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Influence of MXene termination groups on hydrogen interactions

Ashe Mahoney¹, Patrick Ward²

¹ California State University Northridge, Northridge, CA USA

² Savannah River National Laboratory, Aiken, SC USA

Abstract

MXenes are a relatively new class of nanomaterial consisting of alternating layers of transition metals and carbon or nitrogen, capped off on either end by terminal groups, usually from the P-block. They have been considered for a wide range of purposes, including hydrogen storage. In this study, thermogravimetric analysis and mass spectrometry residual gas analysis are performed on $\text{Ti}_3\text{C}_2\text{T}_x$ and Ti_2CT_x to characterize their terminal groups. The hydrogen absorption capabilities of the heat-treated samples are measured using a Sievert apparatus and compared against untreated samples. This reveals that, during heating, the MXenes lose hydrogen, water, fluoride, hydrofluoric acid, and carbon dioxide. Isothermal absorption measurements suggest that the removal of termination groups might improve hydrogen uptake kinetics at high temperatures, but has little effect at room temperatures.

I.) INTRODUCTION

A.) Background

As humanity's demand for energy continues increasing every year, and intermittent renewable energy sources (e.g., wind or solar) take over an increasing share of energy production, it becomes essential to find improved ways of storing that energy. One promising method is to store it in the exceptionally stable bond of the hydrogen molecule. Hydrogen provides an energy density of up to 33 kWh/kg in pure gas form and produces only water as a byproduct of breaking that bond.¹ Of course, as a gas, hydrogen has a very low volumetric energy density, and thus finding a way to store it as a solid is preferred.

MXenes are one material that show some potential for being able to store hydrogen in the solid state. They are one of several carbon-based nanomaterials such as fullerenes and metal-organic frameworks (MOFs) which have recently been the subject of attention in this field. MXenes are 2-dimensional carbide or nitride structures which consist of alternating layers of carbon/nitrogen and a transition metal. They are formed from using an acidic solution, usually hydrofluoric acid, to exfoliate their parent 'MAX phases,' which resemble sheets of MXenes with a layer of a metalloid (usually Al) between them. The transition metal surfaces of MXenes are found to be covered in termination groups leftover from this etching process, usually -F, -OH, or =O.

In theory, the bonding sites being taken up by the termination groups could be used to form bonds to hydrogen instead. Additionally, hydrogen could be bound within the crystalline lattice or strongly physisorbed to the basal plane surface of the MXene. However, no

experimental measurements have been carried out to evaluate the effect that heat-treating MXenes has on their termination group composition or hydrogen absorption capabilities.

MXenes have already been shown to be easily produced at scale,² and several other of their qualities, such as their high mass density compared to fullerenes and MOFs, and their composition of abundant and lightweight materials (such as Ti, C, N, etc.) make these materials good candidates for widespread use in hydrogen storage. Furthermore, the many other uses of MXenes such as catalysis, electromagnetic interference shielding, antibacterial material, sensors, supercapacitors, batteries, electrodes, and more, mean that a deep dive into their composition and properties will be valuable to several fields of development.^{1, 3, 4}

B.) Scope and plan

This paper is only one small section of a larger study of the interactions of hydrogen with MXenes that is ongoing at Savannah River National Laboratory (SRNL) in collaboration with researchers from University of California, Los Angeles (UCLA), California State University, Northridge (CSUN), and Drexel University. For my contribution to this study, I use thermometric and gas sorption techniques to gather data about MXenes. Thermogravimetric analysis, which simultaneously records a sample's mass and temperature as it's heated, was utilized to allow us to see at what temperatures the sample is losing mass to decomposition. The technique was carried out inside of an argon filled glovebox to prevent sample exposure to the atmosphere. This is coupled with residual gas analysis, in which the mass lost from the sample as gas is sent through a mass spectrometer, allowing insight into exactly what compounds are being vaporized off the sample, and at what temperatures.

Finally, isothermal absorption measurements are used to investigate the hydrogen uptake capabilities of the samples and how they change when the MXene is stripped of its termination groups or otherwise altered. Altogether, the data collected through these methods should come together to draw a map of what is happening at the MXene surface as it goes through these treatments, and give direction for further investigation.

