

Direct Observation of Activated Hydrogen Binding to a Supported Organometallic Compound at Room Temperature

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Current interest in the use of hydrogen as a transportation fuel has driven extensive research into novel gas storage materials.^[1] Although physisorption materials can possess technologically viable storage capacities, their isosteric heats are generally below 10 kJ mol⁻¹, limiting these materials to cryogenic temperatures. Chemisorbers, such as metal hydrides or complex hydrides, can store large amounts of hydrogen but require elevated temperatures to release the gas; isosteric heats for hydride systems are typically larger than 40 kJ mol⁻¹. The optimum conditions for viable room-temperature hydrogen storage require materials that possess isosteric heats of adsorption in between that of standard physisorbers and chemisorbers, typically in the 20–30 kJ mol⁻¹ regime.^[2] Theoretical work^[3,4] has shown that the incorporation of transition-metal atoms onto a porous support can provide such binding energies with multiple hydrogen molecules adsorbed. However, despite the very large number of theoretical papers, there is no direct experimental proof of these predictions yet. An early experimental example is the gas-phase hydrogen reaction with Ti–ethylene complexes,^[5] where the gravimetrically measured hydrogen uptake agrees well with theoretical predictions but details of structure, dynamics, and the local chemistry are absent. Herein, we present direct experimental evidence for dihy-

drogen–Ti binding on a silica-supported Ti^{III} organometallic complex (hereafter referred to as Ti-HMS) using detailed sorption and inelastic neutron scattering (INS) measurements. Our experimental findings are further supported by extensive first-principles DFT and reaction path calculations. We show that the Ti^{III} ion is essential for the formation of a dihydrogen complex, and its presence is confirmed by EPR spectroscopy (see Figure S1 in the Supporting Information). Surprisingly, we discover that the H₂–Ti binding is a thermally activated process; exposing the supported organometallic to hydrogen below 150 K results in only physisorption, while near room temperature it forms H₂–Ti moieties that are stable for extended periods of time. Such an activation barrier was missed in earlier DFT calculations, which predicted only the formation of dihydrogen complexes. Though this particular sample does not represent a viable storage material due to its modest uptake and non-optimized support, it does offer a useful benchmark for understanding the underlying hydrogen coordination chemistries.

The sorption performance of the activated Ti-HMS sample measured immediately prior to INS studies (Figure 1) shows an uptake of approximately 12 mg g⁻¹ at 30 bar and 77 K, similar to the bare HMS. This is comparable but somewhat lower than that previously measured^[6] and indicates that some of the active titanium adsorption sites have been lost compared to the as-synthesized complex. This is not unexpected as Ti^{III} alkyls are highly reactive

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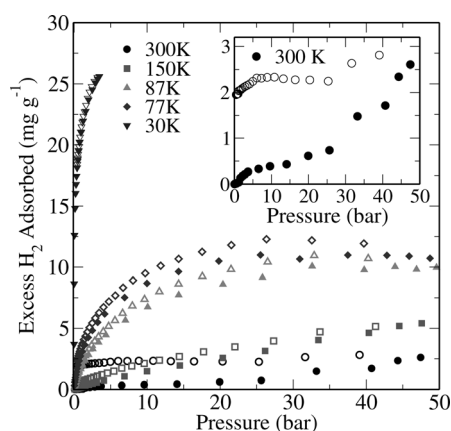


Figure 1. Excess hydrogen isotherms showing reversible physisorption for $T_{\text{dose}} < 150$ K and irreversible adsorption at 300 K (inset).

and have been shown to decompose by disproportionation or through reaction with trace water impurities.^[7] Though some of the most active sites may have been lost, EPR demonstrates that the Ti^{III} ion is stable to heating in inert atmospheres (see Figure S1 in the Supporting Information). Importantly, despite the possible reduction in the number of sites, the specific chemistries that are present (see below) are precisely what was observed previously. At each temperature below 150 K, the hydrogen sorption is completely reversible, consistent with a simple physisorption mechanism.

At room temperature, the adsorption behavior is starkly different. As seen in the inset to Figure 1, the 300 K hydrogen sorption saturates at 3 mg g^{-1} , or approximately 25% of the 77 K capacity. In addition, evacuation of the sample cell at room temperature removes only 1 mg g^{-1} from the material; the remaining 2 mg g^{-1} is stably bound to the host. Comparing this value, approximately 1 mmol H_2 per gram, to the titanium loading (0.6 mmol g^{-1}) yields a ratio of 1.6 H_2 molecules adsorbed per titanium site. The absence of irreversible adsorption below about 150 K implies the presence of an activation barrier. After overcoming the barrier, the hydrogen molecules are stably bound at room temperature as H_2 -metal moieties. The hydrogen that remains in the Ti-HMS sample after room temperature evacuation can be released by heating the sample to approximately 350 K, as seen in Figure S5 in the Supporting Information.

