Research paper

Effect of the particle size and specific surface area of ferric oxide catalyst on the burning rate of AP/HTPB solid propellant

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Abstract

Combustion tests were carried out to investigate the effect of ferric oxide catalyst particle size on the burning rate of a solid propellant consisting of ammonium perchlorate (AP) as an oxidizer and hydroxyl-terminated polybutadiene (HTPB) as a binder. The ferric oxide particle sizes used in the present study varied from nanometer to submicron size. A Crawford-type strand burner was used for the combustion test and the burning rate was calculated by the fuse-wire method. A correlation between the ferric oxide particle size and the burning rate of the propellant sample was confirmed. Moreover, the relationship between the theoretically and experimentally obtained specific surface areas of the ferric oxides and the catalytic efficiency of the propellant sample calculated from the burning rate was also clarified.

Keywords : solid propellant, nano ferric oxide, ammonium perchlorate, catalysis, burning rate

1. Introduction

The burning rate and specific impulse are representative parameters that describe the burning characteristics of solid propellants. In order to design rocket motors, the relationship between impulse and combustion time of the rocket motor, required by the whole rocket system must be satisfied. The basic method used to satisfy the relationship is the adjustment of the burning area by tailoring the grain configuration of the propellant. However, controlling the burning rate more widely by the arrangement of the solid propellant composition would be very advantageous for the design of rocket motors because the restrictions on the grain configuration could be decreased. Various methods to control the burning rate have been investigated to date. Representative methods proposed for currently used composite-type propellants are the addition of a combustion catalyst,[1)-17)] the control of the solid oxidizer particle size,[7),8),18)-21)] and the increase of the thermal conductivity and heat transfer coefficient of the solid propellant.

It is well known that the burning rate of a composite-type propellant that consists of ammonium perchlorate (AP) as an oxidizer and hydroxyl terminated polybutadiene (HTPB) as a binder is enhanced when particular transition metal oxides (TMOs) are added to the composition.[1)-17)] For example, ferric oxide (Fe_2O_3), copper oxide (CuO or Cu_2O), copper chromate ($CuCrO_4$), copper chromite ($CuCr_2O_4$), and manganese oxide (MnO_2) are very effective for enhancement of the burning rate. Of these TMOs, Fe_2O_3 has been the most commonly used, because it is inexpensive and readily available, and therefore, its catalytic effect on the burning rate or thermal decomposition of propellants has been widely researched.[1)-7),13)-15)] Although many researchers have proposed various mechanisms for the effect of Fe_2O_3 on the burning rate of AP-based solid propellants, the exact mechanism still remains unclear.

Research on the effect of general granular combustion catalysts not only Fe_2O_3, has also identified that as decrease in the particle size of combustion catalysts is effective for enhancing the burning rate of the solid propellant. However there have been few studies in which the particle size effect was confirmed experimentally. Recently, nanosized particles have become available at relatively lower prices, due to significant progress in nanotechnology. However nanosized particles have only just begun to be applied to solid propellants as combustion catalysts.

13)–17)

Nano- and submicron-sized Fe_2O_3 particles were used as combustion catalysts for AP/HTPB solid propellant and the effect of the two Fe_2O_3 particle sizes on the burning rate of the propellant samples was investigated by a series of combustion tests.[15] It was clear that the burning rate was significantly enhanced by reducing the particle size of Fe_2O_3 from submicron to nanometer size. In the present study, the relationship between the particle size of Fe_2O_3 and the burning rate of propellants was investigated. The specific surface areas of Fe_2O_3 particles were determined theoretically and experimentally, so that the relationship between the catalytic efficiency calculated from the burning rate and the specific surface area of Fe_2O_3 could be examined.

2. Experiment

2.1 Materials

The Fe_2O_3 particles used in the combustion tests were FRO-3 and FRO-6 (Sakai Chemical Industry Co., Ltd., Japan) with particle sizes of approximately 30 and 60 nm, respectively. The basic composition of the solid propellant sample was AP : HTPB = 84 : 16 (w/w). Propellant samples were also prepared by adding1part of FRO-3 and FRO-6 as combustion catalysts to the basic composition. The composition of the propellant samples also includes a small amount of curing agent and plasticizer. The propellant samples were cut into strand-shaped for use in the combustion tests.

