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Assessing the reactivity of TiCl_3 and TiF_3 with hydrogen

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ABSTRACT

TiCl_3 and TiF_3 additives are known to facilitate hydrogenation and dehydrogenation in a variety of hydrogen storage materials, yet the associated mechanism remains under debate. Here, experimental and computational studies are reported for the reactivity with hydrogen gas of bulk and ball-milled TiCl_3 and TiF_3 at the temperatures and pressures for which these additives are observed to accelerate reactions when added to hydrogen storage materials. TiCl_3 , in either the α or δ polymorphic forms and of varying crystallite size ranging from ~5 to 95 nm, shows no detectable reaction with prolonged exposure to hydrogen gas at elevated pressures (~120 bar) and temperatures (up to 200 °C). Similarly, TiF_3 with varying crystallite size from ~4 to 25 nm exhibits no detectable reaction with hydrogen gas. Post-exposure vibrational and electronic structure investigations using Fourier transform infrared spectroscopy and x-ray absorption spectroscopy confirm this analysis. Moreover, there is no significant promotion of H_2 dissociation at either interior or exterior surfaces, as demonstrated by H_2/D_2 exchange studies on pure TiF_3 . The computed energy landscape confirms that dissociative adsorption of H_2 on TiF_3 surfaces is thermodynamically inhibited. However, Ti-based additives could potentially promote H_2 dissociation at interfaces where structural and compositional varieties are expected, or else by way of subsequent chemical transformations. At interfaces, metallic states could be formed intrinsically or extrinsically, possibly enabling hydrogen-coupled electronic transfer by donating electrons.

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Introduction

Metal hydrides are attractive hydrogen storage media due to their theoretical high gravimetric and volumetric hydrogen densities and possible reversibility [1,2]. Nevertheless, most

bulk hydrides suffer from unfavorable thermodynamics and slow kinetics. Reversible hydrogen storage materials have been based on Mg (e.g., MgH_2), Al (e.g., NaAlH_4 , LiAlH_4 , AlH_3), N (e.g., LiNH_2/LiH), B (e.g., $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$) and C (C/Pt). The kinetics associated with the hydrogen storage reactions of

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desorption and re-hydrogenation in these materials are typically slow for reasons that are poorly understood. Empirically, it is found that TiF_3 or TiCl_3 mixed with the storage material at the ~2–5 mole % level acts to accelerate hydrogen storage reactions for Mg-based [3–9], Al-based [10–26], B-based [27–34], N-based [35,36] and C-based [37] materials. It is remarkable, given the difference in chemistries of Mg, Al, N, B and C, that this commonality of function would be observed for TiCl_3 and TiF_3 , suggesting that there might be a common catalytic agent operative in these systems.

The identity of the catalytic species that accelerates the hydrogen storage reactions remains unknown in almost all cases. Typically, the TiF_3 or TiCl_3 additives are ball-milled into the base hydrogen storage material, producing a 2–5 mole % mixture with particle sizes ~1 μm diameter or less. The additive/host composite mixture is then processed thermally, desorbing hydrogen at ~200 °C or higher with subsequent rehydrogenation at elevated temperature and H_2 pressure. This thermal processing introduces the possibility of activating the TiF_3 or TiCl_3 molecules themselves, or inducing chemical reactions between the additive and the host storage material. Prior work with these additives has identified the formation of MgF_2 and TiH_2 in the MgH_2 system [4–6,8]; Ti_2Al_5 , TiAl_3 , TiAl , alloys of the form $\text{Ti}_{(1+x)}\text{Al}_{(1-x)}$, LiCl , NaCl , zero valent Ti metal and TiH_2 in the Al-based materials [10,12,15,16,18,23–25]; LiF , TiB_2 and TiH_2 in the B-based materials [28,31]; LiCl and TiN in the Li-N-H system [35,36]; and catalytic F-C bonds in C-based materials [37]. Nonetheless, there is no direct evidence that any of these products have catalytic or promotion activity. On the contrary, when these products are intentionally introduced into their hydrogen storage hosts from the start, no significant improvement in reaction kinetics is observed. This has been found for tests of TiH_2 , TiN and MgF_2 for MgH_2 [6,8]; zero valent Ti metal, TiAl_3 and TiH_2 for Al-based materials [18,21,23,24]; and LiF and TiH_2 in B-based materials [31]. In other cases, the catalytic inactivity of these products can be inferred because their production by thermal treatment and cycling coincides with a loss of kinetic and capacity performance, as seen in Al-based [38,39], B-based [31] and N-based materials [35]. Still one should remain open to the general possibility that the catalytic species is a reaction product between the additive and the host hydrogen storage material.

