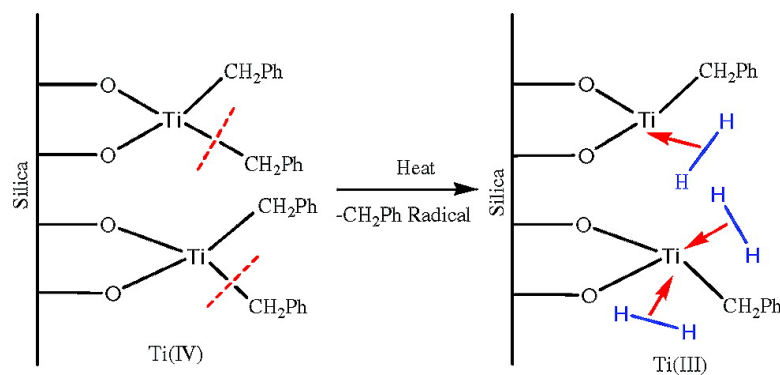


## H Storage Materials (22KJ/mol) Using Organometallic Ti Fragments as #-H Binding Sites

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## H<sub>2</sub> Storage Materials (22KJ/mol) Using Organometallic Ti Fragments as $\sigma$ -H<sub>2</sub> Binding Sites

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**Abstract:** Low-coordinate Ti (III) fragments with controlled geometries designed specifically for  $\sigma$ -H<sub>2</sub> binding were grafted onto mesoporous silica using tri- and tetrabenzyl Ti precursors. The hydrogen storage capacity was tested as a function of precursor and precursor loading level. At an optimal loading level of 0.2 mol equiv tetrabenzyl Ti the total storage capacity at  $-196$  °C was 21.45 wt % and 34.10 kg/m<sup>3</sup> at 100 atm, and 3.15 wt % and 54.49 kg/m<sup>3</sup> for a compressed pellet under the same conditions. The adsorption value of this material was 1.66 wt %, which equates to an average of 2.7 H<sub>2</sub> per Ti center. The adsorption isotherms did not reach saturation at 60 atm, suggesting that the theoretical maximum of 5 H<sub>2</sub> per Ti in this system may be reached at higher pressures. The binding enthalpies rose with surface coverage to a maximum of 22.15 kJ/mol, which is more than double that of the highest recorded previously and within the range predicted for room temperature performance. The adsorption values of 0.99 at  $-78$  °C and 0.69 at 25 °C demonstrate retention of 2.4 H<sub>2</sub> and 1.1 H<sub>2</sub> per Ti at these temperatures, respectively. These findings suggest that Kubas binding of H<sub>2</sub> may be exploited at ambient temperature to enhance the storage capacities of high-pressure cylinders currently used in hydrogen test vehicles.

### Introduction

An ideal hydrogen storage material<sup>1</sup> must display fast adsorption/desorption kinetics, function near ambient temperature, and possess low density, high gravimetric/volumetric capacity, and high tolerance for recycling. Metals<sup>2</sup> and various metal hydride alloys<sup>3</sup> have been studied which can adsorb between 2 and 7 wt % of hydrogen between 100 and 200 °C.<sup>4</sup> Although many of these materials have high volumetric capacities close to the 2015 DOE system goal of 80 kg/m<sup>3</sup>, they fall well short of the 9 wt % gravimetric storage goal. Another major drawback is the high activation barriers of the ca. 80 kJ/mol M-H bonds that must be broken to liberate H<sub>2</sub>. This creates problems with release kinetics and performance temperatures, and often necessitates elaborate heat exchange systems in a practical design. For this reason, many researchers are turning to high surface area porous materials as hosts for H<sub>2</sub> storage. Such materials adsorb H<sub>2</sub> on the surface through a 5–10 kJ/mol physisorption mechanism under cryogenic conditions. The leading materials in this technology are carbon-based structures<sup>5–9</sup> and microporous metal–organic frameworks (MOFs).<sup>10–12</sup> This method of storage is of increasing interest because the technology needed for transportation of large quantities of liquid hydrogen already exist in the rocket industry and many

of these materials have shown promising hydrogen uptake.<sup>7,10</sup> However, the energy lost in cooling and from boil-off is a serious challenge, and no material comes close to meeting the DOE 2015 system targets for temperature or volumetric capacity. To surmount the problems associated with heat exchangers and cooling, materials with binding enthalpies between those of cryogenic materials and metal hydrides must be developed. Calculations by Zhao et al.<sup>13</sup> have predicted high storage capacities and ideal enthalpies for room temperature performance of 20–30 kJ/mol for hypothetical Sc and Ti modified C60 moieties based on Kubas binding of the H–H bond to the metal center.<sup>14</sup> Yildirim has predicted similar performance benefits in Ti-decorated carbon nanotubes.<sup>15</sup> Recent advances within our group<sup>4,16,17</sup> indicate that mesoporous transition metal oxides<sup>18–20</sup> may serve as hosts

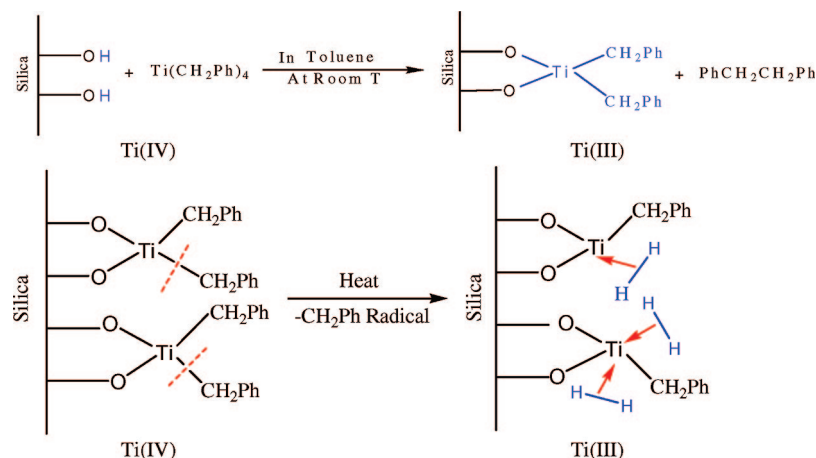
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**Scheme 1.** Schematic Representation of the Grafting of Benzyl Ti Species onto the Surface of Mesoporous Silica and the Subsequent Formation of Tunable Low-Coordinate H<sub>2</sub> Binding Sites with Enthalpies over 20 kJ/mol