2.2 Combustion tests

A series of combustion tests was carried out to measure the burning rate of propellant samples with a Crawford-type strand burner. The combustion tests were conducted at room temperature under a nitrogen atmosphere using the fuse-wire method, where wires are passed through a strand of propellant samples at 17 and 40 mm from the top of the strand. The burning rate was calculated by measuring the time interval between severing of the two wires during combustion. Measurements were made at 5 pressure (0.1, 0.4, 1.0, 4.0 and 10.0 MPa) and the number of trials was n=2.

2.3 Measurement of specific surface area

If the catalytic reaction that enhances the burning rate of propellants proceeds on the surface of Fe_2O_3 particles, then the catalytic effect should be directly related not only to the particle size, but also to the surface area of the Fe_2O_3 particles. Specific surface area measurements were carried out using the Brunauer-Emmett-Teller (BET) method (one point method) for both types of Fe_2O_3 particles used in this study and previous study[15] respectively. An automatic surface area analyzer, (Betasorb model 4200, Nikkiso Co., Ltd., Japan) was used for these measurements. When the measurement atmosphere consists of 30% nitrogen and 70% helium, the following relationship is found :

$$S = K\left(1 - \frac{p}{p_0}\right)V \tag{1}$$

where S is the total surface area of samples (m^2), K is the gas constant (= 4.29 in this apparatus under nitrogen at standard temperature and pressure), P/P_0 is the relative pressure of nitrogen gas as the absorbate gas (= 0.29 in this apparatus), V is the volume of absorbed and desorbed nitrogen gas (cm^3). After V is measured for the sample, the mass m, which was weighed in advance, then S/m, that is to say, specific surface area S_{BET} ($m^2\ g^{-1}$) can be calculated. Silicon nitride with known specific surface area was used to calibrate the apparatus. Specific surface area was measured twice for each sample and S_{BET} was determined as the mean value.

3. Results and discussion

3.1 Combustion characteristics of propellant samples

The relationship between the burning rate of propellant samples and pressure obtained from the combustion tests is shown in Fig. 1. For comparison, results for propellant samples prepared in a similar manner with different particle size Fe_2O_3 from our previous study[15] are also shown. The addition of Fe_2O_3 significantly enhanced the burning rate of the propellant samples, regardless of the particle size. The burning rate tends to increase linearly as the particle size of Fe_2O_3 is decreased, which is in accordance with the general view that catalysts are more effective as the particle size is decreased.[13)–17)] Generally, the burning rate of solid propellants and pressure exhibit linear characteristics called Vieille's law :

$$r = ap^n \tag{2}$$

where r is the burning rate of propellants samples, a is constant, p is pressure, and n is pressure exponent. The pressure exponent is the parameter that represents the effect of the change of pressure on the burning rate. From Fig. 1, the calculated pressure exponent increases from 0.43 for the propellant sample without catalyst to 0.47–0.50 with the addition of catalysts. It is assumed that the reactions in combustion of the propellant samples followed to

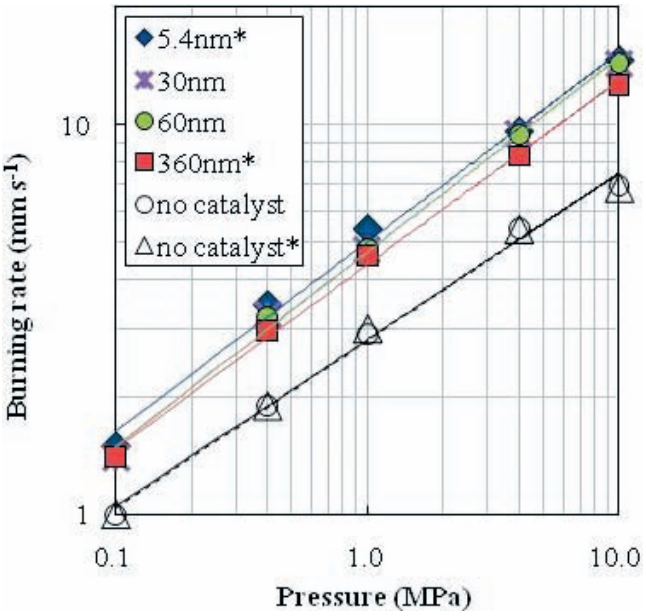

Fig. 1 Burning rate characteristics of propellant samples (*indicates data from a previous report[15]).

