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Stabilization of Volatile $\text{Ti}(\text{BH}_4)_3$ by Nano-Confinement in a Metal-Organic Framework

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Liquid complex hydrides are new class of hydrogen storage materials with several advantages over solid hydrides, e.g. flexible in shape, a flowing fluid and the convection facilitates the heat transport. The physical and chemical properties of a gaseous hydride change when the molecules are adsorbed on a material with a large specific surface area, due to the interaction of the adsorbate with the surface of the host material and the reduced number of collisions between the hydride molecules. In this paper we report on the synthesis and stabilization of the gaseous $\text{Ti}(\text{BH}_4)_3$. The compound was successfully stabilized through adsorption in nano-cavities. $\text{Ti}(\text{BH}_4)_3$ upon synthesis in its pure form spontaneously and rapidly decomposes into diborane and titanium hydride at room temperature in an inert gas, e.g. Argon. The $\text{Ti}(\text{BH}_4)_3$ adsorbed in the cavities of the metal organic framework is stable for several months at ambient temperature and remains stable up to 350 K in vacuum. The adsorbed $\text{Ti}(\text{BH}_4)_3$ reaches approximately twice the density of the gas phase. The specific surface area (BET, N_2 adsorption) of the MOF decreased from 1200 m^2/g to 770 m^2/g upon $\text{Ti}(\text{BH}_4)_3$ adsorption.

Introduction

Materials for energy storage and conversion are key elements that drive the evolution of the energy landscape. The energy efficiency strategies of existing processes and solutions for energy-storage challenges¹ are being intensely investigated. However, sustainable solutions may only be implemented if conventional fossil-based energy sources are replaced with renewable energy fluxes. The intermittency of these fluxes implies that the reversible storage of energy carriers is fundamental for a realistic and reliable alternative to the fossil-fuel-based society².

Because of its energy density (142 MJ/kg), hydrogen has been widely studied as a potential energy vector that could enable the transition to renewable energy sources². While the economic and technological challenges of the entire hydrogen cycle have been addressed, including its production, detection and delivery, hydrogen storage with a high gravimetric and

volumetric hydrogen density has remained one of the main challenges for the implementation of a hydrogen-based economy. The storage of hydrogen in the form of metal or complex hydrides exhibits very high volumetric hydrogen densities up to twice the density of liquid hydrogen³. MgH_2 ^{4,5}, LiBH_4 ^{6,7} and $\text{Mg}(\text{BH}_4)_2$ ^{8,9} have been intensively studied as storage materials. However, most of these high hydrogen-density solid compounds are too stable to spontaneously release hydrogen close to ambient conditions. Instead, they release hydrogen at conditions that do not match the requirements for practical applications, for instance, in combination with proton-exchange membrane (PEM) fuel-cell technology^{10,11}. An alternative approach is to use less stable hydrides that are gaseous or liquid under ambient conditions^{12,13}. The advantage of having a spontaneous hydrogen emitting reaction at room temperature is counteracted by the practical problems of handling such compounds. For example, $\text{Ti}(\text{BH}_4)_3$ and $\text{Al}(\text{BH}_4)_3$ spontaneously decompose into hydrogen and other products within hours, minutes or seconds^{14,15} and are highly flammable in contact with air.

Inspired by the confinement of acetylene molecules in microporous materials¹⁶, several successful attempts to stabilize unstable complex hydrides have been achieved via matrix encapsulation or inorganic complexing^{17–19}. The drawback of these previous investigations is that irreversible chemical reactions between the matrix and the complexes with the hydrides inhibit the reversible use of the matrix and change the decomposition reaction pathway of the hydrides. In addition, their use of catalysts and/or structural modifications may lead to the formation of transient states

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during stabilization, which are difficult to detect. Rapidly evolving species (RES) is a general term that describes thermodynamically unstable phases evolving from chemical reactions that spontaneously react/transform on a short time scale. To determine the mechanisms of multi-step reactions, the role of the involved intermediates or transient species must be clarified. Examples of reactions where the formation of transient or intermediate species can alter the overall process include the adsorption of molecules on a surface²⁰ or catalytic processes, such as gas conversion and reduction^{21–24}. Structural and thermodynamic information is indispensable for controlling and engineering reaction pathways, which is a crucial issue for reliable and safe energy conversion and storage.

