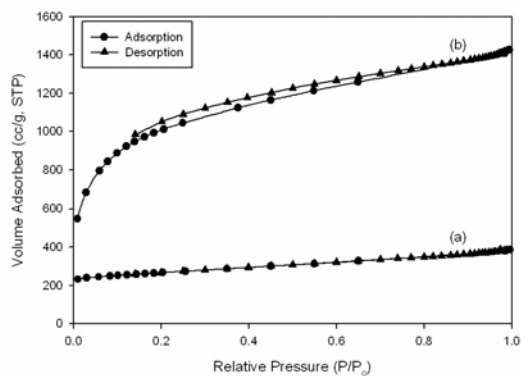


Fig. 8 N_2 adsorption-desorption isotherms of (a) zeolite Y and (b) microporous carbon

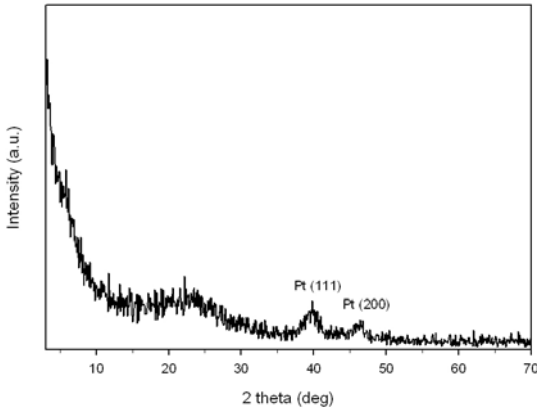


Fig. 9 XRD pattern of Pt/MC

into microporous carbon (MC) by liquid-phase impregnation augmented with ultrasonication, where H_2PtCl_6 was used as Pt source. In the XRD pattern of Pt/MC presented in Fig. 9, two broad XRD peaks at 2θ of 39° for Pt(111) and 46° for Pt(200) were observed, which is characteristic of the cubic Pt metal particle.

Finally, The H_2 storage capacities of MC and Pt/MC were measured using the same technique applied for MOF-5 and Pt/MOF-5. As a result, MC showed H_2 uptake of 0.59 wt% at 298 K and 94 bar and Pt/MC 0.68 wt% at 298 K and 92 bar (Fig. 4). Although these H_2 uptakes are lower than those of MOF-5 and Pt/MOF-5, Pt loading into microporous carbon can indeed increase H_2 uptake, same as the case of MOF-5.

3.3 H_2 adsorption on hybrid material

In order to increase hydrogen storage capacity at room temperature, the hydrogen spillover process was undertaken using hybrid material. Physical mixture of Pt-carbon with MOF-5 would facilitate H_2 spillover. Here, Pt-carbon was the primary receptor for hydrogen spillover, and MOF-5 as the secondary spillover receptor

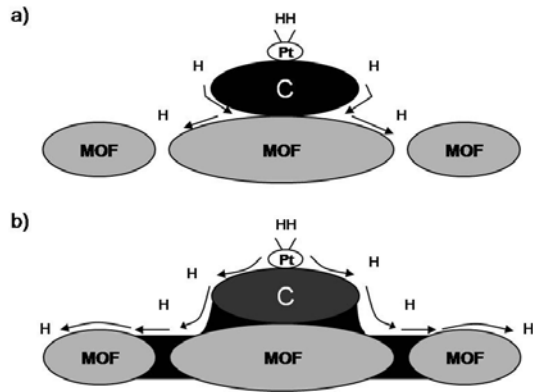


Fig. 10 (a) Spillover of atomic hydrogen from Pt to the carbon support and secondary spillover to the MOF receptor. (b) Carbon bridges facilitated spillover on carbon and secondary spillover on MOF⁸⁾

(Fig. 10). The process includes the dissociative adsorption of hydrogen molecules on Pt metal and subsequent spillover to its support, where the carbon bridge would help hydrogen atoms to spillover to the porous material¹¹⁾.

Secondary spillover requires intimate contacts between the two materials. The bridge building technique could increase the contact of two materials and hence facilitate secondary spillover. In this study, carbon bridges were formed by carbonization of sucrose as a precursor that was introduced into a physical mixture of the MOF-5 and Pt/MC, consequently producing a hybrid material.

To determine the spillover-involved effect on hybrid material, the hydrogen adsorption capacity was measured under the same condition utilized for MOF-5 and MC. The H_2 uptakes of all samples prepared in this study were summarized in Table 1, where similar measurement pressures were chosen for comparison. As can be seen in Fig. 4 and Table 1, the hybrid material showed the hydrogen storage capacity of 1.01 wt% at 298 K and 94

Table 1 H₂ adsorption capacities of samples prepared in this study*

	H ₂ adsorption capacity	Pressure
	(wt%)	(bar)
MOF-5	0.68	80.5
Pt/MOF-5	0.77	93.8
	0.85	82.1
MC	0.94	92.4
	0.54	80.0
Pt/MC	0.59	94.1
	0.65	83.2
Hybrid material	0.68	92.9
	0.93	82.2
	1.01	94.6

*Temperature for measuring H₂ uptake: RT

bar which is higher 1.1 and 1.45 times than those of Pt/MOF-5 and Pt/MC, respectively. Therefore, it would be believed that the H₂ storage capacity is enhanced via the secondary spillover of H atoms to MOF-5 as secondary receptor. Furthermore, as shown in Fig. 4, there is no apparent saturation value as the H₂ uptake is in a linear relationship with the pressure, suggesting that further increase in the H₂ adsorption capacity of hybrid material can be expected at more than 100 bar.

4. Summary

In this study, we demonstrated that, although hydrogen molecules can be adsorbed onto the adsorbent such as MOF and MC itself, the loading of noble metal such as Pt is necessary to enhance the H₂ storage capacity since H₂ molecules can be dissociatively adsorbed on Pt metal and migrated to high-surface-area adsorbent via the primary spillover.

In addition, the hybrid material have been prepared coupling MOF-5 with Pt/MC through carbon bridges formed by sucrose polymerization/carbonization. That this material showed the

highest H₂ uptake at room temperature and about 100 bar is believed to be associated with the secondary spillover effect. Thus, such a strategy is very promising in developing H₂ storage technology using porous adsorbents. However, further experiments should be carried out to explore the choice of bridge carbon, the hybridization method, the dispersion technique of noble metals, etc.

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