for hydrogen storage. Reduction of the Ti oxide based mesoporous framework with Li, Na, or bis(toluene) titanium leads to enhanced H<sub>2</sub> binding to the surface to a high of 4.94 wt % gravimetric storage and 40.46 kg/m<sup>3</sup> volumetric storage capacity. The proposed mechanism for enhancement involves Kubas binding of H<sub>2</sub> to Ti, because this interaction is strongly dependent on the reduction level of the metal center and its ability to back-bond through  $\sigma$ -interaction into the antibonding H-H orbital.<sup>14</sup> This enhancement effect in our system was more important than the surface area, and the binding enthalpies showed an unprecedented increase with surface coverage from 2.5 to 8.08 kJ/mol. However, these enthalpies fall short of those necessary for room temperature performance, and the presence of multiple Ti sites of oxidation states between II and IV suggests that only a fraction of the Ti centers act as binding sites while the rest only add excess weight and decrease the storage capacity. To overcome this problem we developed a new system which uses very light and inexpensive mesoporous silica as a host for single site Ti centers tailored specifically to bind a maximum number of H<sub>2</sub> molecules through a Kubas interaction. Here we present a study of the cryogenic and room temperature hydrogen storage properties of these materials and show how this new method of hydrogen storage may be valuable in increasing the capacity of compressed hydrogen tanks at room temperature.

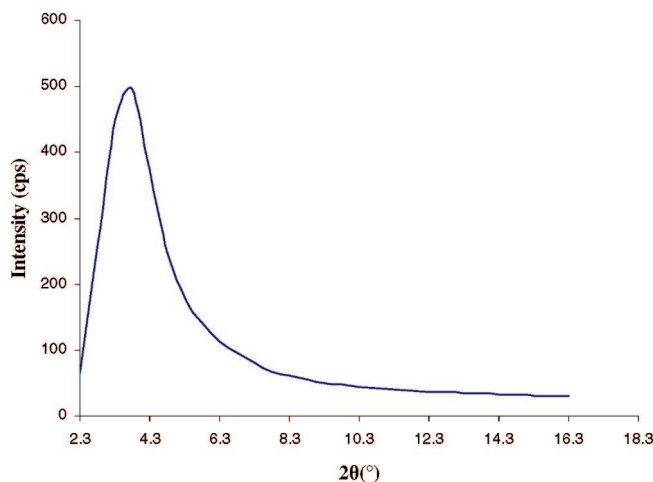
## Results

Mesoporous silica possessing a pore size of 23 Å and a BET (Brunauer, Emmett, Teller) surface area of 1219 m<sup>2</sup>/g was synthesized using a dodecylamine template according to the neutral templating method.<sup>21</sup> Tris- and tetrabenzyl titanium was grafted onto the surface of the mesoporous oxide as described previously for this compound on amorphous silica.<sup>22</sup> When tris- or tetrabenzyl Ti reacts with the OH groups on the surface of the silica, one or two toluene ligands, depending on the

proximity of surface OH groups, are eliminated resulting in the formation of a four-coordinate Ti(IV) benzyl siloxy species anchored to the surface. Heating the material at 180 °C results in reductive cleavage of one of the remaining Ti-C bonds and elimination of benzyl radicals, which then couple and are subsequently removed in vacuo. Benzyl Ti on porous silica has been used widely in olefin polymerization, and previous spectroscopic studies confirmed complete conversion to three-coordinate Ti(III) units on the surface.<sup>22,23</sup> According to the 18-electron rule, these Ti moieties can bind as many as five H<sub>2</sub> ligands via a Kubas interaction. Our synthetic strategy is shown in Scheme 1.

The X-ray diffraction pattern (Figure 1 for all treated materials after heating) showed complete retention of the mesostructure as evidenced by a single broad reflection at  $d = 23$  Å. The nitrogen adsorption/desorption isotherms (Figure 2) for these samples revealed a type IV isotherm consistent with a mesoporous system and surface areas ranging from 720 to 1294 m<sup>2</sup>/g. The pore volume for these materials ranged from 0.7819 to 1.4201 mL/g, while the pore sizes were all in the 20–23 Å range.

Hydrogen storage (including compressed gas) and adsorption (excess storage) measurements were conducted at -196 °C to determine the optimal loading level and precursor. The results are summarized in Table 1 with adsorption and storage isotherms



**Figure 1.** Representative X-ray diffraction pattern of mesoporous silica treated with 0.2 equiv of tetrabenzyl titanium.

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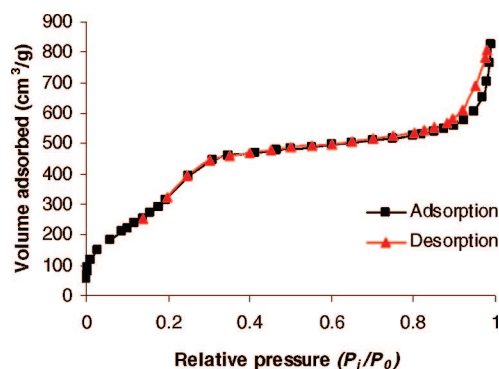
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**Figure 2.** Representative nitrogen adsorption/desorption isotherm of material from Figure 1.