In this work, we investigate the stabilization of a gaseous RES via physisorption in the nanocavities of a metal-organic framework (MOF), as schematically shown in **Figure 1**. The MOF contains and stabilizes the gaseous molecules, and the RES shows no structural changes over months. Moreover, the eventual decomposition reaction pathway is dramatically changed, underlining the fact that a thermodynamic alteration has occurred.

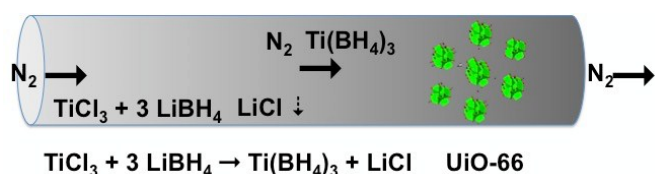


Figure 1. Schematic representation of the gas adsorption by a MOF. The gas molecules ($\text{Ti}(\text{BH}_4)_3$) were synthesized in a reactor and adsorbed on the MOF (UiO-66) via N_2 flow.

$\text{Ti}(\text{BH}_4)_3$ was selected as the gas molecule for this study because of its interesting properties for energy storage (containing 13 wt% hydrogen). It is a highly unstable gas under ambient conditions and can be obtained as the metathesis product of LiBH_4 and TiCl_3 ¹³. In this synthetic approach, nitrogen flow carried newly synthesized $\text{Ti}(\text{BH}_4)_3$ molecules from the reactor to a cold trap containing the adsorbent MOF, UiO-66^{25,26} (see Methods). The zirconium-based MOF UiO-66 was chosen due to its exceptional thermal stability (up to 770 K)²⁷, the suitability of its cage size (1.6 - 1.7 nm diameter)²⁷ for confining the $\text{Ti}(\text{BH}_4)_3$ molecules, and its white color, which facilitates the detection of any color changes due to guest additions. The exploitation of porous materials experienced a breakthrough in the past decade, once the properties of metal-organic frameworks as adsorbents were discovered^{28–32}. The major effort to date has been in finding materials with increased gas storage capacity and/or selectivity^{33–37}. However, the peculiarity of the present case lies in the fact that the adsorbed molecule is thermodynamically unstable; therefore, the strategic goal is controlling its rapid decomposition.

Experimental

All chemicals were purchased from Sigma Aldrich and were used without further purification.

UiO-66 ($\text{Zr}_6\text{O}_4(\text{BDC})_6$, BDC=1,4-benzenedicarboxylate) was prepared using the facile synthetic route developed by Farha *et al.*²⁶. First, 123 mg of 1,4-benzenedicarboxylic acid was mixed with 125 mg of ZrCl_4 , 1 cm^3 of hydrochloric acid and 15 cm^3 of dimethyl formamide (DMF) in a scintillation vial. The reaction mixture was allowed to react at 350 K overnight. The product was filtered, and the remaining unreacted reagents were removed while the high-boiling point DMF was exchanged to tetrahydrofuran (THF) overnight at 430 K using a Soxhlet apparatus. Prior to further use, UiO-66 was activated for 16 h in vacuum at 490 K.

$\text{Ti}(\text{BH}_4)_3$ was produced by metathesis between LiBH_4 and TiCl_3 (3:1 molar ratio) via ball milling for 10 minutes in a PQ-N04 planetary mill (Across International) using a stainless steel vial (100 mL) and stainless steel balls (diameter: 10 mm). It was then captured in the UiO-66 within a cold trap at 200 K. First, the cold trap was filled with UiO-66 in an Ar glovebox to avoid exposure to air. Then, the trap was sealed and allowed to cool in a dry-ice–acetone bath to ca. 200 K under a constant N_2 flow (1.5 bar). After milling, the reaction mixture was inserted into a flow reactor at room temperature, and the nitrogen flow was allowed to carry the gaseous $\text{Ti}(\text{BH}_4)_3$ from the reactor to the trap, enabling gas adsorption on the MOF surfaces. To separate unwanted volatile side products (e.g. diborane), we made use of the differences in their boiling points (T_b diborane = 181 K, whereas $\text{Ti}(\text{BH}_4)_3$ is in a condensed state at 200 K); thus, the dry ice cold trap allowed for the selective condensation of the desired product. The $\text{Ti}(\text{BH}_4)_3$ -loaded UiO-66 was then kept at room temperature and pressure in a glove box for further investigations.