To gain better insight into the resulting hydrogen-Ti-silica complex, we conducted INS measurements (Figure 2). INS has been shown to be extremely powerful in probing the structure of the original dihydrogen Kubas complexes, with a wealth of rotational and vibrational modes in the low to intermediate (0.1 meV to 100 meV) energy range.^[8] The use of INS is essential for our material as the paramagnetic Ti^{III} complex prevents the use of NMR techniques. The INS spectrum of the sample in which the hydrogen is loaded at low temperature (50 K) is quite similar to that of hydrogen on bare HMS (see Figure S2 and S3 in the Supporting Information), both of which can be understood by considering the hydrogen as a simple physisorbed rotor. Both Ti-HMS

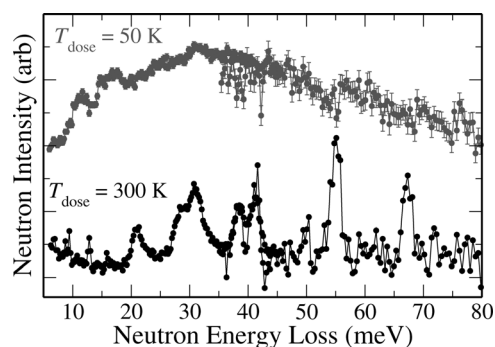


Figure 2. Comparison of the INS spectra collected at 4 K, showing the low-energy modes from H_2 adsorbed at low temperature (50 K, top) and at room temperature (300 K, bottom). Sharp features that appear below 15 meV in the bottom spectrum arise from $\lambda/2$ scattering from the PG monochromator and are equivalent to the primary features. Error bars represent $\pm 1\sigma$ due to counting statistics.

and HMS contain a dominant recoil background that appears as a steplike function starting near 15 meV, accompanied by two sets of features. As in HMS, there are a pair of broad features at 12 meV and 17 meV that arise from a splitting of the 14.7 meV H_2 rotational level due to surface interactions. This indicates that some of the hydrogen is interacting with bare HMS-like surfaces, though the feature is slightly broader in Ti-HMS, indicating a more heterogeneous adsorption surface. In Ti-HMS, there is also a weak feature at 14.7 meV due to a largely unperturbed H_2 rotor, likely due to physisorption of the hydrogen near the residual benzyl ligands. Thus, for low-temperature adsorption (< 150 K), the titanium centers provide only modest improvements in the sorption performance.

Room-temperature sorption of hydrogen leads to dramatically different spectra as compared to the spectrum from the hydrogen that was adsorbed at low temperature (see Figure 2). The signatures of molecularly adsorbed hydrogen, namely the low-energy (ca. 12 meV to 17 meV) rotational peaks and recoil background, are entirely absent. Instead, there are several vibrational bands in the 20 meV to 100 meV range (Figure 2 and Figure S4), which are too low in energy to be attributable to titanium hydride formation.^[9] These modes are in addition to those present in the starting compound, which confirms that there is no reduction in the number of benzyl ligands. Both of these features strongly suggest the formation of an intermediate energy dihydrogen complex. These modes remain unchanged after the sample has been heated above the vapor point under vacuum, confirming that the modes are not due to physisorbed molecular hydrogen and suggesting that these are stable complexes. Further, the dihydrogen complex was stored for 40 days under vacuum at room temperature and then re-measured by INS; the spectrum was quantitatively unchanged, confirming the stability of the complex (see the Supporting Information). We also collected INS spectra after the sample was dehydrogenated by heating under vacuum at 350 K. All hydrogen-related modes have now been removed, however, comparison of the desorbed spectra with that of pristine Ti-HMS (Figure S4) shows that some of the Ti-benzyl vibrational modes also disappear, suggesting some reconstruction of the Ti-benzyl groups with thermal cycling. This is again consistent with the known instability of Ti^{III} complexes under some conditions (see the Supporting Information).