II.) METHODS

A.) TGA/RGA

Samples of MXene, either $\text{Ti}_3\text{C}_2\text{T}_x$ or Ti_2CT_x , were weighed into a stainless steel crucible on a TGA instrument in amounts ranging from 3 mg to 11 mg. In each run, the samples were heated from 30 °C to 900 °C at ramp rates ranging from 10 °C/min to 30 °C/min, and were held at 900 °C for times ranging from 10 minutes to 30 minutes. Their current mass compared to their starting mass was constantly recorded. During all of these runs, the off-gas from each sample was sent to a mass spectrometer for analysis to help identify the compounds responsible for the samples' mass loss during heating. The mass spectrometer was run in secondary electron multiplier (SEM) detection mode with ionization energies varied from 70 eV to 20 eV to allow detection of parent ions. All measurements took place in an argon environment with either argon or nitrogen purge gas, depending on which ions we were looking for and to prevent ion overlap with species of interest.

B.) Annealing the MXenes

In order to compare the MXenes' hydrogen absorption capabilities with and without their functional groups, heat-treated samples had to be prepared. In order to do this, either $\text{Ti}_3\text{C}_2\text{T}_x$ or Ti_2CT_x , was weighed into a clean pressure composition temperature (PCT) vial, which was

sealed in a high-temperature reaction vessel inside the argon glovebox before being attached to the PCT. The temperature controller on the PCT was then set to ramp and soak, taking two hours to ramp up to 900 °C, and then staying at 900 °C for at least one hour, all under vacuum. After this annealing step, the reaction vessel was disassembled inside the glovebox to avoid exposure to air, and the heat-treated sample was collected from the PCT vial. “Untreated” MXenes were still heated to 150 °C for 2 hours to drive off residual moisture and leftover etchant.

C.) Isothermal hydrogen absorption measurements

Isothermal absorption measurements were run on heat-treated $\text{Ti}_3\text{C}_2\text{T}_x$, heat-treated Ti_2CT_x , untreated $\text{Ti}_3\text{C}_2\text{T}_x$, and untreated Ti_2CT_x . These measurements were performed by weighing a known amount (ranging from 200 mg to 1 g) of sample into a clean PCT vial, setting up the reaction vessel the same way as was done for heat-treatment, and then allowing the PCT to run cycles consisting of 2 hours of desorption/evacuation and 3 hours of absorption, for about one day per sample. For all measurements, the hydrogen supply reserve was set to 60 bar, which lowered to about 35 bar once pressure equilibration from the PCT reservoir to the sample chamber occurred. A leak test using helium was performed prior to every measurement, as was a volume calibration of the sample holder. Hydrogen uptake was measured at 30 °C, and then at 600 °C for each sample. For some samples, the temperature was simply raised to 600 °C during the ongoing measurement, meaning no volume calibration at 600 °C was performed (to perform a scoping study). Generally, the difference in temperature only resulted in a ~4% (~240 mL at 600 °C and ~250 mL at 30 °C) difference in volume.

III.) RESULTS AND DISCUSSION

A.) Identity of termination groups

The heating that took place during TGA/RGA measurements evidently stripped the MXenes not only of compounds physically trapped between their sheets, but also stripped several types of termination groups from their surfaces. Typically, $\text{Ti}_3\text{C}_2\text{T}_x$ samples lost about 10-15% of their mass during heating, and Ti_2CT_x samples lost about 25-30% of their mass during heating, indicating significant vaporization of some compounds that had been attached to the MXenes. The mass spectrometry analysis of the heated samples' off-gas corroborates this by showing m/z peaks that align with certain expected compounds. For each of the two MXenes, two of the most informative graphs are shown below in Figure 1.