X-ray diffraction (XRD) data were collected in the Bragg-Brentano geometry using a Bruker D8 Advance diffractometer ($\text{CuK}\alpha$ radiation). Samples were loaded into XRD low background (Si single crystal) sample holders in an argon glove box and sealed within a poly(methylmethacrylate) (PMMA) airtight holder to prevent oxygen/moisture contamination during data collection.

The chemical composition of the $\text{Ti}(\text{BH}_4)_3$ -loaded UiO-66 was verified by probing the Ti:Zr ratio by energy-dispersive X-ray spectroscopy (EDX) using a Zeiss EVO 40 XVP scanning electron microscope equipped with an Oxford Instruments energy dispersive X-Ray spectrometer (EDS) at an accelerating voltage of 20 kV. The samples were briefly (<1 min) exposed to air and were not coated prior to measurement.

Equilibrium N_2 adsorption isotherms at 77 K were acquired on activated samples, using a Micromeritics Tristar II 3020 instrument, measuring 20 data points during both adsorption and desorption. The Brunauer–Emmett–Teller surface area were calculated with the help of the Micromeritics software

package and using the linear region of the adsorption isotherms (data points up to $0.2 p/p_0$). Barrett-Joyner-Halenda pore size and volume analysis was performed using the Micromeritics software package.

Raman spectra were acquired using a WITec alpha 300SAR confocal Raman microscope system (WITec GmbH, Ulm Germany). All Raman measurements were performed with a frequency-doubled Nd:YAG laser with an excitation wavelength of 532 nm and the 100x objective of the confocal microscope (Zeiss EC "Epiplan-Neofluar" 100x NA = 0.9; WD = 0.31 mm). In total, 10 - 1000 spectra were acquired with an integration time of ca. 80 ms. Spectral resolution of this instrument is $\pm 3 \text{ cm}^{-1}$. The spectra were corrected using the built-in background subtraction function of the system.

Decomposition of $\text{Ti}(\text{BH}_4)_3$ was monitored with the aid of a temperature-programmed sealed autoclave coupled to a mass spectrometer (TPD-MS), which allowed for the detection of volatile species. Mass spectra were collected using a Stanford Research Systems (SRS) residual gas analyzer (RGA 300) quadrupole mass spectrometer. The $\text{Ti}(\text{BH}_4)_3$ -loaded UiO-66 was placed in a sealed AISI316 VCR sample holder, outgassed at 3×10^{-7} bar and 300 K overnight. While still under vacuum, the samples were heated to 460 K at a heating rate of 0.5 K min^{-1} . The evolved gases were constantly monitored from 1 to 100 atomic mass units (AMU).

Multivariate curve resolution (MCR) is a method for analysing the evolution of spectral peaks. In this case, the analysis is applied to the temperature evolution of the MS spectra. The matrix of MS spectra is expressed as the product of a fixed number of simulated spectra and their concentrations. Each of the simulated spectra represents the emission of a specific group of species. For the analysis, the MATLAB software package was used, adopting the so-called MCR-ALS script^{43,44}. In this case, the best fit of the MS data was achieved using 2 simulated spectra, which means that the reaction has two steps, each of which is associated with the emission of specific fragments. The result of the fit gives the concentration of the two simulated spectra as a function of temperature and, thus, the temperature evolution of the associated species.

Results

Adsorption of thermodynamically unstable gas molecules on MOF nanocavities

Various methods were used to confirm the successful incorporation of $\text{Ti}(\text{BH}_4)_3$ into the porous structure of the MOF. Complete reaction of the starting materials to produce $\text{Ti}(\text{BH}_4)_3$ was verified by X-ray diffraction (XRD) of the residue powder in the reactor, showing that LiCl was the only crystalline phase after the metathesis reaction, as previously reported¹³ (Supplementary Figure S1). Visibly, the MOF powder underwent a white-to-grey color change upon exposure to gaseous $\text{Ti}(\text{BH}_4)_3$ (Supplementary Figure S2). Energy-dispersive X-ray (EDX) spectroscopy of the loaded MOF revealed the

presence of Ti (Supplementary Figure S3), which is not present in the MOF pre-exposure. The Brunauer–Emmett–Teller (BET) surface area of the loaded MOF, determined by nitrogen adsorption at 77 K, was found to be roughly half that of the pristine MOF prior to loading: $770 \text{ m}^2/\text{g}$ (Supplementary Figure S4). The Barrett-Joyner-Halenda (BJH) pore-size analysis³⁸ probing the variation of the average pore diameter of UiO-66 after the addition of $\text{Ti}(\text{BH}_4)_3$, revealed a decrease in the average pore width after loading of 3.44 \AA (Supplementary Table S1).