shown in Figures 3 and 4. The storage isotherms (Figure 5a) for all materials rose at low pressure and continued to rise in a linear fashion from 10 onward to 60 atm. Extrapolation to 100 atm, a feasible pressure for cryogenic storage tanks, yields values as high as 21.45 wt % and 34.10 kg/m<sup>3</sup> for the sample synthesized with 0.2 mol equiv of tetrabenzyl Ti with respect to Si. This compares to a value of 9.84 wt % and 20.34 kg/m<sup>3</sup> for pure mesoporous silica and 11.96 wt % and 39.23 kg/m<sup>3</sup> for carbon AX-21 recorded under the same conditions. While much of this 21.45 wt % consists of compressed gas, this is the highest gravimetric storage value recorded under these conditions, and compressed gas in the void space of a material is usable as fuel. The adsorption for this material was 1.66 wt % as compared to 1.21 wt % in the untreated silica and 4.5 wt % for AX-21. For a full explanation of excess storage or adsorption versus total storage, see the Experimental Section. On the basis of 4.08% Ti determined by inductively coupled plasma (ICP), the difference between these values translates into 2.7 H<sub>2</sub> per Ti, short of the maximum of 5 H<sub>2</sub> allowed by the 18 electron rule, assuming three-coordinate Ti(III). Elemental analysis revealed 11.28% C, corresponding to an average of 1.45 benzyl ligands remaining per Ti, indicating a mix between disiloxy benzyl and dibenzyl siloxy Ti(III) species. On the basis of the surface area and the %Ti of this sample (see Experimental Section) a surface coverage of 0.4275 Ti per nm<sup>2</sup> can be calculated for this 0.2 mol equiv sample. The adsorption isotherms for treated materials did not saturate at 60 atm (Figure 5b). This behavior is unusual, given that physisorption materials generally saturate at low pressure and increase very little or even decrease at higher pressures. A possible explanation is that a complex pressure-dependent equilibrium exists in which the

Ti units can have zero, one, two, three, four, or five H<sub>2</sub> ligands bound to the surface in a Kubas-type fashion. Increasing the pressure leads to a higher predominance of Ti units with more H<sub>2</sub> ligands, according to Le Chatelier's principle, and higher pressures than 60 atm are required to force the extra H<sub>2</sub> ligands into the Ti coordination sphere. A 20 run cycle of adsorption and desorption at -196 °C and 60 atm showed no change in the maximum gravimetric uptake (Figure 6). The isotherms returned on desorption to zero without any hysteresis (Figure 7). While hysteresis might be expected on the basis of the high binding enthalpies, such a prediction is overly simplistic and does not take into account equilibration times for each point or the entropy changes in the system and surrounding on gas expansion or compression. Storage measurements of a compressed pellet of this material showed gravimetric and volumetric densities of 3.15 wt % and 54.49 kg/m<sup>3</sup> at 77 K and 100 atm, demonstrating that densification of this material gives a large increase in volumetric density with a corresponding penalty in gravimetric density. Nitrogen adsorption measurements were performed on the pellet and yielded a surface area of 720 m<sup>2</sup>/g with retention of the pore structure after compression. The decrease in surface area is likely due to loss of external surface area of the mesoporous particles on compression into tightly bound clusters of particles. Some collapse of pores with thinner walls may have also occurred. This indicates that the Ti units in the pores of the compressed pellets are largely intact and active, while those on the surface of the particles are no longer accessible and therefore inactive.

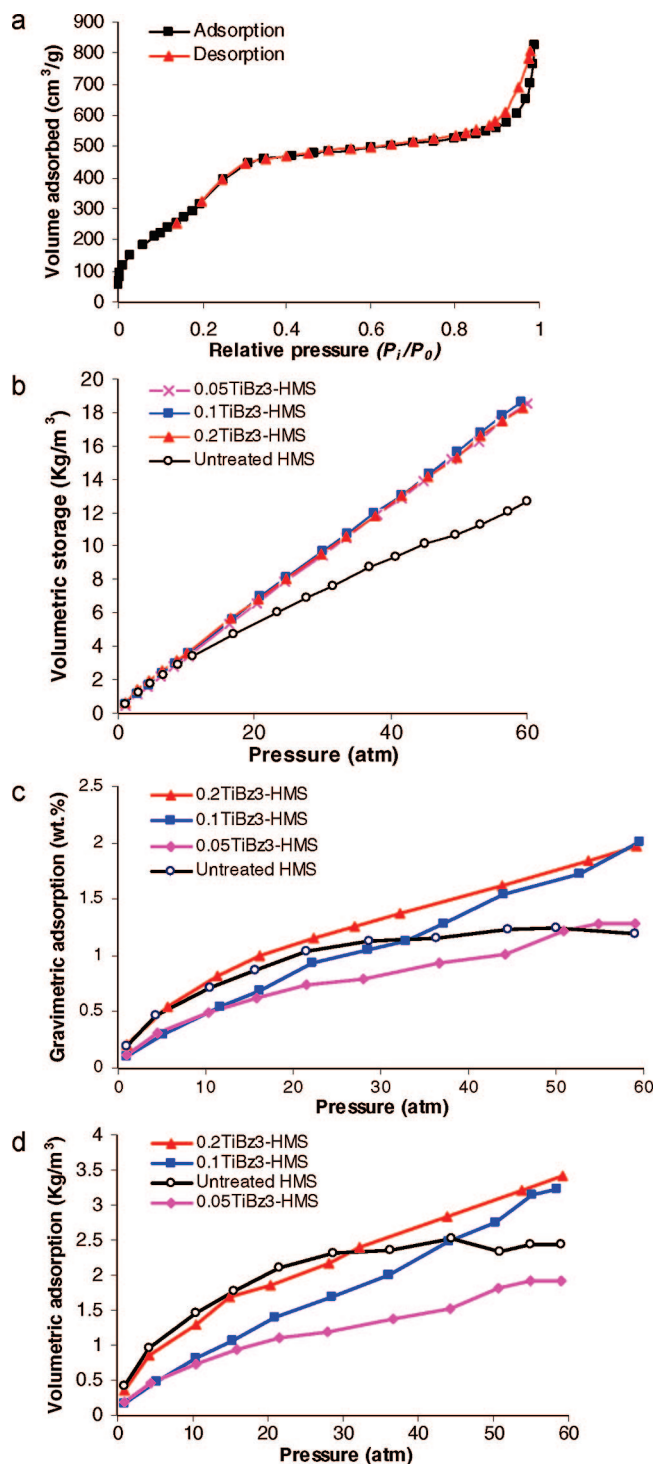
Materials prepared with 0.1, 0.2, 0.3, and 0.5 mol equiv of tetrabenzyl Ti were also studied (Table 1). In general, the gravimetric and volumetric capacities drop from the optimal loading level of 0.2 mol equiv, however there are some anomalies. For example, the 0.3 mol equiv tetrabenzyl titanium material has a higher gravimetric adsorption (2.04 wt %) but lower volumetric storage (33.07 kg/m<sup>3</sup>) than its 0.2 mol equiv tetrabenzyl titanium analogue. Also, the skeletal densities of the treated materials fall in the range of 0.94–1.99, but there are no clear trends with Ti-loading across the range of materials, suggesting that both the skeletal weight and the skeletal volume are affected on anchoring various organometallic fragments to the surface in ways that are difficult to predict at this stage. Since hydrogen storage in this system relies heavily on the oxidation state and coordination sphere of the Ti units, it is crucial that there be maximum surface coverage without any disruption of the structural integrity of the anchored sites. In the case of the 0.1 mol equiv sample, it is likely that there are