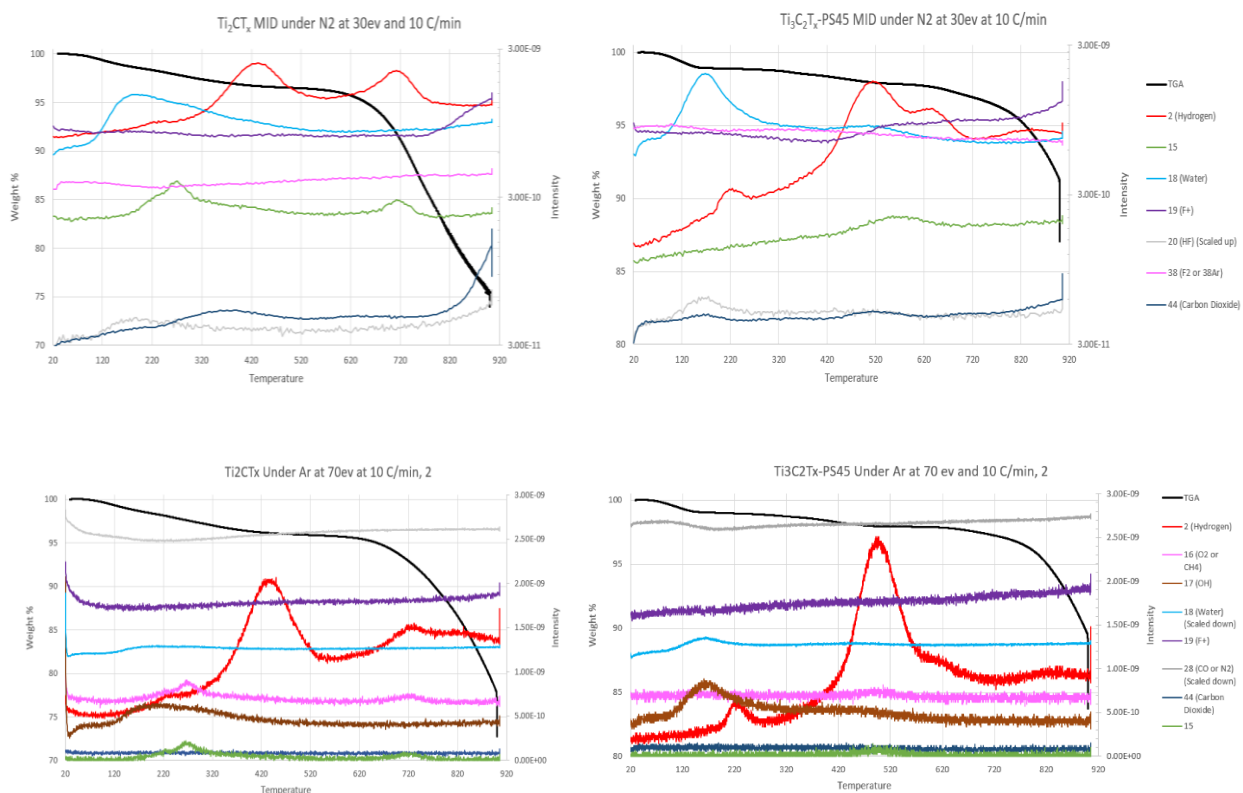


FIG. 1. Top row: TGA graph at 10 °C/min under nitrogen purge gas of Ti_2CT_x (left) and $\text{Ti}_3\text{C}_2\text{T}_x$ (right) overlaid

with the respective RGA graphs from multiple ion detection at 30 eV ionization energy searching for $m/z = 2, 15, 18, 19, 20, 38,$ and 44 . Bottom row: TGA graph at $10\text{ }^{\circ}\text{C}/\text{min}$ under argon purge gas of Ti_2CT_x (left) and $\text{Ti}_3\text{C}_2\text{T}_x$ (right) overlaid with the respective RGA graphs from multiple ion detection at 70 eV ionization energy searching for $m/z = 2, 15, 16, 17, 18, 19, 28,$ and 44 .

The earliest peaks, at $m/z = 17, 18,$ and 20 , indicate the loss of compounds leftover from etching, namely water (H_2O^+ and the fragment OH^+) and hydrofluoric acid (HF^+). The low temperature needed to remove them indicates that they are physically absorbed in the MXene structure rather than chemically bonded to it, reinforcing the idea that they are simply leftover etchant. Notably, there is no more detectable loss of H_2O or OH after this initial loss of leftover etchant. There were also no observable peaks at $m/z = 32$ (O_2^+). Thus, there is no evidence of any oxygen-containing termination groups being removed from the MXene before $900\text{ }^{\circ}\text{C}$.

