



# Hydrogen-enhanced combustion of a composite propellant with $ZrH_2$ as the fuel



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## ABSTRACT

The reaction mechanisms of metal hydrides in the combustion of solid propellants are closely related to their effects on the energetic and combustion properties of propellants. Here, we report a first attempt to investigate the reaction mechanisms of  $ZrH_2$ , a promising candidate for fuels, in the combustion of HTPB propellants using ammonium perchlorate ( $NH_4ClO_4$ , AP) as the oxidizer.  $ZrH_2$  is determined to possess a good resistance to the direct oxidation by AP. Thus, it would dehydrogenate independently to generate  $H_2$  and metallic Zr, which is believed to be very favorable for decreasing the gaseous molecular masses. On the other hand, due to the attachment of gaseous reactants to it,  $ZrH_2$  was found to tune the decomposition behaviors of AP by enhancing the generation of NO in the high-temperature decomposition stage. More interestingly, the hydrogen released from  $ZrH_2$  is evaluated to promote the combustion reactions in gaseous phases and be responsible for the two-stage combustion behaviors of the corresponding propellant, which are distinct from those when metallic Al is used as the fuel. The findings in this work validate the potential of  $ZrH_2$  as a fuel for high-energy solid propellants.

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## 1. Introduction

In solid rocket propulsion for both civil and military applications, the pursuit for longer range necessitates the development of novel materials to improve the energetic and combustion performances of solid propellants [1,2]. Metal hydrides, which are also very useful for a range of applications including hydrogen storage [3–6], hydrogen generation [7,8] and reducing agents [9–11], have attracted sustainable attentions as a series of promising metal fuels for solid rocket propellants. It is supposed that, the metal hydrides are capable of providing simultaneously high energy from metal oxidation and low gaseous molecular mass due to hydrogen ( $H_2$ ) released during the combustion processes [12–14], thus resulting in enhanced specific impulses of solid propellants. Considerable efforts have been devoted investigating the applications of promising metal hydrides in propellants, such as aluminum hydride (alane,  $AlH_3$ ) [15–19], beryllium hydride ( $BeH_2$ ) [20], magnesium hydride ( $MgH_2$ ) [17,21], titanium hydride ( $TiH_2$ ) [22,23], lithium hydride ( $LiH$ ) [24] and ammonia borane ( $NH_3BH_3$ ) [25]. Especially, aluminum hydride ( $AlH_3$ ), which is proposed to be a promising al-

ternative to the most widely used metal fuel aluminum (Al), was found to be capable of increasing the specific impulse and decreasing the two-phase flow losses [12,15]. However,  $AlH_3$  is a fuel with relatively low density ( $1.477\text{ g/cm}^3$ ), which is significantly lower than those of aluminum ( $2.70\text{ g/cm}^3$ ) and conventional propellants (about  $1.60\text{--}1.70\text{ g/cm}^3$ ). Thus, if  $AlH_3$  is adopted to replace Al in the aluminized propellants, the volumetric loading of the resulting propellants would be evidently reduced. Obviously, this is unfavorable for their practical applications. Zirconium hydride ( $ZrH_2$ ), which is now under intense investigations in several fields including hydrogen storage [26,27], neutron shielding [28], blowing agents for foaming metals [29] and moderator in nuclear reactors [30], on the other hand, possesses a much higher density of  $5.61\text{ g/cm}^3$ . Therefore, the introduction of  $ZrH_2$  to propellants is proposed to be capable of providing both high energy and low gaseous molecular mass without reducing the densities [31].

As stated above, the high energy and low gaseous molecular mass offered by metal hydrides originate from the hydrogen and metal generated upon their dehydrogenation. However, it is well-known that, metal hydrides are reductive due to the existence of  $H^{\delta-}$  in them, thus resulting in a high possibility of the occurrence of interactions between metal hydrides and the strong oxidizers in solid propellants, such as ammonium perchlorate (AP), cyclotetramethylene-tetranitramine (HMX) and cyclotrimethylene-

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**Table 1**  
Main ingredients of the HTPB propellants.

Compositions		Contents (mass%)	Contents (mass%)	Contents (mass%)	Contents (mass%)
HTPB	Binder	10.22	10.22	10.22	10.22
Ammonium perchlorate	Oxidizer	71	71	71	71
Aluminium	Metal fuel	15	10	5	
ZrH <sub>2</sub>	Metal fuel		5	10	15
DOS	Plasticizer	3	3	3	3
TDI	Cross-linking agent	0.68	0.68	0.68	0.68

trinitramine (RDX). Furthermore, the above interactions are believed to result in the direct oxidation of metal hydrides, which would give rise to the generation of metal oxides and water instead of the expected H<sub>2</sub> and metals. Obviously, occurrence of the redox reactions between hydrides and oxidizers is very unfavorable for lowering the gaseous molecular mass and increasing the specific impulse of propellants. On the contrary, the independent dehydrogenation of metal hydrides in the existence of oxidizers to give H<sub>2</sub> and metals would benefit the energetic performances of solid propellants. As a consequence, for metal hydrides used as the fuels for solid propellants, it is of great importance to determine their interaction characteristics with the oxidizers. In addition, the role of hydrogen in hydride, which is believed to be very critical for propellant combustion, should be also evaluated. Previously, Lempert et al. investigated theoretically the specific impulses, densities and combustion temperatures of several ZrH<sub>2</sub>-based composite propellants with different oxidizers and binder [31,32]. However, little is known about the interaction characteristics of ZrH<sub>2</sub> with the oxidizers and especially, the role of hydrogen in ZrH<sub>2</sub>.