Most importantly, the incorporation of $\text{Ti}(\text{BH}_4)_3$ into the pores of the MOF was unambiguously demonstrated by solid-state Raman spectroscopy of the loaded material. The vibrational modes appearing in the $2400 - 2550 \text{ cm}^{-1}$ range correspond to the B-H stretching mode of the BH_4 unit in $\text{Ti}(\text{BH}_4)_3$, in agreement with previous observations on solid complex hydrides³⁹. The intensity of the B-H stretching mode at 2435 cm^{-1} is approximately 10% of the primary MOF mode at 1611 cm^{-1} , giving a qualitative indication of the success of the gas adsorption. **Figure 2** shows the Lorentzian fitted Raman spectrum at room temperature of the as-prepared UiO-66 (spectrum a) and the same material after exposure to $\text{Ti}(\text{BH}_4)_3$ gas (spectrum b), where the B-H stretching modes are evident, in the region between $2400 - 2550 \text{ cm}^{-1}$; the raw data and fit parameters are given in Supplementary Figure S5. The vibrational modes of UiO-66 are present in all spectra. The modes between 650 and 1700 cm^{-1} can be attributed to the organic linkers^{40–42}. These modes are not significantly altered upon $\text{Ti}(\text{BH}_4)_3$ adsorption (within the instrumental spectral resolution of $\pm 3 \text{ cm}^{-1}$), likely due to their much larger number compared to adsorbed molecules in this work.

The adsorbed $\text{Ti}(\text{BH}_4)_3$ is stable over time, when kept in an argon glove box at ambient pressure and temperature. Raman spectroscopy of the $\text{Ti}(\text{BH}_4)_3$ -exposed material after several months demonstrated that the stabilized gas remained adsorbed in the nanocavities of the MOF, as shown in Figure 2. This implies that a remarkable increase in stability was achieved, since pure $\text{Ti}(\text{BH}_4)_3$ decomposes in less than a few hours under an argon atmosphere at ambient pressure and temperature¹³.

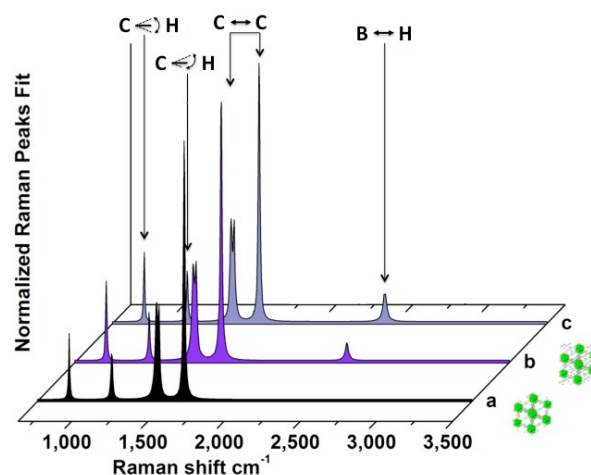


Figure 2. Fitted Raman spectra showing successful gas adsorption on the MOF and the stabilization of the gas molecule. Fitted Raman spectra at room temperature for (a) the pristine MOF, (b) the loaded MOF and (c) the loaded MOF after 1 month in argon atmosphere at ambient pressure and room temperature. The illustrations represent the pristine and loaded MOF. The vibrations are assigned as follows: 650 - 900 cm^{-1} C-H out-of-plane bending; 1140 cm^{-1} C-H in-plane bending; 1430 - 1625 cm^{-1} C-C stretching; and 2435 cm^{-1} B-H stretching, visible only in the loaded sample⁴⁰.

Stabilization of the thermodynamically unstable gas molecules

The incorporation of $\text{Ti}(\text{BH}_4)_3$ into the nanocavities of the MOF not only stabilizes the borohydride with respect to time, as discussed above, but also makes it more thermally stable. The mechanism of the adsorbed complex-hydride decomposition was investigated using temperature-programmed desorption combined with mass spectrometry (TPD-MS) and Raman spectroscopy (Figure 3 and 4, respectively). The loaded MOF was heated in vacuum ($< 10^{-3}$ mbar), and the mass spectra of the evolved gases were acquired as a function of temperature of the sample, as shown in Figure 3b. Unlike of the case of pure $\text{Ti}(\text{BH}_4)_3$ decomposition¹³, no signal from diborane was

