Hydrogen adsorption properties of platinum decorated hierarchically structured templated carbons

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A B S T R A C T

In this report, the possibility of Pt catalytic activity for the dissociation of hydrogen molecules and subsequent hydrogen adsorption on sucrose templated carbon at ambient temperature has been studied. In order to investigate Pt catalytic effect for hydrogen storage solely, 6.8 wt.% Pt-doped (Pt/TC) and pure templated carbon (TC) possessing almost identical specific surface area (SSA) and pore volume (Vp) have been successfully synthesized. Since both Pt/TC and TC shares for their textural properties (e.g. SSA and Vp), any difference of hydrogen adsorption characteristic and storage capacity can be ascribed to the presence of Pt nanoparticles. Both samples are characterized by various techniques such as powder X-ray diffraction, ICP-OES, Raman spectroscopy, transmission electron microscopy, cryogenic thermal desorption spectroscopy, low-pressure high-resolution hydrogen and nitrogen BET and high-pressure hydrogen adsorption isotherms in a Sieverts’ apparatus. By applying hydrogen and deuterium isotope mixture, cryogenic thermal desorption spectroscopy point to a Pt catalytic activity for the dissociation of hydrogen molecules. Furthermore, the hydrogen adsorption isotherms at RT indicate an enhancement of the initial hydrogen adsorption kinetics in Pt-doped system. However, the hydrogen storage capacity of Pt/TC exhibits a negligible enhancement with a strong hysteresis, suggesting no connection between the spillover effect and a feasible hydrogen storage enhancement.

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1. Introduction

Concerning climate change, resource depletion and energy security, a growing pressure exists to search for a replacement for fossil fuels. Among various sustainable energy sources, hydrogen has been concerned as a clean energy carrier especially for mobile applications. Although hydrogen has an excellent gravimetric energy density of around 142 MJ/kg, the volumetric energy density is very low compared to current fuels (e.g. 1 kg of H2 required 11 m³ at STP) [1]. Therefore, the efficient storage of hydrogen is the bottleneck for moving to a future hydrogen economy including the on-board hydrogen storage media. Unfortunately, current technology for mobile application such as very high pressure (~700 bars) or cryogenic liquid storage suffer from major safety and low efficiency obstacles [2]. One promising approach to overcome these obstacles is to store hydrogen into solid state materials via either physical [3,4] or chemical methods [5]. In recent years, the development of microporous and mesoporous materials, such as activated carbon and metal organic frameworks, for physisorption have emerged as promising technique for cryogenic hydrogen adsorption tank systems, since the gravimetric hydrogen storage capacity at 77 K under moderate pressure already reached industrial demands for mobile applications [6]. However, in the case of hydrogen storage at room temperature, the physisorption mechanism is not able to achieve enough capacity for practical application due to the weak van der Waals interaction, i.e., low isosteric heats for hydrogen sorption. For increasing the interaction, various methods such as incorporating a high number of unsaturated metal centers, ligand exchange and metal doping have been proposed for enhancing the hydrogen storage capacity [7–11]. Recently, as a part of this, feasible hydrogen storage method at room temperature has been proposed by Yang et al., which ascribes hydrogen sorption enhancements to the so-called “spillover” effect [12,13].

‘Hydrogen spillover’ is well-known phenomenon in catalysis, which the dissociative chemisorption of hydrogen molecules on metal nanoparticles, followed by migration of atomic hydrogen into the high surface area support. In case of hydrogen storage applications, however, this storage enhancement mechanism by decoration of noble metal particles inside high surface area
supports is not yet fully understood and still under debate [14–20] due to the absence of a consistent microscopic picture. Furthermore, measurements of the hydrogen storage capacity scatter from an enhancement of several times to negligible within the experimental uncertainty, which may be caused by different textural properties after metal doping as reduced pore volume and specific surface area. Additionally, other reactions can occur since the metal nanoparticles may be oxidized [21] or residual organics exist from noble metal precursor [22] or an variation of H2 interaction properties at unsaturated atomic site inside carbon support [14,16]. For that reason, a metal doped and pure support possessing same textual properties might be desired in order to minimize undesirable effects and to clarify the influence of the spillover effect on hydrogen storage. Recently both Blackburn et.al., and Puja et.al., have reported spectroscopic (DRIFTS and Raman) evidence of "spiltover" hydrogen atoms on a carbon surface, but with only modest (<15%) enhancements of sorption [10,23].