To understand the H_2 -Ti-HMS interactions further, we performed total-energy calculations from DFT using the plane-wave implementation of the local-density approximation to DFT (see Supporting Information for details). Silica surfaces are notoriously heterogeneous and process dependent, possessing a number of different hydroxyl groups whose concentrations can vary considerably,^[10] and thus we have considered several organometallic/silica bonding motifs in the DFT calculations. We focus here on the structure that best explains the experimental results, with details of the other structures available in the Supporting Information. The HMS surface (Figure 3) is modeled as two layers of SiO_4 tetrahedra derived from the high symmetry cristobalite

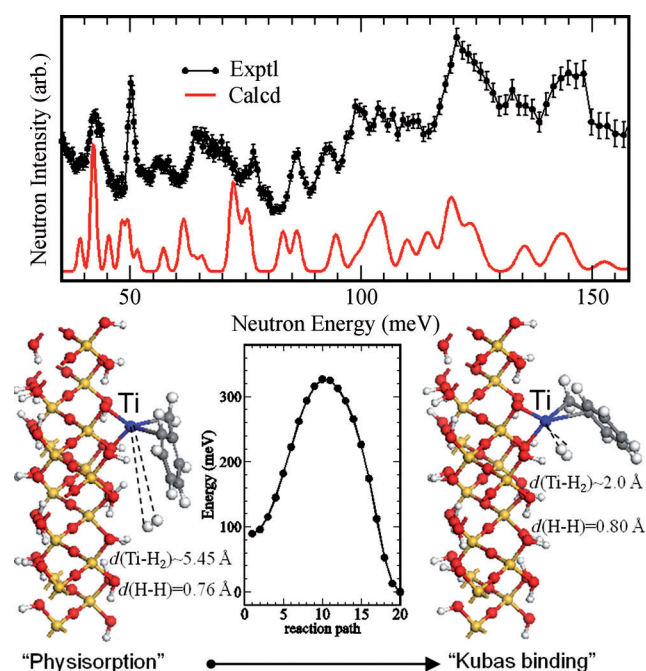


Figure 3. Top: Comparison of the INS spectra of the activated Ti-HMS and a simple DFT model in which Ti–benzyl is attached to two layers of hydrogen-passivated SiO₂. Bottom: The calculated reaction path from physisorption to Kubas-like dihydrogen binding with an activation barrier that is consistent with our measurements. Error bars represent $\pm 1\sigma$ due to counting statistics.

structure of SiO₂. The bottom Si and O atoms are fixed at their bulk positions, whereas the top (i.e. surface) Si and O atoms are fully relaxed. The surface oxygen atoms that do not contribute to the attachment of the organometallic are passivated by hydrogen atoms, which are also fully relaxed. For this case, the Ti atom is attached to a SiO₂ group with geminal hydroxyl groups (i.e. the two oxygens are attached to a single silicon atom); bonding through vicinal (different silicon atoms) and isolated hydroxyl (single Ti–O bond) groups are given in the Supporting Information. Because the INS intensity in this system is dominated by the scattering due to the hydrogenous ligands, the detailed bonding and vibrational structure of the silica host contributes negligibly to the spectra. Though several chemistries are possible and may be present (see the Supporting Information), the best agreement between experiment and DFT calculations is for the case of one benzyl ligand remaining after the sample is activated at 180 °C rather than two ligands (see Figure 3), leaving a highly reactive Ti^{III} that is critical for the dihydrogen coordination; only those structures that possess the Ti^{III} center can support dihydrogen–Ti bonding.^[11] Despite the simplicity of our model, the agreement between experiment and calculations is rather good. The calculations indicate that the Ti^{III} center is stabilized by the remaining benzyl ligand bending down toward the surface, blocking any direct access of hydrogen molecules for possible dihydrogen bonding (Figure 3).

The sterically constraining benzyl coordination would seem to prohibit any hydrogen adsorption, however, our

