TG-FTIR Study on Effects of Titanium Dioxide Nanoparticles on the Decomposition of HAN Aqueous Solutions

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1. Introduction

Finding green liquid monopropellants that can replace hydrazine is necessary for propulsion community due to the ever stricter environmental and safety regulations as well as public health concerns. Potential replacements include H_2O_2 (hydrogen peroxide), $N_2H_5C(NO_2)_3$ (hydrazinium nitroformate, HNF), $NH_4N(NO_2)_2$ (ammonium dinitramide, ADN) and NH_4NO_3 (ammonium nitrate, AN), and $NH_3OH(NO_3)$ (hydroxylammonia nitrate, HAN). With relatively high performance, low vapor pressures, low melting points, and high chemical and thermal stabilities, HAN-based liquid monopropellant is among the more promising green propellant. It has been the green propellant selected for the NASA Green Propellant Infusion Mission (GPIM)[1]. HAN-based propellant can be ignited through thermal, catalytic and electrolytic decompositions [2-10].

It is well known that burning rates of monopropellants can be enhanced by adding nanoparticles of various metal oxides, such as silica, titania, and alumina. The research group at Texas A & M has recently studied effects of silica and titania nanoparticles on the burning rate of HAN aqueous solutions under elevated pressures [11,12]. The experiments showed that burning rates significantly increased with the presence of nanoparticles in the solutions. However, the exact mechanism that leads to burning rate enhancement is still far from clear.

In the present study, synchronized thermogravimetric and Fourier Transform Infra-red spectroscopy (TG-FTIR) measurements were performed to analyze the decomposition characteristics of HAN aqueous solutions with titanium dioxide (titania) nanoparticles. The weight loss rates as well as gas generation rates of with various TiO_2 mass loadings in HAN aqueous solutions were obtained. The measurements may be instrumental for better understanding of the influence of nanoparticles on thermal decomposition of HAN-based propellants.

2. Experimental Setup

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HAN aqueous solutions used in the present work is prepared in-house through acid-base titration of 25% nitric acid solution and 50% hydroxylamine at low temperatures. The low concentration HAN aqueous solution obtained from the titration process was then concentrated to various concentrations (density) using a rotary evaporator. Mean diameter of TiO_2 nanoparticle was 25 nm, and the nanoparticles were dispersed into the solution via ultrasonication. Figs 1 show the appearances of HAN aqueous solution before and after adding TiO_2 nanoparticles. The mass loading of TiO_2 in the solution shown in Fig. 1(b) was 0.657% , and the originally transparent HAN solution became opaque even with the relatively low TiO_2 mass loading.

(a) (b)

Fig. 1 (a) ρ=1.5117 g/cm^3 of HAN aqueous solution, and (b) the solution after adding 0.657 wt% TiO_2 nanoparticle

Thermal decomposition tests were performed using a synchronized TG-FTIR (PerkinElmer STA8000 and PerkinElmer, Spectrum Two). The sample weight loaded for each test was 10±0.5 mg, and the sample was heated from 30 °C to 300 ° C at 10 ° C / min in the TG-FTIR furnace. The purge gas was nitrogen. Resolution of the FT-IR spectrum was 4 cm^{-1} to allow higher sampling frequency of the decomposed gas.

3. Results and Discussions

Results of thermogravimetric measurements of HAN aqueous solution and HAN solution with 0.657% TiO_2 were shown in Fig. 2. The decomposition temperature was drastically reduced from 172 ºC to 120 ºC with the addition of TiO_2 nanoparticles although the mass loading is far less than the value reported in Ref. [12]. The enhancement of derivative weight, which corresponded to the decomposition rate of the solution, was even more dramatic. The peak rate increased by 31 times, from 100%/min to 3100%/min. Fig. 3 further showed the influence of TiO_2 nanoparticles addition on the heat release during HAN decomposition. It was found that the addition of TiO_2 nanoparticles resulted in not only the reduction of decomposition temperature, but also more intense heat release. The narrower heat release peak is consistent with the evolution of derivative weight in Fig. 2. The areas below peaks of the two curves in Fig. 3 which represent total heat release remains the same. Considering the significant reduction of transparency after adding TiO_2 nanoparticle, radiation heat transfer to the aqueous solution during heating process can be largely promoted and may be the cause of the effects observed.