In this report, Pt-doped (Pt/TC) and pure templated carbon (TC) possessing almost identical specific surface area (SSA) and pore volume (Vp) have been successfully synthesized, showing one of the very rare examples possessing identical textural properties despite of Pt decoration. This enables the study of Pt catalytic activities, dissociation of hydrogen molecules and hydrogen adsorption kinetics on sucrose templated carbon (TC) at ambient temperature by using various analysis techniques.

2. Experimental section

2.1. Preparation of the carbon materials

The mesoporous carbon in this work has been synthesized by templating of a mesoporous silica, which in turn was obtained by a microemulsion-templated method as described elsewhere [24]. Procedure details of mesoporous carbon synthesis are also shown in Scheme 1 and in the Supporting information. The hierarchically porous particles of silica, which served as the template of the carbon, have been obtained by procedure described by Carroll et al. [24] at UNM in a 5 g powder batch and used as described below. The silica template was impregnated with an aqueous solution of sucrose and sulfuric acid. After all solution was added to the silica particles, they were dried at RT overnight. Next day, a heat treatment was performed in oven at 100–150°C under air. In case of Pt decorated carbon preparation, aqueous solution of chloroplatinic acid hexahydrate, sucrose and sulfuric acid was additionally added to achieve an 8 wt.% Pt infiltration into the sample. This was followed by pyrolysis at 800°C at nitrogen atmosphere for 4 h, with a heating rate of 3°C per min. After pyrolysis, the silica template was removed by dissolving (etching) in 6 M KOH for 4 days. The material was then filtered, washed 8 times with DI water, and dried in the oven at 70°C overnight.

2.2. Characterization

2.2.1. ICP-OES analysis

The precise Pt amount was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The determined Pt content in carbon sample was 6.8 ± 0.4 wt.% which is in good agreement with stoichiometric input of Pt prior to the synthesis (8 wt.%).

2.2.2. X-ray diffraction patterns

The crystal structure of pure carbon (TC) and Pt@carbon (Pt/TC) were identified by powder X-ray diffractometer (PXRD) using Cu
Kα radiation. Measurements were carried out in transmission mode and by using glass capillaries.

2.2.3. Transmission electron microscopy measurements

Transmission electron microscopy (TEM) images were acquired using a FEI Tecnai G2 operated at 200 kV. High resolution scanning transmission electron microscopy (HRSTEM) images as well as the energy-dispersive X-ray spectroscopy elemental maps were collected using a FEI Titan 80–300 microscope operated at 300 kV and equipped with EDAX retractable Si(Li) X-ray detector and aberration-correctors for the imaging lens and the probe forming lens. Samples were prepared by dispersing the powder in ethanol, and placing several drops of the dispersion onto a holey carbon grid. Electron tomography was performed by collecting a tilt series of 2-dimensional images using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) over an angular range of ±70° with 2° tilt increments. After alignment, a 3-dimensional reconstruction was obtained using the simultaneous iterative reconstruction technique (SIRT) implemented in the FEI Inspect3D software package. Amira 5.2.1 (Visage Imaging GmbH) was used to obtain the volume renderings of the tomogram in order to provide 3-D visualizations of the reconstructed data. The movie of the volume rendered tomogram can be found in the Supporting information.

2.2.4. N2 BET measurement

Specific surface area measurements at 77 K were carried out using Quantachrome Autosorp-1 MP instrument with N2 gas using optimized protocols, the TC and Pt/TC samples (~100 mg) were priorly degassed at 420 K for overnight. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method. The total pore volume and the micropores volume were computed from the density functional theory (DFT) method and the MP micropore method, respectively. The pore size distribution (PSD) was obtained from the adsorption branch of the nitrogen isotherm using the non-local density functional theory (NLDFT).

2.2.5. Cryogenic H2 BET measurement

The hydrogen adsorption isotherms of TC and Pt/TC at 19.5 K was measured with laboratory-designed volumetric adsorption equipment with temperature controlled cryostat and is described in details elsewhere [25]. Around 20 mg of TC and Pt/TC was activated under ultra-high vacuum at 420 K for overnight prior to each measurement. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method. The specific pore volume (SPV) was calculated according to Gurvich’s rule [26].

\[
SPV = \frac{n_{\text{max}}}{\rho_{\text{liq}}}
\]

where \(n_{\text{max}}\) is the maximum uptake per material mass before liquefaction and \(\rho_{\text{liq}}\) is the density of the liquid.