**Table 1.** Hydrogen Storage Capacities of Mesoporous Silicas at 77 K with Different Surface Areas Synthesized Using Various Molar Ratios of Tribenzyl and Tetrabenzyl Titanium<sup>a</sup>

sample name	surface area (m <sup>2</sup> /g)	skeletal density (g/mL)	apparent density (g/mL)	gravimetric H <sub>2</sub> adsorption at 77 K (wt %) <sup>b</sup>	gravimetric H <sub>2</sub> storage at 100 atm (wt %) <sup>c</sup>	volumetric H <sub>2</sub> storage at 100 atm (kg/m <sup>3</sup> ) <sup>c</sup>
plain HMS	1219	1.6	0.206	1.21	9.84	20.34
0.05TiBz <sub>3</sub> -HMS	799	1.38	0.15	1.38	20.56	30.67
0.1TiBz <sub>3</sub> -HMS	889	0.94	0.16	1.99	19.26	31.14
0.2TiBz <sub>3</sub> -HMS	895	0.93	0.17	2.02	17.48	30.37
0.1TiBz <sub>4</sub> -HMS	1140	1.96	0.17	0.95	17.68	30.02
0.2TiBz <sub>4</sub> -HMS	1294	1.45	0.16	1.66	21.45	34.10
0.3TiBz <sub>4</sub> -HMS	913	1.99	0.17	2.04	19.67	33.07
0.5TiBz <sub>4</sub> -HMS	746	1.86	0.20	0.26	13.04	26.59
0.2TiBz <sub>4</sub> -HMS Pellet	720	1.82	1.73	1.55	3.15	54.49
AX-21	3225	2.10	0.33	4.19	11.96	39.23

<sup>a</sup> Instrument was calibrated to AX-21 at 4.5 wt % at -196 °C and 65 atm. <sup>b</sup> Saturation was not reached at 60 atm except for that of plain silica, 0.1TiBz<sub>4</sub>-HMS, and 0.5TiBz<sub>4</sub>-HMS. <sup>c</sup> Hydrogen measurement is at the temperature of 77 K and 60 atm extrapolated to 100 atm with goodness of fit ( $R^2 = 0.9966\sim 0.9995$ ).





**Figure 3.** Hydrogen storage and adsorption isotherms at 77 K for mesoporous silica treated with various molar equivalents of tribenzyl titanium: (a) gravimetric storage density; (b) volumetric storage density; (c) gravimetric adsorption density; (d) volumetric adsorption density.

not enough Ti moieties on the surface to affect the capacities to the same extent as the 0.2 mol equiv sample, but for the higher loading levels the explanation is not so clear, as the surface coverage of 0.4275 Ti per nm<sup>2</sup> of the 0.2 mol equiv sample should allow for more Ti units given the size of the benzyl ligands. Perhaps the available surface OH groups are already used at a loading level of 0.2 mol equiv, and the addition of more tetrabenzyl titanium begins to form dimeric species on

the surface, which are less able to bind H<sub>2</sub> because of steric or electronic factors.<sup>23</sup>

Table 1 also shows results from using a tribenzyl titanium precursor. The gravimetric and volumetric storage capacities are uniformly lower at a given loading level than those prepared with tetrabenzyl titanium, however the adsorption levels are higher for the tribenzyl material (2.02 wt % vs 1.66 wt % at 0.2 equiv).

In MOF materials it has been proposed that H<sub>2</sub> can bind to the metal linker and that this feature is just as important as the surface area and pore size in determining storage capacity.<sup>24</sup> For some of these materials the Kubas interaction was proposed to be operative at the metal center. The maximum enthalpy observed for any MOF is 10.1 kJ/mol,<sup>25</sup> recorded for a manganese benzenetristetrazolate MOF. For comparison, the  $\Delta H$  values for amorphous carbon are normally in the range of 5–8 kJ/mol.<sup>26</sup> In previous work we found that reduction of the surface of mesoporous Ti oxide with bis(toluene) titanium led to an increase in binding enthalpies from 2.5 to 8.08 kJ/mol. The enthalpy data also showed an unprecedented rise with surface coverage, suggesting a different mechanism than simple physisorption, but the values fell far short of the predicted 20 kJ/mol for room temperature binding. In physisorption systems operating at 77 K, higher binding enthalpies are undesirable because this means heat is released by the system on cycling and this creates an energy penalty in term of the coolant required to maintain 77 K. However, higher binding enthalpies also mean stronger H–H bonds to the surface, which may translate into retention of storage capacities at higher temperatures. Figure 8 shows the binding enthalpies of untreated HMS silica, and silica treated with 0.2 mol equiv of tribenzyl titanium before and after heating as calculated by a variant of the Clausius–Clapyron equation<sup>27</sup> from hydrogen adsorption data at 77 and 87 K (Figure 9). The pristine silica material shows a linear progression from 3.5 kJ/mol with decreasing slope on increasing coverage. The material treated with tetrabenzyl titanium before heating starts at 0.15 and increases sharply to 13.15 kJ/mol. This rising slope behavior suggests that the Ti(IV) units, which have no special affinity for H<sub>2</sub>, have already been partially reduced to Ti(III). This is not unexpected given that tetrabenzyl titanium is both heat and light sensitive<sup>23</sup> and must be stored in the dark at –30 °C to prevent reductive cleavage of the C–Ti benzyl bond.<sup>22</sup> The same material after heating shows a gradual progression from 2.65 to 22.15 kJ/mol. This is the highest value ever recorded for a porous material under cryogenic conditions, more than double that of any previous material, and suggests that this material should retain hydrogen at room temperature. The difference between the heated and unheated materials illustrates that it is the Ti(III) centers and not the benzyl groups that provide the high enthalpy binding sites. The rising slope can be rationalized by either adsorption at multiple sites of different enthalpies and activation barriers, or a progressive change in adsorption enthalpy on H<sub>2</sub> ligand binding to the Ti centers. The latter was predicted by Zhao<sup>13</sup> and Yildirim<sup>15</sup> and can be viewed