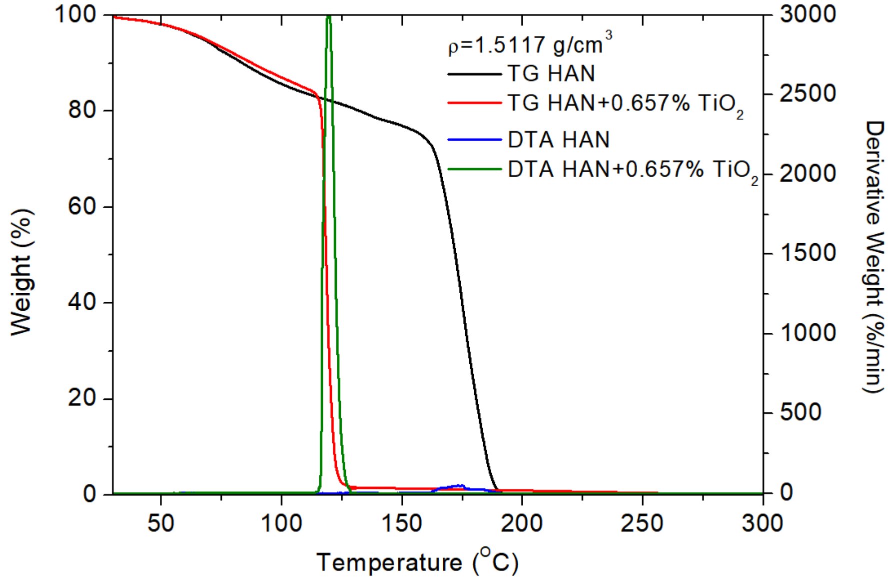

Fig.2 Comparison of HAN aqueous solutions with and without TiO_2 nanoparticle.

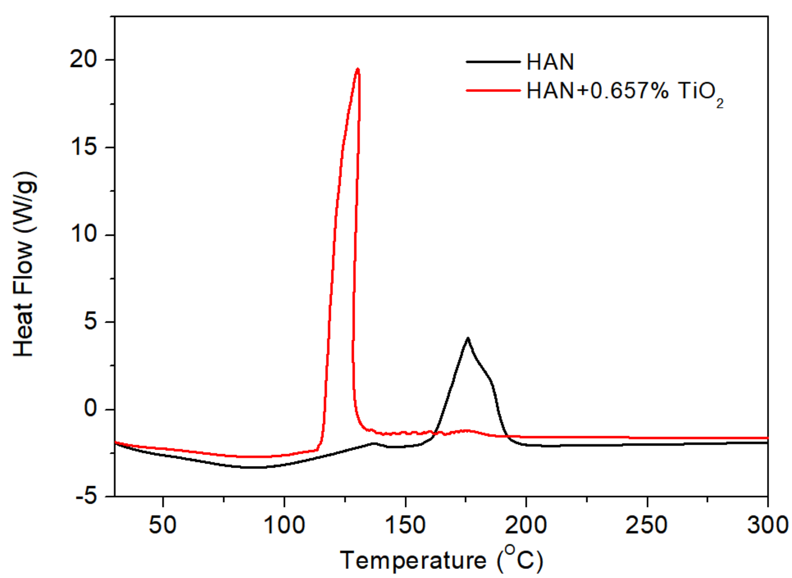

Fig. 3 Heat flow of HAN aqueous solution with and without TiO_2 nanoparticles (ρ_{HAN} = 1.5117 g/cm^3).