the Arrhenius equation :

$$\ln k = \ln A - \frac{E}{RT} \tag{3}$$

where E is the activation energy, A is the frequency factor, R is the ideal gas constant, and T is the temperature. The frequency factor relates the amount of collisions that need to occur in an unit time to carry out the reaction[22]. The frequency factor of reactants in the gas phase increases as the pressure rises, so that the burning rate also increases. The addition of catalyst increases the collision frequency of reactants and catalyst ; therefore, it is expected that the pressure exponent for the propellant samples with catalysts will increase, as evidenced by Fig. 1.

For comparison of the results from this and the previous study, the catalytic efficiency η_c is defined by Eq. (4) :

$$\eta_c = \frac{r_c - r_n}{r_n} \tag{4}$$

where r is the burning rate of propellant samples, subscripts c and n denote propellants with and without catalyst, respectively. This relationship can decrease the slight difference of the combustion characteristics caused by the difference of the time or the material lot for the preparation of propellant samples. The relationship between the catalytic efficiency and the particle size of Fe_2O_3 at 10 MPa is shown in Fig. 2. This pressure value (10 MPa) was selected because it is closest to the pressure during operation of rocket motor. The point at the origin represents a propellant sample without catalyst and the catalytic efficiency increases to 0.8−1.1 by the addition of catalysts. The catalytic efficiency is higher for smaller particle sizes. The small particle size suggests a larger surface area of catalyst. Therefore, it was confirmed that the catalytic activity by the addition of Fe_2O_3 particles is due to the active sites only on the surface of Fe_2O_3 particles.

Table 1 Specific surface area of Fe_2O_3 particles.

Particle size (nm)	S_{BET} ($m^2\ g^{-1}$)	S_{th} ($m^2\ g^{-1}$)
5.4	203	212
30	38	38
60	28	19
360	16	3

3.2 Specific surface area of Fe_2O_3 particles

The results of the BET specific surface area measurements for the 4 types of Fe_2O_3 particles are shown in Table 1. The theoretical specific surface area S_{th}, which is the specific surface area calculated from the particle size using Eq. (5) and assuming spherical particles, is shown as a reference.

$$S_{th} = \frac{6 \times 10^3}{\rho \times d} \tag{5}$$

where d is the Fe_2O_3 particle size (nm) and ρ is the density of Fe_2O_3 (5.24 g cm^{-3} from ref. 23). The S_{BET} values are in good agreement with S_{th} for small Fe_2O_3, but S_{BET} is larger than S_{th} for larger Fe_2O_3 particles. This discrepancy suggests that the shape of the particles deviates from spherical and becomes more influenced by the unevenness of the surface. The SEM micrographs of Fe_2O_3 particles[15] also support this statement.

3.3 Relationship between catalytic efficiency and specific surface area of Fe_2O_3

The relationship between the catalytic efficiency and the specific surface area of Fe_2O_3 at 10 MPa is shown in Fig. 3. The point at the origin represents a propellant sample without catalyst. The catalytic efficiency was increased as both the S_{BET} and S_{th} specific surface areas of the catalysts increased, and then approached a constant value. The value where the catalytic efficiency plateaus is

