

Hydrogen Storage in Chemically Reducible Mesoporous and Microporous Ti Oxides

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Today's raising concerns of global warming and environmental pollution have spurred an interest in alternative fuels. Hydrogen is energy rich¹ and when used in a fuel cell produces only water as a byproduct. A major concern is the development of a safe storage and transport system for this highly flammable gas. To overcome this problem, solids which adsorb hydrogen under various conditions have been investigated. Many metals² and metal hydride alloys³ adsorb between 2 and 7 wt % of hydrogen between 100 and 200 °C,⁴ while carbon based nanotubes^{5–9} and microporous metal–organic frameworks (MOFs)^{10–12} have shown promise for cryogenic hydrogen storage. Since the U.S. Department of Energy has defined 9 wt % and 81 kg/m³ as the 2015 system targets, these materials have so far fallen short of expectations. Recent advances within our group suggest that mesoporous Ti oxides may serve as hosts for hydrogen storage.⁴ These materials possess extremely high surface areas, tunable pore sizes, and the capacity for coordinative unsaturation and variable oxidation states of the Ti center,^{13–15} a feature not present in MOFs, zeolites, or porous carbon. These properties are important because the binding of H₂ to transition metals is strongly dependent on the electron density at the metal center and its ability to back-donate through a π -interaction into the antibonding H–H orbital.^{16,17} Recent calculations by Zhao et al. have predicted high storage capacities and ideal enthalpies of 20–30 kJ/mol for hypothetical Sc and Ti modified C₆₀ moieties based on a Kubas-type binding of the H–H sigma bond to an electron rich coordinatively unsaturated metal center;¹⁷ however, to date, there is no experimental study demonstrating the feasibility of this approach. With this goal in mind, we report a comprehensive study of H₂ storage at 77 K for pristine and chemically reduced amine-templated Ti oxides.

Hydrogen pressure-composition isotherms were recorded at 77 K for a series of five pristine micro- and mesoporous Ti oxide materials, synthesized as described previously¹⁵ from C₆, C₈, C₁₀, C₁₂, and C₁₄ amine templates possessing B.E.T. surface areas ranging from 643 to 1063 m²/g (Figure S2, Supporting Information). The XRD (Figure S3), nitrogen adsorption desorption isotherm (Figure S4), and TEM (Figure S5) are shown for the materials synthesized with hexylamine (C6-Ti). The pore sizes of these materials decreased monotonically from 26 to 12 Å as described previously for a similar series of porous Nb oxides.¹³ The isotherms for all materials gently rise sharply at low pressure and continue to rise in a linear fashion from 10 atm onward to 65 atm and then return on desorption without significant hysteresis. Equilibration is immediate, implying a very low activation barrier for adsorption/desorption. Extrapolation to 100 atm, a feasible pressure for cryogenic storage tanks, yields total storage values as high as 5.36 wt % and 29.37 kg/m³ for C6-Ti. In MOF materials it has been proposed that H₂ can bind to the metal linker and that this feature

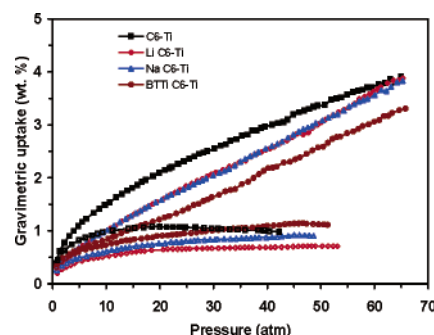


Figure 1. High-pressure H₂ isotherms for pristine and reduced microporous titanium oxides synthesized using hexylamine as the template at 77 K in gravimetric uptake. Filled markers represent storage capacity and open markers denote adsorption capacity.

is just as important as the surface area and pore size in determining storage capacity.¹⁸ It is therefore possible that such σ binding of H₂ to Ti can occur in our system, where the Oh MX₄L₂ Ti centers¹⁴ present at the surface and in the walls are nominally electron deficient 12 electron species possessing vacant t_{2g} orbitals. A schematic representation of a monolayer portion of the wall is shown in Figure S6, in which H₂ molecules can potentially bind to the Ti centers via a side-on interaction to the d⁰ center through the Ti t_{2g} set,^{16,17} or can exist as a compressed gas phase within the pore structure of the material. While anatase and rutile are poor hydrogen storage materials, the low-density amorphous structure of the walls in our materials preserves a degree of coordinative unsaturation while also allowing easy access of the H₂ to the Ti centers.

To explore the role of Ti oxidation state in H₂ storage capacity, C6-Ti was reduced with a variety of organometallic species. Figure 1 shows the H₂ sorption isotherms at 77 K for C6-Ti, C6-Ti reduced with 1.0 mol equivalent of Li naphthalene (Li C6-Ti), C6-Ti treated with 1.0 mol equivalent of Na naphthalene (Na C6-Ti), and C6-Ti reduced with excess bis(toluene) Ti (BTTi C6-Ti). The results are summarized in Table 1, complete with extrapolations to 100 atm. Direct measurements of AX-21 are shown for comparison. The adsorption values reflect the amount of hydrogen bound to the surface of the porous structure, while the total storage is a sum of the adsorption and the compressed H₂ in the pores. The former value is useful in studying surface binding, while the latter is a measure of the total H₂ available as fuel in any system. Reduction of C6-Ti with Li leads to an increase in gravimetric storage capacity from 5.36 to 5.63 wt % and an increase in the volumetric storage capacity from 29.37 to 31.30 kg/m³ at 77 K and 100 atm. The Na-reduced material exhibits a slight decrease in gravimetric storage over the Li-reduced material, but possesses a higher volumetric storage capacity of 31.58 kg/m³. Treatment of C6-Ti with bis(toluene) Ti leads to a decrease in the gravimetric storage to 4.94