detected at room temperature. The mass-to-charge (m/z) signals from Ti-B-H containing fragments appear near 350 K. B-H fragments (BH_4 $m/z = 15$; $(\text{BH}_4)_2$ $m/z = 30$; $(\text{BH}_4)_3$ $m/z = 45$ or B_5H_9 $m/z = 58, 59$) and Ti containing species ($\text{Ti}^{10,11}\text{B}_2\text{H}_4$ $m/z = 72, 73$ and $\text{Ti}^{10,11}\text{B}_3\text{H}_{10}$ $m/z = 90, 91$) are discernible, which is a distinctly different behavior from that which was previously observed for the decomposition of pure $\text{Ti}(\text{BH}_4)_3$ in either ultra-high vacuum or at ambient pressure, both of which yielded diborane as the main decomposition product at room temperature¹³. To correlate and identify the formation of intermediate species during the decomposition of $\text{Ti}(\text{BH}_4)_3$, multivariable curve resolution (MCR) analysis was performed on the TPD-MS data^{43,44}. The results of the analysis are shown in Figure 3a and 3c, where the matrix of the TPD-MS spectra is expressed as the product of a fixed number of calculated spectra (Figure 3a) multiplied by their concentrations (Figure 3c). TPD-MS data are best fitted with two simulated spectra (percent of variance at the optimum = 99.5659), which differ mainly in the 55 - 65 and 90 - 95 m/z regions (Figure 3a). The plot of the simulated spectra's concentrations as a function of temperature (Figure 3c) reveals a two-step process. No emission of species was detectable below 350 K apart from impurities. The black curve in Figure 3c represents the emission of intermediate species (such as B_5H_9) that disappear