Figures.4 (a) and (b) showed the absorption spectra of evolved gas released from decomposition of HAN aqueous solutions with or without TiO_2 nanoparticle, respectively. The density of HAN aqueous solution for the test shown was 1.5117 g/cm^3. Spectra at key temperatures were selected to be shown in the figures. Absorption peaks from gas species including N_2O (2140-2285 cm^{-1}), H_2O (3500-4000 cm^{-1}, 1250-1352 cm^{-1}), NO (1762-1795 cm^{-1}), NO_2 (1483-1578 cm^{-1}) are observed on the spectra. In Fig. 4(a), strong absorption bands at 1250-2000 cm^{-1}, and 2000-2500 cm^{-1} were found at 173 °C, the temperature corresponded to the highest weight loss rate for solutions without TiO_2, indicating that gas phase decomposition products of

HAN aqueous solution composed of NO, NO_2, and N_2O. Fig. 4 (b) showed absorption spectra of gaseous products from solution with TiO_2 nanoparticles. Identical gas species, NO, NO_2, and N_2O were found in the decomposition product; however, the absorption peaks appeared at a low temperature, and the intensities were much higher.

(a)

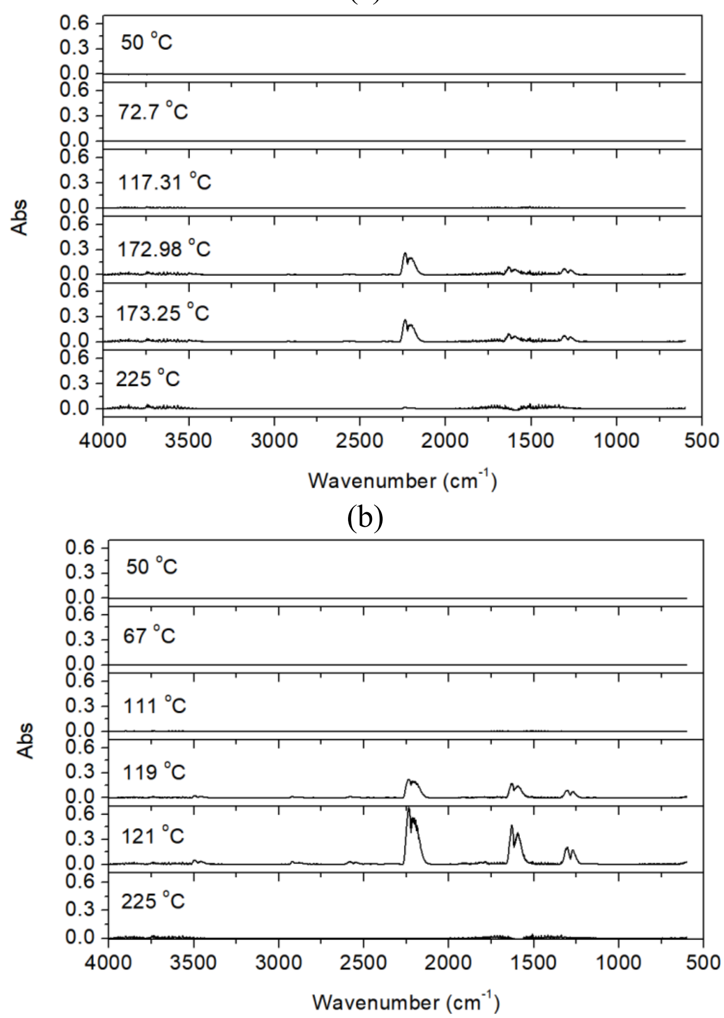

Fig. 4 Absorption spectra of evolved gas from the decomposition of ρ=1.5117 g/cm^3 HAN aqueous solution (a) without (b) with TiO_2 nanoparticle

Semi-quantitative analysis of the evolved gas species was performed by integrating the area below the spectra curves in Fig. 4 within the quantification window of each species. The results were shown in Figs. 5(a) and (b). It is found that concentrations of N_2O and H_2O was increased by 10% after adding TiO_2, while NO and NO_2 were less affected. Besides, the induction time of decomposition was shortened with the addition of titania nanoparticles.