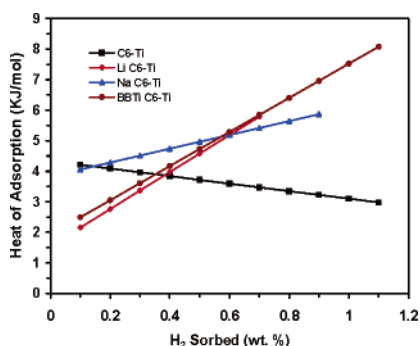
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Table 1. Hydrogen Sorption Capacity of C6-Ti Materials and AX-21

sample name	apparent density (g/mL)	skeletal density (g/mL)	gravimetric adsorption (77 K, wt %)	gravimetric storage at 100 atm ^a (wt %)	volumetric adsorption (77 K, kg/m ³)	volumetric storage at 100 atm ^a (kg/m ³)
C6-Ti	0.548	2.698	1.08	5.36	5.918	29.37
Li C6-Ti	0.556	2.508	0.71	5.63	3.948	31.30
Na C6-Ti	0.565	2.741	0.92	5.58	5.198	31.58
BTTi C6-Ti	0.819	2.835	1.14	4.94	9.337	40.46
AX-21	0.328	2.103	4.19	11.96	13.75	39.23

^a Hydrogen storage measurement is at the temperature of 77 K and 65 atm extrapolated to 100 atm with goodness of fit (R^2) = 0.9963 ~ 0.9995.

**Figure 2.** Enthalpy of H₂ adsorption for pristine and reduced microporous titanium oxides synthesized using hexylamine as the template.

wt % and an increase of the volumetric storage to 40.46 kg/m³, higher than that measured for AX-21 and the highest volumetric capacity we know of under these conditions. The adsorption data show a decrease from 1.08 wt % and 5.918 kg/m³ in C6-Ti to 0.71 wt % and 3.948 kg/m³ in Li C6-Ti and 0.92% and 5.198 kg/m³ in Na C6-Ti, and an increase to 1.14 wt % and 9.337 kg/m³ in BTTi C6-Ti. Equilibration for all reduced materials is immediate and there is no hysteresis between the adsorption and desorption cycles. An increase in temperature is not required for full discharge. At room temperature, this material has a hydrogen gravimetric storage capacity of 1.3 wt % at 100 atm. Previous XPS studies^{19,20} show a progressive reduction in the surface Ti species from Li to Na to bis(toluen) Ti (Table S1), however establishment of a uniform trend relating Ti oxidation state to H₂ capacity is difficult because of the differing densities, surface areas, and void space volumes of these materials. Despite this uncertainty, it is clear from the data that treatment with bis(toluen) Ti leads to the most dramatic overall increase in performance, possibly because of its greater degree of reduction and additional Ti binding sites (C6-Ti is 38% Ti; BTTi C6-Ti is 51% Ti).¹⁹ Cycling studies of this material conducted at 77 K and 65 atm demonstrate that the material does not lose any of its storage capacity after 10 cycles (Figure S7). The binding enthalpies were calculated by a variant of the Clausius–Clapyron equation²¹ from hydrogen adsorption data at 77 and 87 K (see Figure 2). The plot for C6-Ti decreases with increasing capacity, typical for physisorption, while the plots for all reduced materials show an increase in ΔH with H₂ capacity, a behavior which is highly

unusual and may reflect a different mechanism of surface binding than simple physisorption, possibly involving a Kubas-type interaction. The maximum ΔH for C6-Ti is 4.21 kJ/mol, similar to the value calculated for amorphous carbon.²² Li C6-Ti possesses a ΔH of 5.79 kJ/mol, while Na C6-Ti has a ΔH of 5.87 kJ/mol. BTTi C6-Ti has a ΔH of 8.08 kJ/mol, which compares well with values determined by Kaye et al.²³ for MOFs materials, in which transition metals are thought to act as H₂ binding sites, but falls far short of the 20 kJ/mol value proposed for porous materials to function effectively at ambient temperature.¹⁸

In summary, micro- and mesoporous Ti oxide materials with a range of pore sizes from ca. 12 to 26 Å and surface areas from 643 to 1063 m²/g were prepared and screened for H₂ storage capacity. While surface area and pore size had some effect on storage, surface Ti reduction provided an even greater increase in performance, possibly because of a Kubas-type interaction. These results suggest that reduction by the appropriate organometallic reagent may lead to even greater storage densities at temperatures higher than 77 K with more precise control over the enthalpies of adsorption.

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Supporting Information Available: Detailed experimental procedures, H₂ sorption measurements, the methods used to calculate H₂ adsorption enthalpies, powder X-ray diffraction pattern, N₂ adsorption/desorption isotherm and TEM image. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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