2.2.6. Thermal desorption spectroscopy (TDS)

An in-house designed experimental set-up, previously described [27], was rebuilt and further improved. The sample chamber is a UHV chamber where the sample holder is screwed tightly to a Cu block, which is surrounded by a resistive heater, and can be connected to a cold finger of a flowing helium cryostat, which allows cooling to 20 K. The TC and Pt/TC powder were activated at 420 K. For the thermal desorption experiment the sample was exposed to a 10 mbar 1:1 H2/D2 isotope mixture at room temperatures. Afterwards, it was cool down to 30 K and the gas molecules that had not been adsorbed were pumped out until HV is reached again. Then the sample was heated with a rate of 0.1 K/s from 30 K to 140 K and the desorbing gas was continuously detected by a quadrupole mass spectrometer.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Initial sample mass</th>
<th>Final sample mass</th>
<th>Skeletal density</th>
<th>(H_2) uptake at RT, 20 bar</th>
<th>(H_2) uptake at 77 K, 20 bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC</td>
<td>138 mg</td>
<td>129 mg</td>
<td>1.88 g/cm³</td>
<td>0.29 ± 0.01 wt.%</td>
<td>2.2 wt.%</td>
</tr>
<tr>
<td>Pt/TC</td>
<td>138 mg</td>
<td>127 mg</td>
<td>2.04 g/cm³</td>
<td>0.30 ± 0.02 wt.%</td>
<td>2.2 wt.%</td>
</tr>
</tbody>
</table>

**Fig. 1.** PXRD patterns of (a) Pt/TC and (b) TC.
2.2.7 Hydrogen-adsorption/desorption measurements

The automated Sievert’s type apparatus (PCTPro-2000) was used with a so-called micro-doser (MD) from HyEnergy. The adsorption and desorption isotherms (0–20 bar) were measured at 298 K and 77 K (liquid nitrogen) in a sample cell volume of ≈1.3 ml using ultra high purity hydrogen gas (99.999%). Before the hydrogen-uptake measurements, the 138 mg of TC and Pt/TC were loaded into the sample cell and were heated for several hours at 150 °C in vacuum (4.5 × 10⁻³ bar) in order to remove any adsorbed gas from the surface. After activation and the adsorption measurements, the final sample mass was determined to 129 mg (TC) and 127 mg (Pt/TC), respectively (see Table 2), and these values were used to calculate the uptake in wt.%.

In order to quantify uncertainty in H₂ isotherm at RT, TC and Pt/TC samples are measured three times in adsorption and desorption (see Figs. S4 and S5, SI) under identical P, T condition. From these six values, the standard deviation is calculated and is used for an error bar in H₂ isotherm at RT. The uncertainty of the measurement at RT is therefore given by:

\[
\text{StdDev}(P,T) = \sqrt{\frac{(1\text{st measurement} - \text{average})^2 + (2\text{nd measurement} - \text{average})^2 + (3\text{rd measurement} - \text{average})^2}{N_{P,T}}} \]

Average \( (P,T) = \frac{(1\text{st measurement} + 2\text{nd measurement} + 3\text{rd measurement})}{N_{P,T}} \)

where function “sqrt(·)” denotes to non-negative square root of its argument. Hence, our experimental set up provides less than
0.01 wt.% and 0.02 wt.% reproducible precision for TC and Pt/TC, respectively.

To remove an influence of the temperature gradient between cooled sample cell (77 K) and gas reservoir with pressure transducer (298 K) during isotherm measurement at 77 K, non-adsorbing samples (sea sand) possessing the same volume was measured under identical conditions. By subtracting these two measurements, the influence of the temperature gradient as well as systematic errors cancels out. Thus, the excess amount of hydrogen \( n_{\text{exc}}(p,T) \) adsorbed can be calculated by:

\[
n_{\text{exc}}(p,T) = n_{\text{experiment}}(p,T) - n_{\text{sea sand}}(p,T)
\]

The adsorbed amount is reported in wt.% which is defined as mass of hydrogen \( m_{\text{ads}} \) per mass of the system, which consists of the sample mass \( m_s \) and the adsorbed hydrogen.

\[
\text{Hydrogen uptake (wt.\%)} = \frac{m_{\text{ads}}}{m_s + m_{\text{ads}}}
\]

2.2.8. Raman spectroscopy

The Raman spectra were taken in backscattering geometry in aJobinYvon LabRam 1800 single-grating spectrometer equipped with a razor-edge filter and a Peltier-cooled CCD camera. We used a green laser with a wavelength of 532 nm for excitation. The laser beam was focused through a 50× microscope objective to a ~5 μm diameter spot on the sample surface.