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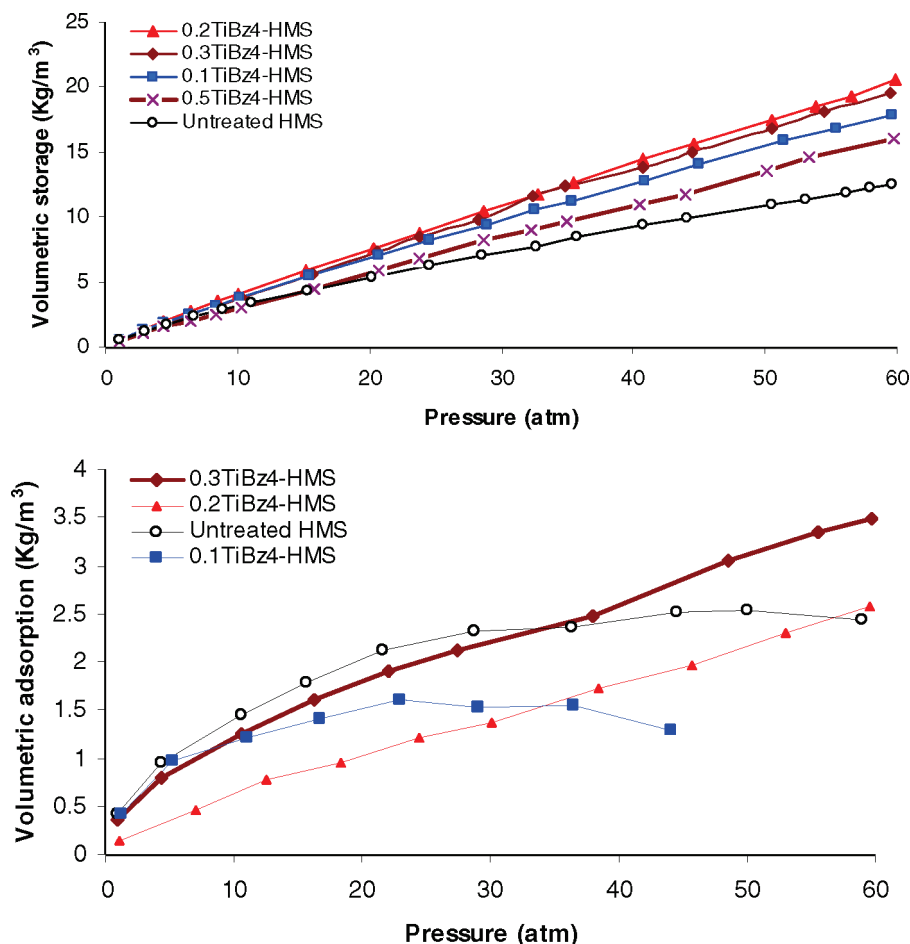
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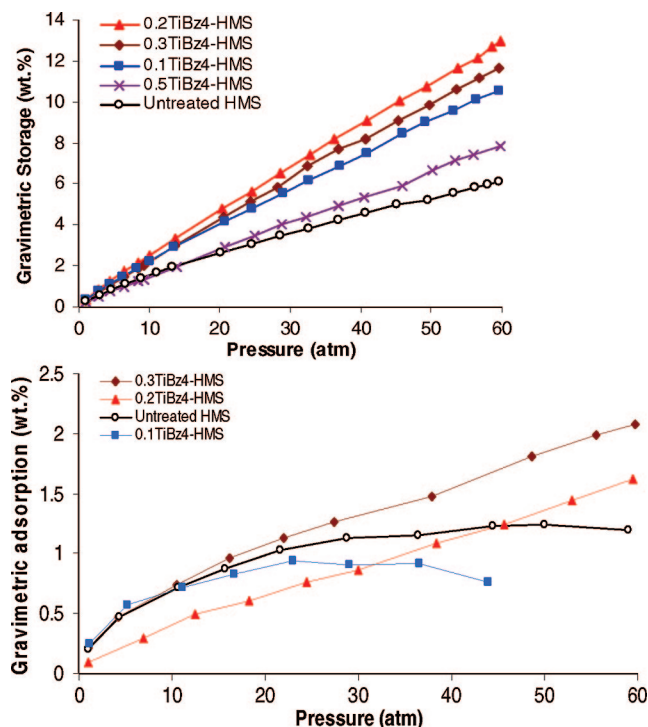
**Figure 4.** Hydrogen storage and adsorption isotherms at 77 K for mesoporous silica treated with various molar equivalents of tetrabenzyl titanium: (a) volumetric storage density; (b) volumetric adsorption density.

as a result of cis and trans ligand effects on the electronic environment of the Ti centers. With an increasing number of H<sub>2</sub> ligands on the Ti centers, the metal becomes more electron rich because of  $\sigma$ -donation from the H–H bond, thus facilitating  $\Pi$ -back bonding from the metal into the H–H antibonding orbital. The enthalpy of the 0.3 tetrabenzyl titanium material was also calculated by this method and rises with coverage to 22.04 kJ/mol, demonstrating that high enthalpies are general in these materials and not specific to one set of samples or a particular composition.

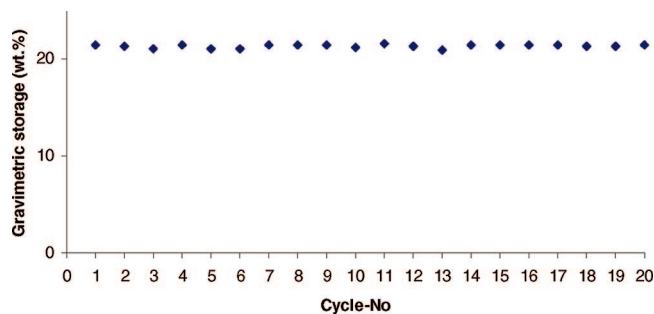
Table 2 shows a comparison in storage capacities at  $-196$ ,  $-78$ , and  $25$  °C at 100 atm between pristine mesoporous silica and mesoporous silica treated with 0.2 equiv of tetrabenzyl titanium after heating. The values for the compressed pellets are also shown. There is a decrease in total storage from 21.45 to 8.39 and 5.05 wt % with increasing temperature in the treated material. This is accompanied by a drop in volumetric capacity from 34.10 to 14.84 and 8.93 kg/m<sup>3</sup>, respectively, with increasing temperature. These numbers compare to 32, 12.5, and 8 kg/m<sup>3</sup>, calculated for compressed hydrogen at 100 atm for these temperatures. The most intriguing numbers are the adsorption values, which drop from 1.21 to 0.58 and 0.44 wt % with increasing temperature for pure HMS silica, and 1.66 to 0.99 and 0.69 wt % for the treated material. Taking into account the 4.08% Ti from ICP and the densities of the materials, this corresponds to 2.4 H<sub>2</sub> per Ti at  $-78$  °C and 1.1 H<sub>2</sub> at ambient temperature. There is thus very little loss of H<sub>2</sub> binding capacity at the Ti centers at  $-78$  °C, and only 59%