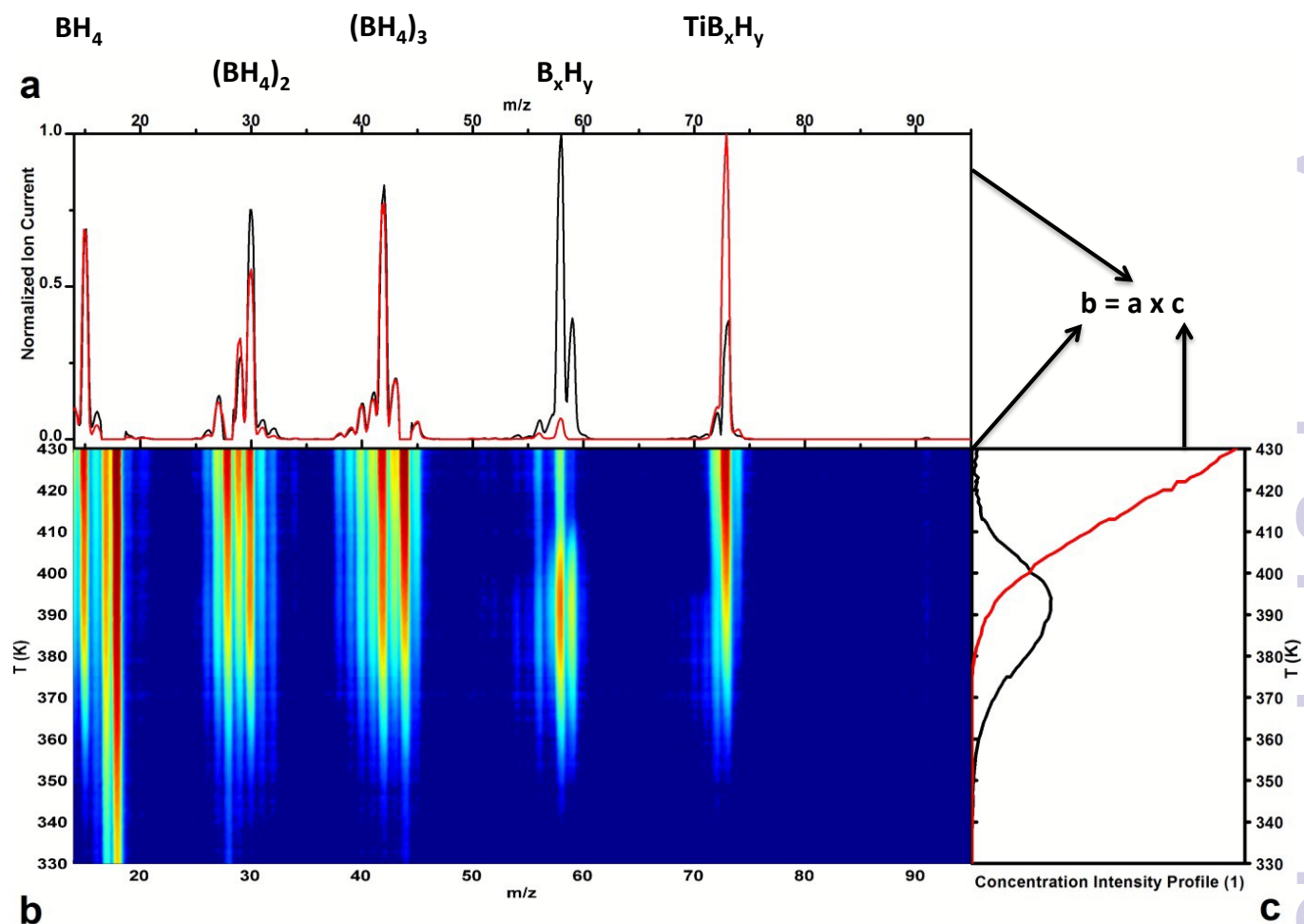


Figure 3. TPD-MS, Raman spectroscopy and MCR analysis showing the decomposition reaction of the adsorbed gas molecules from the MOF. The TPD-MS matrix (panel b) is expressed as the product of the simulated spectra (panel a) and their concentrations (panel c). In detail, panel a: Simulated TPD-MS spectra from MCR analysis (impurities have been removed from the input data). The experimental data in panel b were best fitted with two simulated spectra (black and red curves). Panel b: Experimental TPD-MS spectra of the adsorbed sample during the heating ramp. The intensities of the signals in arbitrary units are represented by a range of colors from blue (Ion Current = min) to red (Ion Current = max). Panel c: Concentration profiles of the simulated TPD-MS spectra in panel a^{43,44} as a function of temperature from MCR analysis.

at approximately 410 K. The red curve represents the continuous emission of species (e.g., B-H units) up to 430 K, when the sample is completely decomposed. This result suggests that the decomposition of the adsorbed $\text{Ti}(\text{BH}_4)_3$ proceeds via an intermediate step.

To better characterize these decomposition products, *ex-situ* Raman spectra of the loaded MOF were acquired at room temperature after the TPD-MS treatment. Figure 4 shows the Lorentzian fitted Raman spectrum of the UiO-66 as prepared (spectrum a), after $\text{Ti}(\text{BH}_4)_3$ gas exposure (spectrum b) and after TPD-MS treatment up to 470 K and cooled back to room temperature (spectrum c). In the post-decomposition MOF sample (spectrum c), the B-H stretching mode at 2435 cm^{-1} disappears, and two modes at 2245 and 2950 cm^{-1} appear. The high energy of the latter mode could correspond to transient C-H interactions; however, there is no further indication of changes in the MOF structure, i.e., in the C-H bending region. Both modes might be assigned to B-H stretching modes of intermediate species and products from the evolution of the BH_4 unit. The B-H bond can stretch and shift its characteristic vibration frequencies upon distortion of the BH_4 unit, as previously demonstrated by Raman spectroscopy studies of borohydrides⁴⁵. Raw data and the fit parameters are given in Supplementary Figure S6.

The additional modes observed in the Raman spectrum of the loaded MOF after decomposition of the adsorbed $\text{Ti}(\text{BH}_4)_3$ disappear upon prolonged laser irradiation or air exposure (Figure 4 spectrum d). The fully decomposed spectrum is identical to that of the pristine MOF (comparing Figure 4 spectrum d to Figure 4 spectrum a). No B-H stretching modes remain, and the Raman modes corresponding to the pristine MOF do not present any apparent changes (complete raw data and fit parameters are given in Supplementary Figure S6), indicating that the MOF did not undergo any structural changes upon guest adsorption and release. XRD measurements (Supplementary Figure S7) of the MOF before and after guest adsorption reveal that no significant structural changes have occurred in the specimen. While chemisorption of $\text{Ti}(\text{BH}_4)_3$ on the UiO-66 may occur to some extent, our experimental data strongly suggest that the framework remained intact upon guest sorption. Visibly, the MOF reverts

to its original white color after decomposition of the $\text{Ti}(\text{BH}_4)_3$, or after release of the adsorbed gas to air.