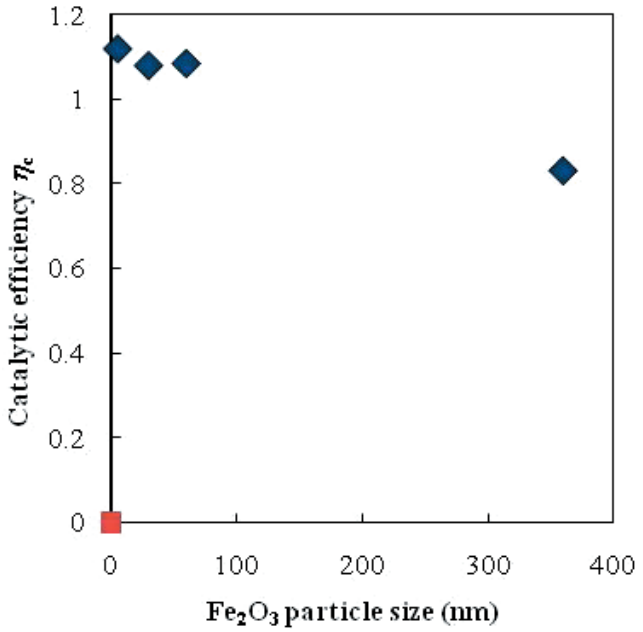

Fig. 2 Effect of Fe_2O_3 particle size on the catalytic efficiency of propellant samples.

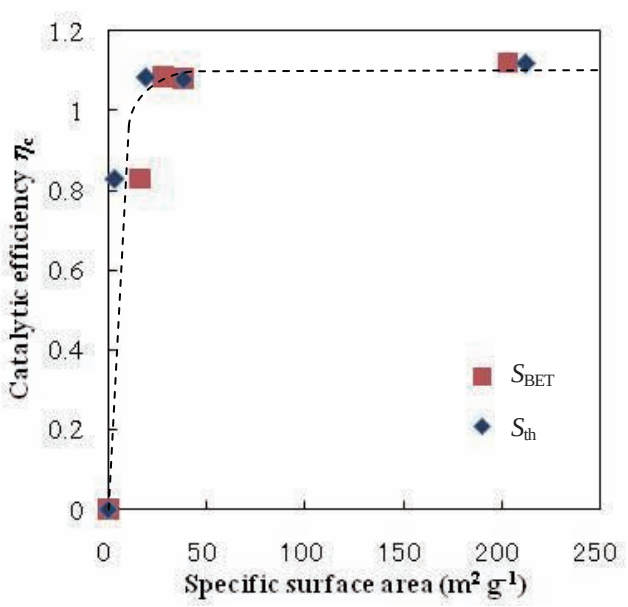

Fig. 3 Relationship between the specific surface area of Fe_2O_3 and the catalytic efficiency of propellant samples.

approximately 1.15. As noted in section 3.1, the catalytic reaction by the addition of Fe_2O_3 particles proceeds on the surface of catalyst particles. The reason that the catalytic efficiency plateaus as the surface area of catalyst increases is considered to be due to the rate-determining step, which is the diffusion of AP, HTPB, and intermediates of partial decomposition products to the catalyst surface. That is, the entire surface area of the catalyst is not utilized effectively, because the catalysts pass through the reaction zone more rapidly than the reactant reaches and covers the entire surface of the catalyst. It is possible that the agglomeration of catalyst particles during combustion is increased for smaller particle size. The effect of agglomeration could be confirmed if the Fe_2O_3 particles remaining after propellant combustion could be collected. The subject should be considered in future.

4. Conclusions

Combustion tests were carried out to investigate the effect of ferric oxide catalyst particle size on the burning rate of AP/HTPB solid propellant. A correlation between the particle size of ferric oxide particles and the burning rate of the propellant sample was confirmed. The relationship between the theoretically and experimentally specific surface areas obtained for the ferric oxide samples and the catalytic efficiency calculated for the propellant samples from the burning rate was also clarified. The catalytic efficiency increased as the specific surface area of Fe_2O_3 increased, then approached a constant value.

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酸化鉄触媒の粒径と比表面積がAP/HTPB系固体推進薬の燃焼速度に与える効果

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酸化鉄触媒粒子の粒径が過塩素酸アンモニウム(AP)酸化剤と末端水酸基ポリブタジエン（HTPB）バインダーから成る固体推進薬の燃焼速度に与える効果を調べるために，燃焼試験を実施した。本研究で使用した酸化鉄の粒径は，ナノメートルサイズからサブミクロンサイズである。燃焼試験ではクロフォード型ストランド燃焼試験装置を使用し，ヒューズワイヤ法により燃焼速度を算出した。結果として，推進薬サンプルの燃焼速度と酸化鉄粒子の粒径の相関を得ることができた。さらに，理論的および実験的に酸化鉄粒子の比表面積を求め，燃焼速度から算出した触媒効率との関係についても明らかにした。

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