first-principles reaction path calculations indicate that as the hydrogen molecule nears the Ti center, the benzyl ligand moves away, much like a trap door, costing approximately 240 meV in energy before allowing the dihydrogen–Ti complex to form. As is expected for a dihydrogen complex, the H₂–Ti distance is reduced from a typical van der Waals distance of approximately 3 Å, indicative of physisorption to a distance of approximately 2 Å and is accompanied by an elongation of the H–H bond from 0.76 Å to 0.80 Å.^[12] Recently published DFT calculations have derived a similar starting structure as illustrated in Figure 3, however the absence of reaction-path calculations caused the activation barrier and experimentally observed dihydrogen complex to be missed.^[13] The calculated energy barrier is consistent with the experimental observation of an activation barrier to stable complex formation and is similar to the energy barrier found in Ti–ethylene complexes,^[3c] suggesting that the barrier is a common property of these systems. Given the heterogeneous nature of the experimental surface chemistries, we have also performed DFT calculations assuming slightly different surface chemistries (see the Supporting Information). In these calculations, it is shown that dihydrogen interacting with other Ti^{III} chemistries also exhibits activated coordination, though with slightly different energy profiles, while a Ti^{IV} variant shows completely nonbonding interactions. Each Ti^{III} chemistry is qualitatively consistent with the experimental observations, namely activated formation of a (meta)stable dihydrogen complex, and it is possible that the high reactivity of Ti^{III} complexes may lead to a time-dependent change in the relative abundance of each surface chemistry, with corresponding changes to the activation barriers to the dihydrogen state. Nonetheless, we believe that the structure presented in Figure 3 best explains all of the experimental data presented in this work. Though we cannot explicitly preclude the possibility of dihydride complex formation at this point, the calculated H–H bond lengths strongly indicate that the coordination is dihydrogen in nature.^[12a] Interestingly, due to competing Ti–benzyl and Ti–H₂ interactions, the final dihydrogen complex has a similar ground-state energy, being lower by approximately 90 meV. Indeed, exposure of Ti-HMS to 120 °C H₂ gas is consistent with earlier studies suggesting protonation of the Ti^{III} ion by substitution of hydrogen for the benzyl ligand (see Figure S1 in the Supporting Information).^[7c] Thus, higher temperatures destabilize the dihydrogen complex and removal of hydrogen from the complex should be possible under relatively mild conditions, since it passes a similar energy barrier as the initial adsorption. In practice, this allows hydrogen charging by using excess pressure, while using temperature to remove the hydrogen as was observed by INS and sorption measurements.

Lastly, we return to the experimental INS spectra shown in Figure 2. INS investigations of the original Kubas complexes were analyzed based on a pure rotational model in which the coordinated dihydrogen is treated as a simple surface-adsorbed quantum rotor and the measured modes correspond to transitions between rotational energy states. The

INS spectrum in Figure 2 cannot be rationalized based on this simple model. Based on our DFT–molecular dynamics simulations, the hydrogen dynamics in these systems are quite complex, involving strongly coupled rotation–translation dynamics. The original Kubas complexes possessed relatively open faces for dihydrogen bonding, such that the quasi-2D rotations of the coordinated dihydrogen are a reasonable description of the local environment.^[8,14] In our case, the dihydrogen is in a sterically constrained environment such that there are likely strong perturbations to rotations in the coordination plane as well as strong coupling to the center of mass motion of the H₂ molecule. We have performed classical DFT calculations (see the Supporting Information) using a simplified model of the calculated final dihydrogen complex structure (see Figure S12), which qualitatively agree with the experimentally measured spectra. Fully quantum calculations on the final structure in Figure 3 are ongoing to provide more quantitative comparison with the experimental INS spectra.

In conclusion, we have shown that grafting Ti^{III} complexes into a porous matrix provides active sites for room-temperature Kubas-like adsorption of dihydrogen. Although the specific complexes studied here do not show sufficient capacity for a viable storage system, it does represent the first to provide direct experimental evidence for the use of supported transition-metal complexes for enhanced dihydrogen binding at room temperature in line with previous theoretical predictions. The formation of the strongly bound H₂–Ti complexes is suppressed by an activation barrier such that low-temperature adsorption offers only physisorbed hydrogen. This surprising finding is very important and it suggests that in the search for new hydrogen storage materials, one should not limit the measurements at 77 K (which is a standard procedure) but also check absorption isotherms at room or higher temperatures for a possible activated binding. In addition to showing that the hydrogen is stably bound for long periods of time at room temperature, we have also shown that it can be released under modest heat treatments. Having experimentally established the efficacy of these supported dihydrogen complexes, future work can be focused on optimizing the surface and volume density of the binding sites through choice of ligands and supports, probing the effect of different transition metals, and enhancing the stability and repeatability of the metal–dihydrogen complexes over multiple cycles.

Experimental Section

The sample used in this study was based on hexagonal mesoporous silica (HMS) that had been grafted with 0.2 molar equivalents of tetrabenzyltitanium (0.2TiBz₄-HMS, hereafter Ti-HMS); details of the synthesis have been presented previously.^[6] The presence of Ti^{III} ions in the surface-grafted complex was confirmed by using EPR spectroscopy. The titanium concentration was measured to be (28 ± 5) mg ((0.6 ± 0.1) mmol) per gram of sample by prompt gamma neutron activation analysis

(PGAA)^[15] at the NIST Center for Neutron Research (NCNR). Gas sorption measurements were performed on a home-built, computer-controlled Sieverts system.^[16] INS measurements were performed at the NCNR on the BT-4 Filter Analyzer Neutron Spectrometer (FANS).^[17] Further details are provided in the Supporting Information.

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