loss at room temperature. This confirms predictions that materials possessing binding enthalpies in the 20 kJ/mol range may find application in room temperature hydrogen storage. While the storage capacities of the powder fall short of practical value at ambient temperature, extrapolation of the capacities to 350 atm, a pressure used in some current model hydrogen vehicle compressed gas tanks, gives 17.82 wt % and 31.52 kg/m<sup>3</sup> for the powder and 3.51 wt % and 60.75 kg/m<sup>3</sup> for the compressed pellet. These compressed pellet numbers are roughly double that of compressed hydrogen under the same conditions and resemble that of many hydrides (i.e., high volumetric with only moderate gravimetric), with volumetric densities approaching the 80 kg/m<sup>3</sup> 2015 DOE goal, yet these materials do not require any heating or heat exchangers for hydrogen release and thus are more advantageous from an automotive design standpoint. The extrapolated capacities for the compressed pellet at 350 atm and ambient temperature are very similar to those at  $-196$  °C and 100 atm, demonstrating that excess pressure can be used in this system to compensate for increased temperature. This gives an obvious advantage in design as well as overcoming problems with boil-off encountered under cryogenic conditions. While these capacities fall short of DOE goals, it is anticipated that by tuning the Ti coordination sphere and oxidation state, as well as optimizing surface coverage and the nature of the support material, further gains can be realized.

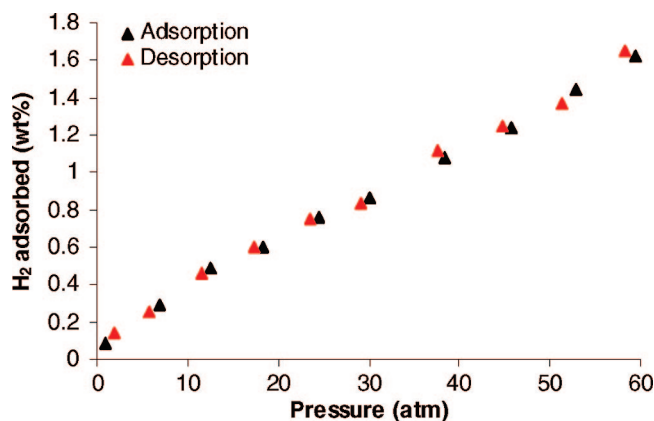
In summary, mesoporous silica was used as scaffolding for well-defined single site 3-coordinate Ti(III) centers capable of binding up to 5 H<sub>2</sub> per Ti through a Kubas interaction. These



**Figure 5.** Hydrogen storage isotherms at 77 K for mesoporous silica treated with various molar equivalents of tetrabenzyl titanium: (a) gravimetric storage density; (b) gravimetric adsorption (excess storage) density. Slight fluctuations at higher pressure in some adsorption isotherms were not related to temperature fluctuations, as this parameter was strictly controlled.

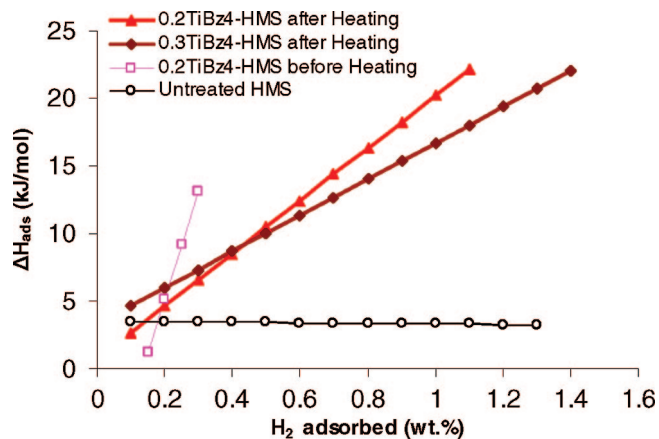


**Figure 6.** Hydrogen storage capacity in a 20 cycle test of mesoporous silica treated with 0.2 mol equiv of tetrabenzyl titanium.



**Figure 7.** Adsorption and desorption isotherms for the material from Figure 6.

materials display binding enthalpies of up to 22.15 kJ/mol and retain 89% of their enhancement at  $-78$  °C and 41% at room



**Figure 8.** Hydrogen binding enthalpies of mesoporous silicas from Table 1: pristine silica (black), the 0.2 molar equiv tetrabenzyltitanium material after heating at 180 °C (red), the 0.3 molar equiv tetrabenzyltitanium material after heating at 180 °C (brown), and the 0.2 molar equiv tetrabenzyltitanium material before heating (pink).

temperature. Under selected conditions volumetric densities as high as 60.75 kg/m<sup>3</sup> were extrapolated at room temperature and elevated pressure, suggesting that these materials may find use for increasing storage capacities of compressed gas cylinders at ambient temperature.

## Experimental Section

**Synthesis of Tetrabenzyl Titanium.**<sup>27</sup> To a solution of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>MgCl (100 mL, 1 M in diethyl ether) at  $-15$  °C was added a solution of TiCl<sub>4</sub> (2.5 mL, 22.8 mmol) in pentane (100 mL) dropwise over 2 h. The mixture was stirred for 3 h at  $-15$  °C and filtered. The solid residue was washed with diethyl ether (2 × 50 mL) and the combined filtrate and washings were reduced in vacuo. The residue was dissolved in pentane (50 mL) and filtered followed by further washing of the residue with pentane (2 × 50 mL). The filtrate and pentane washings were concentrated to approximately 70 mL and cooled to  $-30$  °C overnight to yield a dark-brown red crystalline product.