There were some small peaks of $m/z = 16$ (potentially O^+), but they always coincide with peaks at $m/z = 15$. This particular combination is most likely attributed to CH_3^+ and CH_4^+ , or, in other words, methyl groups. While we are fairly certain about the identity of these methyl groups, we do not know where they are coming from.

Approaching $900\text{ }^{\circ}\text{C}$, there is also a large peak in $m/z = 44$ which represents CO_2 . This is the only evidence for any removal of oxygen terminations, because in the inert atmosphere of the glovebox, the oxygen in CO_2 could only be coming from oxygens breaking off of the MXene itself. The carbon in the CO_2 likely comes from the edges of MXene sheets where the carbon layer is exposed rather than covered by the titanium layer.

Finally, peaks at $m/z = 2$ indicate the removal of hydrogen gas (H_2^+). Several distinct $m/z = 2$ peaks at different temperatures suggests that hydrogen is coming from multiple sources,

or different kinds of chemical bonds to the MXene structure or from other termination groups such as -OH.

Particularly notable are the hydrogen peaks visible at 900 °C when using high ionization energy. When the ionization energy is lowered, peaks at $m/z = 20$ are visible instead, suggesting that HF is present. When an electron ionization energy of 70 eV is used, HF is fragmented into F^+ and H_2^+ , but 30 eV ionizes it into HF^+ and F^+ instead. Since fluorine is bonded to the MXene as a single atom rather than as -HF, and there is no other apparent source of hydrogen at these temperatures, this data suggests the presence of hydrogen termination groups, a possibility which has not been previously discussed. Furthermore, the lack of a peak at $m/z = 38$ at 900 °C shows that F_2 is not being detected; this provides further support for the idea that the MXene is losing not only -F termination groups at 900 °C, but also a large amount of -H termination groups.

B.) Influence of termination groups on hydrogen uptake

At time of writing, only one of the MXenes, $Ti_3C_2T_x$, has been tested in the Sievert apparatus to measure its hydrogen uptake. Two $Ti_3C_2T_x$ samples were tested; one untreated sample and one annealed sample. The isotherms of each sample/temperature combo are averaged, and these averages are graphed together for comparison. These averages leave out the variation between absorption cycles that was observed but are sufficient for a quick comparison between the different samples.