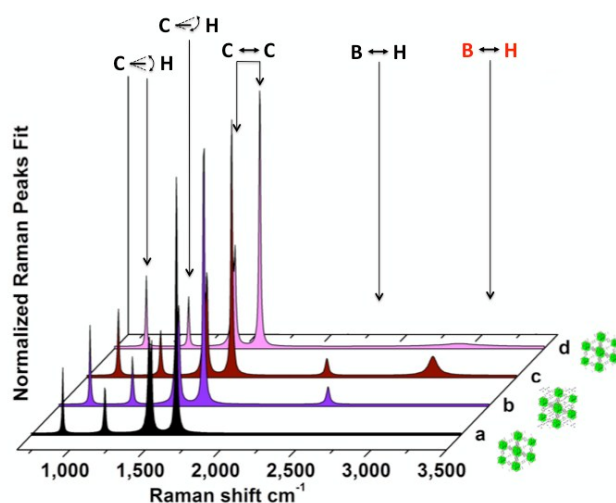


Figure 4. Fitted Raman spectra showing the decomposition of the loaded MOF. Fitted Raman spectra at room temperature for (a) the pristine MOF, (b) the loaded MOF, (c) the loaded MOF after heating in a vacuum to 470 K and (d) the loaded MOF after TPD-MS and air exposure. The illustrations represent the loaded and pristine MOF. The vibrations are assigned as follows: $650 - 900\text{ cm}^{-1}$ C-H out-of-plane bending; 1140 cm^{-1} C-H in-plane bending; $1430 - 1625\text{ cm}^{-1}$ C-C stretching; 2435 cm^{-1} B-H stretching, visible only in the loaded sample⁴⁰; 2245 and 2950 cm^{-1} B-H stretching, visible only in the sample after heat treatment.

Discussion

The presented data show several results: $\text{Ti}(\text{BH}_4)_3$ is incorporated into the MOF, the loaded sample is stable over time if kept in an inert atmosphere (argon, 1 bar, room temperature), and $\text{Ti}(\text{BH}_4)_3$ is released and decomposes at 350 K without diborane emission. The gaseous $\text{Ti}(\text{BH}_4)_3$ molecule is normally thermodynamically unstable. Therefore, the adsorption of $\text{Ti}(\text{BH}_4)_3$ on the MOF alters the stability of the $\text{Ti}(\text{BH}_4)_3$ and enables the characterization of the normally transient species. To interpret this stabilization, we seek its origin in the host-guest interaction.

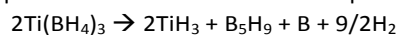
The molecule $\text{Ti}(\text{BH}_4)_3$ decomposes spontaneously at room temperature. This process is favored by collisions with surface phonons, photons or other $\text{Ti}(\text{BH}_4)_3$ molecules. In the loaded MOF, the encapsulated $\text{Ti}(\text{BH}_4)_3$ molecules can diffuse and migrate within the porous structure. However, inter-molecular collisions are hindered when the gas molecules are highly dispersed and thus diluted on a supporting framework. When this is the case, the $\text{Ti}(\text{BH}_4)_3$ molecules are held at a certain distance from one another, and their stabilization would then be achieved by restricting the reactions between two molecules, as for acetylene¹⁶. This behavior would imply that, on average, each $\text{Ti}(\text{BH}_4)_3$ molecule is confined in a pore. When a guest is adsorbed in the pores of a scaffold, the pore size decreases accordingly; indeed we observed a decrease in the

average pore width after loading of 3.44 Å. Because the narrowest diameter of the non-spherical $\text{Ti}(\text{BH}_4)_3$ molecules is approximately 2 \AA^{46} , it is therefore suggested that, on average, there is more than one $\text{Ti}(\text{BH}_4)_3$ molecule per UiO-66 pore, which means that the guest molecules are close enough to replicate the phase-pure reaction and that their stabilization is not due to the dilution of the molecules. This result is supported by the rough estimation of $\text{Ti}(\text{BH}_4)_3$ loading in the MOF, as suggested by the Raman spectroscopy shown in Figure 2. By taking into account such a successful loading process, the $\text{Ti}(\text{BH}_4)_3$ molecules should be able to migrate and react as they would outside of the MOF unless they were adsorbed onto the surfaces of the MOF pores.