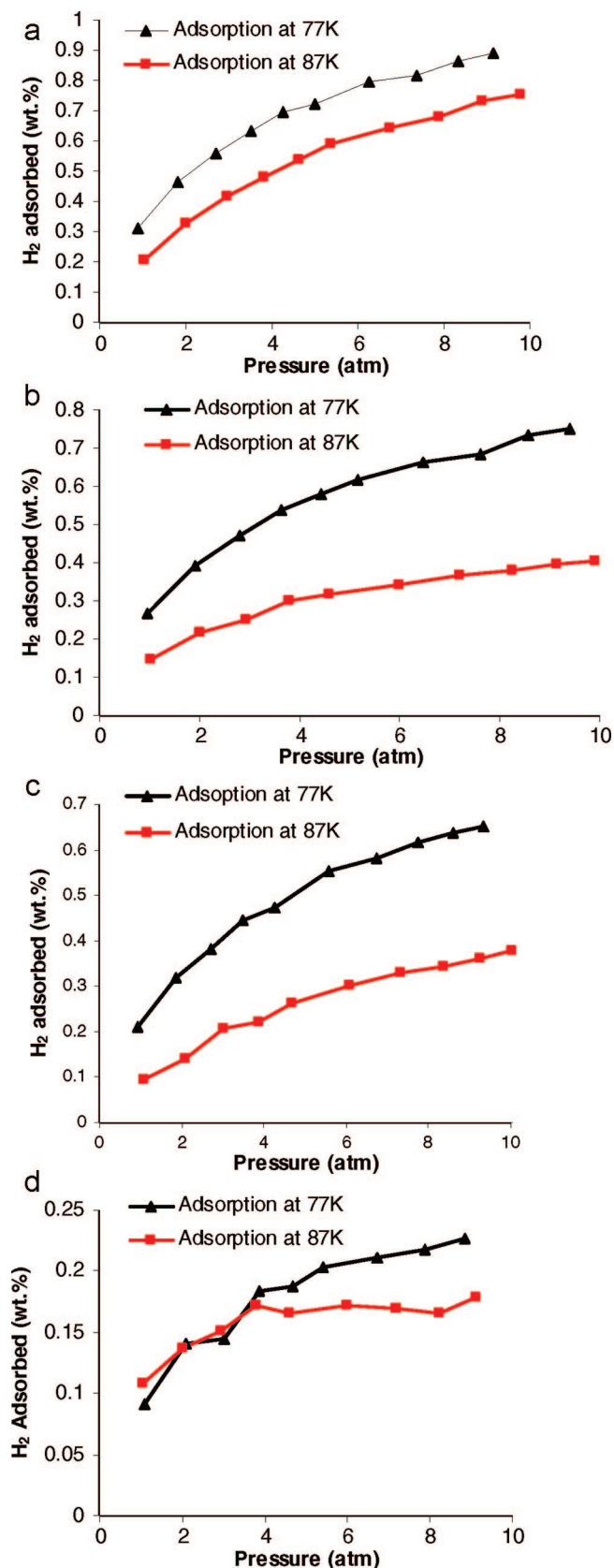
**Concentration of Exposed Ti Metal Sites.** Assuming 1 g of 0.2TiBz<sub>4</sub>-HMS, with a surface area of 1200m<sup>2</sup>/g ( $1.2 \times 10^{21}$  nm<sup>2</sup>): 0.2TiBz<sub>4</sub>-HMS has 4.5 wt % Ti; therefore, in 1 g of 0.2TiBz<sub>4</sub>-HMS there is 40.8 mg Ti ( $8.52 \times 10^{-4}$  moles Ti). Ti coverage = ( $8.52 \times 10^{-4}$  moles Ti ×  $6.02 \times 10^{23}$  Ti/mole)/( $1.2 \times 10^{21}$  nm<sup>2</sup>) = 0.4275 Ti/nm<sup>2</sup>.

**Synthesis of Tribenzyl Titanium.** Tribenzyl titanium was obtained at 0 °C in a toluene solution by the reaction of tetrabenzyltitanium with ethyllithium for 2 h. The resulting benzylolithium was precipitated by carboxylation at  $-78$  °C. A tribenzyl titanium solution was obtained after filtration. Crystallization gave a 65% yield with respect to the initial quantity of tetrabenzyl titanium.

**Synthesis of Hexagonally Mesoporous Silica (HMS).** In a typical preparation, tetraethyl orthosilicate (1.0 mol) was added with vigorous stirring to a solution of dodecylamine (0.27 mol) in ethanol (9.09 mol). The reaction mixture was aged at ambient temperature for 18 h, and the resulting mesoporous silica was air-dried on a glass plate. The template was removed by mixing 1 g of the air-dried HMS with 150 mL of hot ethanol for 1 h. The product was then filtered and washed with a second 100 mL portion of ethanol. This extraction procedure was repeated twice, and the crystalline product air-dried at 80 °C.

**Synthesis of Ti-Grafted Mesoporous Silicas.** A 0.2 equiv portion of tetrabenzyl titanium (or tribenzyl titanium), as calculated on the basis of 33% Si in the porous oxide (ref 21), was added to a suspension of hexagonally mesoporous silica in dry toluene under nitrogen. After 1 day of stirring to ensure complete absorption of



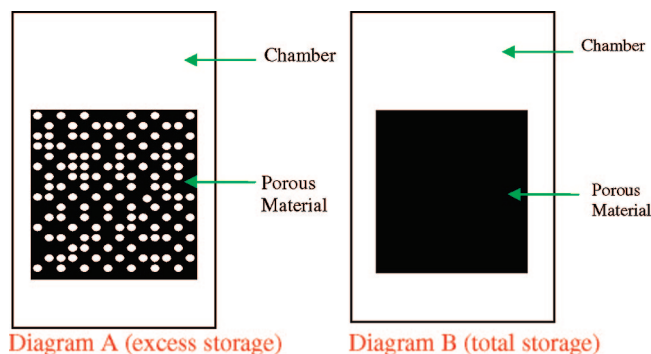


**Figure 9.** Adsorption isotherms for the materials from Figure 2 recorded at liquid argon and liquid nitrogen temperatures: (a) pristine mesoporous silica, (b) silica treated with 0.2 mol equiv tetrabenzyl titanium after heating, (c) Silica treated with 0.3 mol equiv tetrabenzyl titanium after heating, (d) silica treated with 0.2 mol equiv tetrabenzyl titanium before heating.

the organometallic, the reduced material was collected by suction filtration under nitrogen. The resulting material was then heated in toluene at 180 °C for 8 h and washed several times with toluene and finally dried in vacuo at  $10^{-3}$  Torr on a Schlenk line until all volatiles had been removed. This material was used as either a powder or a 1.3 cm diameter pellet compressed in a commercial pellet press at 4 metric tones.