3. Results and discussion

3.1. Sample characterization

PXRD patterns for the templated carbon (TC) and Pt-doped templated carbon (Pt/TC) are shown in Fig. 1. TC is amorphous, but after Pt impregnation, Pt(111), Pt(200), Pt(220), and Pt(222) peaks are clearly found at 2θ = 39.8, 46.3, 67.5, 81.3 and 85.8 in the XRD patterns. One should note that, in addition to the Pt Bragg peaks, a number of very low intensity can be observed in Fig. 1. From PXRD Rietveld refinement of Pt/TC, these low-intensity peaks are determined to be platinum silicide (Pt12Si5) as shown in Fig. S1, SI. Although platinum silicide (Pt12Si5) is detected, the amount of platinum silicide (Pt12Si5) is very small as Si was below the detection limit in the ICP-OES or EDX measurement (see details in Supporting information).

In Fig. 2, the Raman spectrum of TC, measured with an excitation of \( \lambda = 532 \text{ nm} \), shows two broad peaks centered at 1343 and 1596 cm\(^{-1} \), which can be assigned to the disorder induced C–C single bond (sp\(^3\) hybridization) (D-band) and the vibration of sp\(^2\) hybridized carbon (G-band), respectively. In addition, the peak of the G-band slightly shifts downwards by Pt decoration. Nevertheless, the almost identical Raman spectra of Pt/TC and TC show that any impurity effect or different surface chemical composition can be excluded for the study of Pt catalytic effect on \( \text{H}_2 \) storage capacity.

The textural properties of TC and Pt/TC were analyzed by nitrogen adsorption at 77 K. The nitrogen adsorption/desorption analysis and pore size distribution (PSD) of the TC and Pt/TC samples are shown in Fig. 3. In the sorption curve a small hysteresis occurs for both samples over a wide relative pressure range. A broad PSD (between 0.7 and 100 nm) of TC and Pt/TC can be seen as shown in Fig. 3 (inset). The Pt/TC exhibits an almost identical nitrogen uptake and a stronger hysteresis compared to pure TC. The nitrogen BET specific surface area (SSA) for TC and Pt/TC were 877 m\(^2\)/g and 882 m\(^2\)/g, respectively. This is unusual behavior since SSA and pore volume is generally decreased with metal nanoparticle insertion due to the space occupation by metal particles. Thus, there is a possibility that \( \text{N}_2 \) BET might not represent its textural properties since TC possesses micro porosity where nitrogen probe cannot reach. In this regard, the hydrogen BET is a good approach to determine the SSA and pore volume more accurately over the nitrogen BET since hydrogen molecule is much smaller. The hydrogen BET results for Pt/TC and TC are presented in Fig. 4 and Table 1. In order to determine the appropriate pressure range for microporous materials, two consistency criteria should be followed; (1) the straight line fitted to the BET plot must have a positive intercept, and (2) the pressure range should be chosen so that \( n_{\text{ads}}(1 - P/P_0) \) is always increasing with \( P/P_0 \) as shown in Fig. S3, SI. According to this approach, \( \text{H}_2 \) BET SSA of Pt/TC (1364 m\(^2\)/g) and TC (1306 m\(^2\)/g) can be calculated. Considering the difference in size between \( \text{N}_2 \) and \( \text{H}_2 \), the approx. 35% increase of SSA from \( \text{N}_2 \) BET to \( \text{H}_2 \) BET indicates the existence of numerous micropores smaller than nitrogen molecule size. Nevertheless, Pt/TC still exhibits comparable SSA and pore volume to TC and is one of the very rare examples of identical textural properties despite of Pt decoration.

![Fig. 3. Nitrogen sorption curves of TC (square black) and Pt/TC (circle red) at 77 K.](image)

![Fig. 4. Low-pressure high-resolution hydrogen adsorption (closed symbol) / desorption(open symbol) isotherm at 19.5 K for TC (square black) and Pt/TC (circle red).](image)
For a further understanding of the Pt distribution in the porous carbon, TEM study has been carried out (Fig. 5). Bright-field TEM (BFTEM) image reveals the presence of Pt particles that are dispersed throughout the carbon matrix (see Fig. 5a). In addition, it is seen that the size of the particles varies significantly through the matrix, and the large-sized particles often form agglomerates with each other (see Fig. 5a). Such agglomeration of the particles is observed to be less apparent when the size of Pt particles decreases (see Fig. 5b). Chemical information was obtained by elemental mappings with STEM/EDX analysis of the nanoparticles embedded in the porous matrix. The color-mix of both Pt and C elemental maps indicated the distribution of the nanoparticles in the matrix (see Fig. 5b). In addition, HRSTEM images (see Fig. 5c) prove that both smaller and bigger sized particles are single crystals. The lattice fringe spacing of the small sized particle estimated to be \(~2.3\,\text{Å}\), corresponding to the interplanar distance of the (111) planes of platinum.