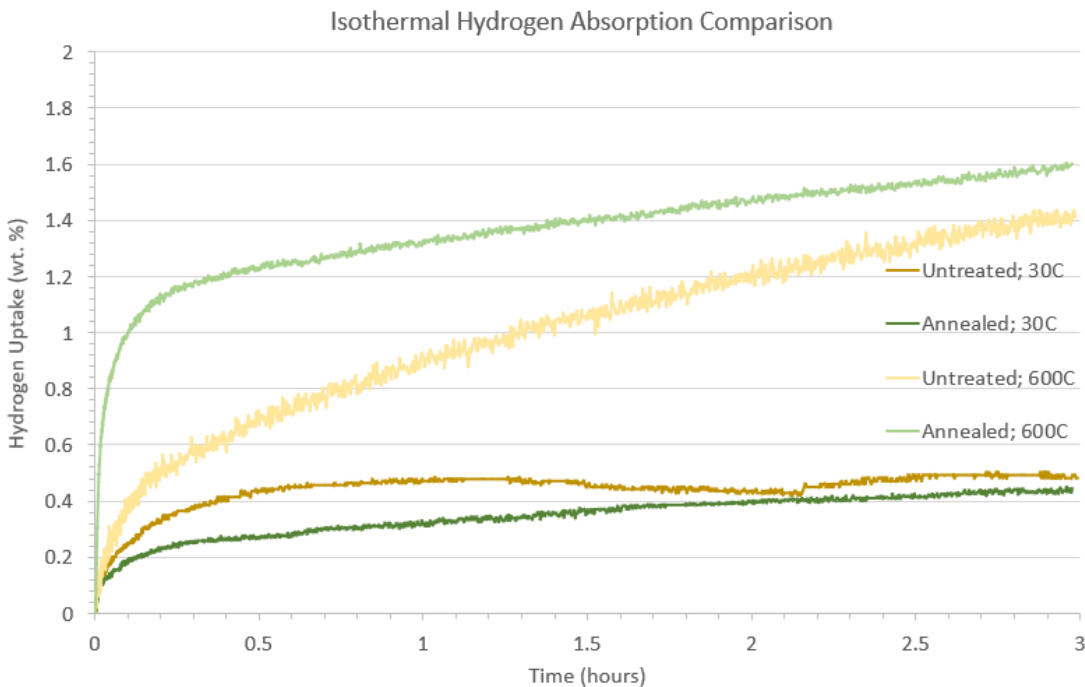


FIG. 2. The average of all isotherms of a given sample and temperature are graphed together for comparison.

In general, it appears that there is little influence of termination group removal on hydrogen uptake at 30 °C. However, a significant increase in the kinetics of hydrogen uptake and minor increase in capacity is observed for annealed samples at 600 °C. These preliminary results are only exploratory and further investigations are ongoing. Furthermore, these averages do not show the variation in measurements between absorption cycles, which can be quite significant, as seen in this summary of the annealed sample:

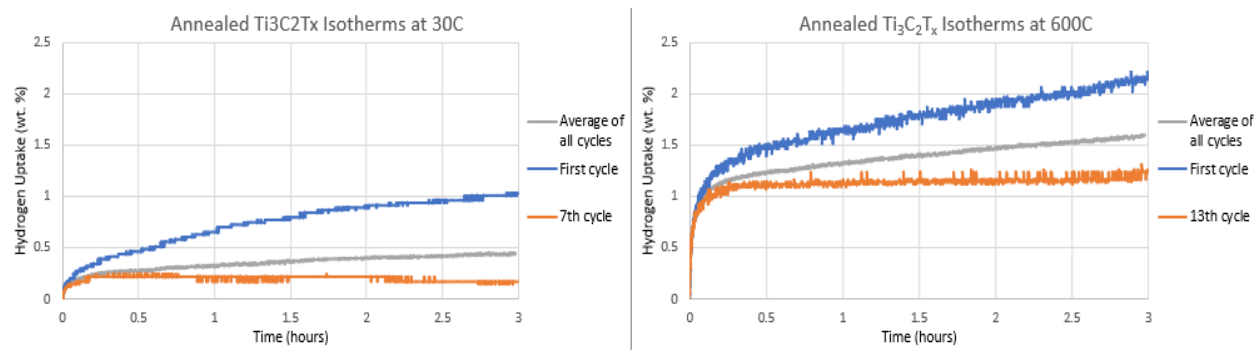


FIG. 3. Graphs of isotherms for the annealed Ti₃C₂T_x at 30 °C (left) and 600 °C (right). Each graph includes the isotherm of the first (highest uptake) cycle, the isotherm of the second-to-last (lower uptake) cycle, and an average of all cycles.

While the last absorption cycle of each sample/temperature did not necessarily show the lowest hydrogen uptake, each sample/temperature did consistently show its highest hydrogen uptake during its first absorption cycle. This is largely unsurprising; not all hydrogen uptake is necessarily reversible. How well these materials maintain their hydrogen uptake capabilities after repeated absorption/desorption cycles is an important piece of information, but is ultimately outside the scope of this paper.

VI.) CONCLUSION

During this work, the first ever evidence of hydrogen termination groups on Ti-C based MXenes was discovered through a systematic TGA/RGA analysis. This changes what we know about the surface of MXenes. The possibility of hydrogen terminations is something that has not yet been discussed in any prior MXene research, despite previous confirmation of HF as a decomposition product of these MXenes at high temperatures.⁵ Other information gained in this study, such as the multiple sources of hydrogen throughout heating, are planned to be investigated further with spectroscopic techniques to identify specifically what kinds of termination groups hydrogen release is originating from. Preliminary PCT results reveal increased hydrogen uptake kinetics at high temperatures upon termination group removal and a slight increase in capacity. Further investigation is currently underway.

Works Cited

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