Alternative mechanistic functions for the added TiCl_3 or TiF_3 have been proposed, including the generation of zero valent Ti “at the Al surface” [15], retention of “grain refinement” and increase in H vacancies (promoting H diffusion) caused by the presence of the additives [16], “point defect hexahydrides” with population promoted by the presence of Ti species [26], and catalytically active F-C bonds [37]. The anions F^- and Cl^- may also play a role in the kinetic promotion [7,40–42]. Finally, it remains unclear how TiF_3 and TiCl_3 can promote hydrogen storage in such a diverse range of materials, when the chemistry of the hosts varies so much.

As part of an effort to understand the fundamentals of how these additives affect hydrogen storage reactions and how they can influence the chemistry of so many different materials systems, it is prudent to start from the simplest point possible, namely the reactivity of the additives themselves with hydrogen. Surprisingly, there have been no prior studies

of the reactivity of TiF_3 and TiCl_3 with hydrogen under the conditions of temperature and hydrogen pressure in which they promote hydrogen storage reactions as additives. In this paper, we investigate the reactivity of TiF_3 and TiCl_3 with hydrogen for commercial (as-received) materials, as well as for ball-milled TiF_3 and TiCl_3 , in order to evaluate the influence of reduced particle size and potential material defects on possible reaction with H_2 . We also investigate the potential for the bulk and ball-milled TiF_3 to dissociate molecular hydrogen using H_2/D_2 isotope exchange experiments, and structure-dependent H_2 dissociation and adsorption energetics using *ab initio* computation.

The focus of these experimental and computational studies is to clarify how TiF_3 or TiCl_3 could affect the kinetics of hydrogen storage reactions after ball-milling with the storage material, but prior to any chemical reaction with the host material. In those systems where the combination of hydrogen and thermal processing produce chemical reaction between the additive and the host, these studies provide information on the unreacted portion that may remain after some chemical reaction has occurred. We also examine through computation how Ti-based additives could promote H_2 dissociation at interfaces where structural and compositional varieties occur, or else by way of subsequent chemical transformation.

In this work we make reference to “additives” rather than to “catalysts.” Whereas pure catalysts affect the kinetics of a chemical reaction without changing what products are generated or the equilibrium constant, we recognize that materials added to hydrogen storage reaction may instead react with the host material, thereby altering the reaction path and the product distribution. We refer to an additive that accelerates hydrogen storage reactions as a “catalytic agent” with this understanding in mind.

Experimental methods

All sample handling and preparation were conducted in an Ar-filled glove-box equipped with a recirculation system that keeps H_2O and O_2 concentrations below 0.1 ppm. Commercial grade TiF_3 and TiCl_3 were obtained from Sigma-Aldrich and Alfa Aesar, respectively. These materials were ball-milled to investigate the effect of reduced particle size and possible material defects and stresses on the reactivity towards hydrogen. Ball-milled material was produced by loading tungsten carbide (WC) mill pots with TiF_3 or TiCl_3 and milling with $\frac{1}{2}$ ” diameter 440C stainless steel balls from SPEX Sample Prep, Inc. The ball/powder mass ratio was 18. In one case, $\frac{7}{16}$ ” diameter WC balls were used with the same ball/powder mass ratio to assess the possible role of milling contamination (principally Fe from stainless steel) on hydrogen reactivity. Milling was conducted under high-purity Ar for 2 h using a SPEX Sample Prep 8000M high-energy mixer mill.

The TiF_3 and TiCl_3 samples (both as-received and ball-milled) were examined during hydrogen exposure with Sieverts uptake measurements to assess hydrogen reaction. Sample masses for the Sievert's measurements were in the 1.2–1.4 g range. Material characterization before and after hydrogen exposure was conducted with x-ray diffraction

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