If the $\text{Ti}(\text{BH}_4)_3$ was adsorbed to the MOF pore surface the molecule's potential would be altered due to the strong host-guest bonds, which is confirmed by Raman spectroscopy. Previous spectroscopic studies on pure gaseous $\text{Ti}(\text{BH}_4)_3$ exhibit two distinct peaks in the B-H stretching range¹³. The splitting of the B-H stretching modes is due to the highly asymmetrical configuration of the BH_4 units, which have three hydrogen atoms (H_b) bridged between the titanium and boron and one terminal hydrogen atom (H_t) bonded uniquely to the boron (tridental configuration). Infrared spectroscopy on $\text{Ti}(\text{BH}_4)_3$ molecules in the gas phase reveals a mode at 2025 cm^{-1} that is assignable to the B- H_b vibration and a mode at 2590 cm^{-1} that is assignable to the B- H_t vibration^{13,47}. Due to the C_{3h} symmetry of the $\text{Ti}(\text{BH}_4)_3$ molecule⁴⁷, these vibrations are also Raman active and therefore should be present in the spectra of the loaded sample. Conversely, in Figure 2, the single B-H stretching peak at 2435 cm^{-1} suggests a symmetrical configuration of the $[\text{BH}_4]^-$ ion, typical of stable complex hydrides^{7,45}. The shift of the B- H_b stretching mode to 17% higher energy reflects a change in binding energy of the B-H atoms⁴⁸. The bond dissociation energy in diatomic B-H is 3.5 eV; therefore, a stabilization of 0.6 eV is achieved. This stabilized system should induce a shift in decomposition temperature of approximately 67 K. Gaseous $\text{Ti}(\text{BH}_4)_3$ molecules decompose at room temperature¹³, while, as shown in Figure 3 by mass spectroscopy, the loaded sample does not decompose below 350 K: approximately 57 K above room temperature and in agreement with the calculation on the stabilization of the molecule.

The lack of $\text{Ti}(\text{BH}_4)_3$ bending modes in the Raman spectrum of the loaded MOF supports the hypothesis of a change in the symmetry of the molecule. In addition, when a molecule is adsorbed on a substrate, the selection rules for Raman activity differ from the ones of the free molecule⁴⁹. The surface-gas interaction also explains the stabilization effect of the MOF on the $\text{Ti}(\text{BH}_4)_3$ molecule: the MOF surface lowers the free energy of the molecule. A similar effect has been observed for microporous siliceous frameworks⁵⁰. The adsorption of transition states or RES on these surfaces is favored even in the absence of specific sites for chemical binding. It may therefore be possible that, as a general rule, the physisorption of transient or thermodynamically unstable species on porous materials provides a significant enthalpy stabilization of the adsorbates⁵⁰. The change in the thermodynamic state of the

$\text{Ti}(\text{BH}_4)_3$ molecule opens the possibility for a new decomposition reaction pathway. The lack of diborane emission is evidence of a modification in the decomposition pathway of the adsorbed molecule. The spectroscopic evidences suggest a decomposition reaction pathway that involves the pentaborane as intermediate step:



and where the pentaborane recombines with the increased temperature to form solid higher boranes. Modification of decomposition reaction pathways has already been observed for melt infiltrated complex hydrides in nanoporous materials and has been attributed to effects due to the confinement of the complex hydride in the pores^{51,52}. The different decomposition mechanism might indicate reversible hydrogen sorption reactions of $\text{Ti}(\text{BH}_4)_3$. Previous studies identified diborane as one of the key elements restricting this process. Therefore, this new system might be reversible due to the lack of diborane emission¹³. These findings open up new opportunities for the thorough investigation of the effects of surfaces on adsorbents.

Conclusions

$\text{Ti}(\text{BH}_4)_3$, a highly reactive gaseous molecule at room temperature, was incorporated into a metal-organic framework and found to be thermodynamically stabilized. The adsorption on a MOF stabilizes unstable $\text{Ti}(\text{BH}_4)_3$ for months and changes the energy configuration of the system. The adsorption is achieved without reaction with the scaffold matrix and is potentially reversible. This new approach allows for safe storage and easy handling of volatile unstable complex hydrides. Additionally, it provides an opportunity for the physical characterization of transient states. The lack of chemical bonding or substitution between the transient species and the framework allows for the release of the species upon heating or air exposure and allows for subsequent guest reload in the framework.

This case study opens a new route for the practical use of a class of transient materials that is interesting for energy storage and, more generally, acts as a proof of concept of the stabilization of rapidly evolving species.

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