For several decades, ammonium perchlorate (AP) has been widely utilized as an oxidizer for solid rocket propellants [33–35]. As a major ingredient of the formulations, its interactions with metal fuels are closely related to the performances of AP-containing propellants. Herein, we investigate the interaction characteristics between ZrH<sub>2</sub> and AP, and especially, the role of hydrogen in the combustion of HTPB propellants containing ZrH<sub>2</sub> as the metal fuel. It is evaluated that, ZrH<sub>2</sub> would not be oxidized directly by AP or its decomposition products. Instead, it dehydrogenates to produce hydrogen and metallic zirconium which would promote the combustion of propellants. The new insights into the reaction mechanisms of ZrH<sub>2</sub> in propellant combustion are very useful for the applications of metal hydrides in solid rocket propellants.

## 2. Experimental section

Ammonium perchlorate is an energetic compound sensitive towards impact and friction. When handling AP, propellant samples containing AP and its mixtures with metal fuels, proper protective measures including ear protection, Kevlar gloves, face shield, body armor, and earthed equipment should be used.

Handling of the hydride was performed in a glove box (MBRAUN 200B) equipped with a circulation purifier to keep the concentration of O<sub>2</sub> and H<sub>2</sub>O below 0.1 ppm. In addition, extra attentions should be paid to the manufacturing of sample propellant containing ZrH<sub>2</sub> since ZrH<sub>2</sub> possesses higher reducing activity than Al.

### 2.1. Materials and sample preparation

The oxidizer ammonium perchlorate (AP, NH<sub>4</sub>ClO<sub>4</sub>, 120 μm), which is obtained from Dalian Gaojia Chemical Co., Ltd, was dried in vacuum at 70 °C for 24 h before use. Zirconium hydride (ZrH<sub>2</sub>, 10 μm) was obtained from Aladdin and used as received. Figure S1 (Supplementary material) exhibits the XRD patterns and FTIR spectra of AP (PDF number: 00-043-0648) and ZrH<sub>2</sub> (PDF number:

01-073-2076). It was found that, both AP and ZrH<sub>2</sub> showed good crystallinity. In addition, no impurities were detected by XRD and FTIR, suggesting their high purities.

Aluminum (Al, 5 μm), which is now the most widely adopted metal fuel in solid propellants, was used for comparison with ZrH<sub>2</sub>. Zirconium (Zr) was also used in evaluating the role of hydrogen in ZrH<sub>2</sub>. The binder, HTPB (hydroxyl-terminated polybutadiene), was obtained from Liming Research Institute of Chemical Industry. Moreover, in this work, dioctyl sebacate (DOS) and 2,4-tolylene diisocyanate (TDI) were utilized as the plasticizer and cross-linking agent, respectively. The compositions of propellant formulations are listed in Table 1 and no combustion catalysts were used in the formulations.

The propellant samples were prepared in 500 g batches using a vertical planetary mixer of 2 L capacity. All batches were mixed and cast under vacuum by a slurry process. After HTPB, DOS and TDI were mixed evenly, AP was carefully introduced into the mixture followed by additional mixing. Then, the fuel (Al, ZrH<sub>2</sub>) was added to the sample and mixed evenly. It is worth mentioning that the addition of ZrH<sub>2</sub> should be conducted under the protection of nitrogen. The propellant samples were cured at 50 °C for 72 h in a water jacketed oven. After that, the propellant densities were measured and densities were determined to be  $(1.75 \pm 0.01) \times 10^3$ ,  $(1.78 \pm 0.01) \times 10^3$ ,  $(1.81 \pm 0.01) \times 10^3$  and  $(1.84 \pm 0.01) \times 10^3$  kg/m<sup>3</sup> for the propellants containing 15 mass% of Al, 10 mass% of Al + 5 mass% of ZrH<sub>2</sub>, 5 mass% of Al + 10 mass% of ZrH<sub>2</sub> and 15 mass% of ZrH<sub>2</sub>. These densities are almost identical to the corresponding theoretical ones of  $1.75 \times 10^3$ ,  $1.77 \times 10^3$ ,  $1.81 \times 10^3$  and  $1.83 \times 10^3$  kg/m<sup>3</sup>, suggesting that the propellant samples possess good quality.

The AP/ZrH<sub>2</sub> combination system used for thermal analyses was prepared by physically mixing AP and ZrH<sub>2</sub> evenly using pestle and mortar.

### 2.2. Structural characterization

Phase identification was conducted using powder X-ray diffraction (XRD) on a PANalytical X'Pert Pro X-ray Diffractometer with Cu Kα radiation ( $\lambda = 1.5418$  Å) at 40 kV and 40 mA. The data were collected from 5° to 90° (2θ) in steps of 0.05° at ambient temperature.

The vibrational characteristics of chemical bonds were determined using a Bruker Tensor 27 Fourier Transform Infrared (FTIR) spectrometer. The spectra of the samples (as KBr pellets with a KBr to sample mass ratio of approximately 30:1) were acquired in the range of 4000–400 cm<sup>-1</sup> in the transmission mode with a resolution of 4 cm<sup>-1</sup>.

X-ray photoelectron spectroscopy (XPS) analyses were performed on an ESCALAB 250 Xi XPS microprobe (Thermo Scientific, U.K.). The sample was prepared by sprinkling powder on a carbon tape which was attached to the sample holder in the glove box. The sample was transferred into the vacuum prep chamber by a commercial transfer vessel with overnight pumping before the measurement. XPS spectra were recorded using monochro-

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