The 3-dimensional dispersion of the Pt nanoparticles within the carbon matrix was investigated using electron tomography. In this study, high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was used to obtain the 2-dimensional projection images. Since the intensity in the projection images acquired using HAADF-STEM scales with the atomic number \(Z\) of the elements present in the sample, it is thus possible to obtain both structural and analytical information. As a result, an intensity difference is expected between the Pt nanoparticles and the carbon matrix. The visualization of the 3-dimensional reconstructions (see Fig. 6a) that were obtained for Pt nanoparticle loaded carbon
Fig. 7. Thermal desorption spectra of 1:1 H₂/D₂ mixture on (a) TC and (b) Pt/TC with heating rate 0.1 K/s. The signal of the mass spectrometer is normalized by the sample mass. H₂ (square black), HD (circle red) and D₂ (triangle blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 8. Excess hydrogen isotherm sorption curves of the TC (square black) and Pt/TC (circle red) at (a) 77 K and (b) RT; Filled symbol: adsorption and open symbol: desorption. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. Rate of adsorption for hydrogen on Pt/TC and TC at 298 K with various pressure; (b) ~1.2 bar, (c) ~3.3 bar and (d) ~5.5 bar versus full equilibrium time at each pressure.
matrix together with a slice through the reconstructed volume (see Fig. 6b and c) reveal how the particles are dispersed in the volume. It is seen that the smaller size particles are dispersed randomly, instead of forming agglomerates with each other within the matrix. This results in the appearance of Pt particles which are well embedded within the carbon matrix. In addition, it is seen that with an increase at the size of the particles, voids come into sight around the bigger size particles (see Fig. 6c). This can be interpreted as the embedded Pt particles are partially agglomerated inside meso-pore silica template before carbonization, and then play a role as a support inside cavity for suppressing any shrinkage during carbonization. Similar shrinkage observations were mentioned by various authors.[28–30] Consistently, the PSD graph in Fig. 3 (inset) also confirmed that (mostly) meso- and (small portion of) micro-pore volume of Pt/TC is increased (Fig. 3 inset region A and C), and consequently decreased micro-pore volume (Fig. 3 inset region B) by occupation of Pt particles. The movie of the volume rendered tomogram can be found in the Supporting information.

3.2. Hydrogen catalytic effect and storage capacity

From the results of PXRD and TEM analysis, it could be confirmed that Pt nanoparticles are successfully embedded within carbon matrix with same textual property of TC although agglomerated Pt also exists sometimes in mesopores. Aiming to further investigate the catalytic effect on hydrogen storage of the so called ‘spillover effect’, thermal desorption spectra (TDS) were recorded after cooling the samples from RT to 30 K in 1:1 hydrogen/deuterium isotope mixture (10 mbar). Before ramping, gas molecules that had not been adsorbed were pumped out of the sample chamber. Fig. 7 shows thermal desorption spectra after adsorption of a 1:1 H2/D2 mixture for TC and Pt/TC in range between 30 K and 140 K, recorded with a heating rate of 0.1 K s⁻¹. TDS spectra show distinct differences in the magnitude of the HD signal between TC and Pt/TC. A strong HD signal for Pt/TC is observed compared to TC (Fig. 7b). This can be an evidence of the catalytic activity of Pt by dissociation of H2 with strong hysteresis by chemical reaction. Table 2 summarizes a hydrogen capacity comparison of these two samples.

4. Conclusions

This study shows a synthesis method of Pt-doped (Pt/TC) and pure templated carbon (TC) possessing almost identical textual properties. By comparison of these materials, the possibility of hydrogen spillover is examined by various techniques. Furthermore, in these templated hierarchically structured carbons possessing small micropores, the hydrogen adsorption kinetics is enhanced by catalytic activity of Pt in the Pt-doped system. It appears, however, that dissociation of hydrogen on Pt leads to an irreversible chemisorption in the storage systems, suggesting limited connection between spillover effect and feasible room temperature hydrogen storage enhancement for these types of materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.micromeso.2013.04.020.

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