A more extensive study on the effects of titania nanoparticles addition on the decomposition of HAN aqueous solution is underway. Parameters including mass loading of the nanoparticles and concentration/density of HAN solution are investigated. Preliminary results (see Table 1) show that enhancement of decomposition rate and reduction of decomposition temperature were observed for all three HAN aqueous solutions tested.

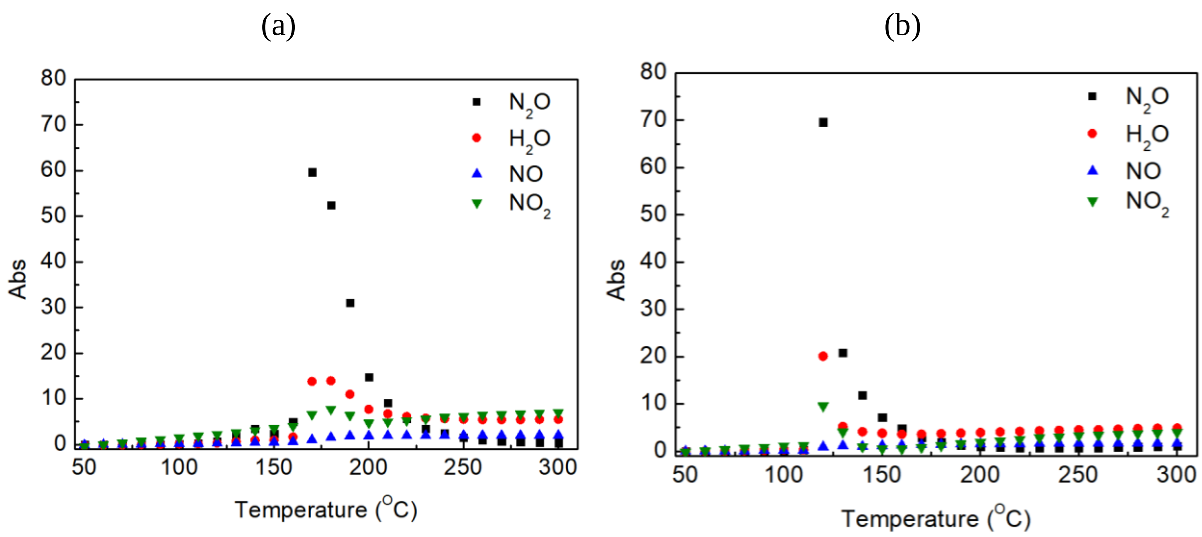

Fig 5 The area of absorbance of different gases by temperature (a) without TiO_2 (b) add TiO_2 nanoparticle

Table 1 Effects of TiO_2 addition on decomposition temperature and maximum derivative weight in TGA tests.

Test Number	HAN Density (g/cm^3)	TiO_2 Mass Loading (wt%)	Total Sample Weight (mg)	Decomposition Temperature (°C)	Maximum Weight Loss Rate (%/min)
1a	1.4083	0	9.95	169.7	94.4
1b	1.4083	0.705	9.84	120.7	1515.0
2a	1.5117	0	10.76	173.2	46.1
2b	1.5117	0.657	10.80	119.2	3554.2
3a	1.6041	0	10.49	178.2	231.0
3b	1.604	0.619	10.07	127.6	3210.8

4. Conclusion

TG-FTIR measurements were performed to study effects of TiO_2 addition to HAN aqueous solution. The test showed that with 0.657% mass loading, the decomposition temperature was reduced to 119 °C from 178 °C, and the decomposition rate was increased by ~ 31 times. Both heat flow measurements and FT-IR spectra of the evolved gas verified the reduction of decomposition temperature and the enhancement of decomposition rate. Species including NO, NO_2, N_2O and H_2O were identified in the decomposition product through FTIR measurements. The absorption spectra also indicated that peak concentrations of N_2O and H_2O in the evolved gas became higher with the existence of TiO_2 nanoparticles in the liquid phase.

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