**Measurements.** Nitrogen adsorption and desorption data were collected on a Micromeritics ASAP 2010. Hydrogen uptake is measured with a commercial pressure-composition isotherm (PCI) unit provided by Advanced Materials. Highly purified hydrogen (99.9995% purity) was used as the adsorbent. Before all measurements the materials were activated in vacuo at 573 K to remove any physisorbed water or volatile impurities. Hydrogen storage measurements on a standard AX-21 sample (4.5 wt %) were performed to ensure proper calibration and functioning of the instrumentation. Leak testing was also performed during each measurement by checking for soap bubbles at potential leak points. These measurements are necessary to ensure the veracity of the isotherms. In the  $H_2$  adsorption–desorption experiments complete reversibility was observed for all samples across the whole range of pressures. Samples were run at liquid nitrogen temperature (77 K) and liquid argon temperature (87 K) to 60 atm and extrapolated to 100 atm with a goodness of fit of 0.9966~0.9995 and 0.9988~0.9994, respectively.

The skeletal density was measured using a Quantachrome Ultracycrometer. When the skeletal density was used for the hydrogen uptake measurement, the compressed hydrogen within the pores is treated as part of the sample chamber volume. Therefore only the hydrogen physisorbed to the walls of the structure will be recorded by the PCI instrument as the adsorption capacity of the material (see diagrams A and B).



In diagram A,  $H_2$  adsorption (excess storage isotherm) is measured. The black area represents the space occupied by the porous solid. The instrument uses the weight of the sample and the skeletal density from the pycnometer to calculate the volume occupied by the solid (black area). The white area (pores + void volume in the chamber) is subtracted out and only the hydrogen within the boundaries of the black area is used in calculating the volumetric and gravimetric densities. In diagram B the black area also represents the area occupied by a porous solid; however, this time for the measurement of the total storage in which the pore volume within the solid is NOT subtracted out. The total macroscopic desktop density is measured, which ignores the presence of pores inside the material, and this number is used with the sample weight to calculate the volume occupied by the solid (black area). The colorless area (representing the chamber void only) is then subtracted out and ONLY the hydrogen contained within the boundaries of the black area is used to calculate the gravimetric and volumetric densities. Because it uses desktop density, this number will change according to the compression of the sample. The total storage can seem high in many materials owing to the very low density and high porosity of the sample and inclusion of the compressed gas component, but this measurement is necessary



**Table 2.** Hydrogen Storage Capacities of Pristine and Ti-Grafted Mesoporous Silica at Different Temperatures<sup>a</sup>

sample name	apparent density (g/ml)	skeletal density (g/ml)	gravimetric H <sub>2</sub> adsorption (wt %) <sup>b</sup>	gravimetric H <sub>2</sub> storage at 100 atm (wt %)	volumetric H <sub>2</sub> storage at 100 atm (kg/m <sup>3</sup> ) <sup>d</sup>
plain HMS at -196 °C	0.206	1.6	1.21 <sup>b</sup>	9.84	20.34
plain HMS at -78 °C	0.206	1.6	0.58 <sup>c</sup>	7.37	11.79
plain HMS at 25 °C	0.206	1.6	0.44 <sup>c</sup>	5.55	8.88
0.2TiBz <sub>4</sub> -HMS at -196 °C	0.17	1.45	1.67 <sup>c</sup>	21.45	34.10
0.2TiBz <sub>4</sub> -HMS at -78 °C	0.17	1.45	0.99 <sup>c</sup>	8.39	14.84
0.2TiBz <sub>4</sub> -HMS at 25 °C	0.17	1.45	0.69 <sup>c</sup>	5.05	8.93
0.2TiBz <sub>4</sub> -HMS pellet at -196 °C	1.73	1.82	1.55	3.15	54.49
0.2TiBz <sub>4</sub> -HMS pellet at -78 °C	1.73	1.82	0.82	1.28	22.14
0.2TiBz <sub>4</sub> -HMS pellet at 25 °C	1.73	1.82	0.59	0.86	14.88

<sup>a</sup> Instrument was calibrated to AX-21 at 4.5 wt % at -196 °C and 65 atm. <sup>b</sup> Hydrogen adsorption isotherms reached saturation below 60 atm. <sup>c</sup> Hydrogen adsorption isotherms did not reach saturation at 60 atm. <sup>d</sup> Hydrogen storage measurement is at 60 atm extrapolated to 100 atm with goodness of fit ( $R^2$ ) = 0.9966~0.9995.

so that engineers can determine the total amount of hydrogen present in a tank filled to capacity with these materials.

Taking both the 77 K and 87 K hydrogen adsorption data, enthalpies of adsorption were calculated using a variant of the Clausius–Clapeyron equation (ref 23):

$$\ln\left(\frac{P_1}{P_2}\right) = \Delta H_{\text{ads}} \frac{T_2 - T_1}{RT_1 T_2} \quad (1)$$

where  $P_n$  = pressure for isotherm  $n$ ,  $T_n$  = temperature for the isotherm  $n$ , and  $R$  = gas constant.

Pressure as a function of the amount adsorbed was determined by using exponential fit for each isotherm; the first 10 points of

the isotherms were picked up and fit to the exponential equation. This exponential equation gives an accurate fit over the pressure up to 10 atm with the goodness of fit ( $R^2$ ) above 0.99. The corresponding  $P_1$  and  $P_2$  values at a certain amount of H<sub>2</sub> adsorbed at both temperatures can be obtained by the simulated exponential equation. Inputting these numbers into the eq 1, we then calculate the enthalpies of the adsorption.

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