

Engineering Notes

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Catalytic Activity of Ignition Catalysts in Hybrid Propellant Combustion

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Nomenclature

- E_g = band gap
 e = electronic charge
 K = Boltzmann constant
 k = dielectric constant of the catalyst
 l = mean free path
 m = mass of the electron or hole
 N_f = number of species adsorbed on the surface of the semiconductor
 n = concentration of electrons
 n_0 = charge carrier concentration
 p = concentration of holes
 T = temperature
 U = universal constant
 V_f = height of Fermi level at equilibrium

MINIMUM ignition delay coupled with smooth burning is one of the desirable characteristics of liquid and hybrid rocket propellants. Ignition catalysts^{1,2} have been used to reduce the ignition delay of liquid and hybrid propellants. During our recent ignition delay studies of aniline formaldehyde-fuming nitric acid hypergolic hybrid propellant system,³ it has been observed that ammonium vanadate and ammonium dichromate when dissolved in acid reduce the ignition delay from 1.8 sec to 2.5 and 27 millisecc respectively. The present paper reports the attempts made to explain the higher catalytic activity of ammonium vanadate over ammonium dichromate in reducing the ignition delay.

Experiment

Pellets of ammonium vanadate and ammonium dichromate (length 0.3 cm. and area of cross section 1.839 cm²) were prepared by pressing their respective powders under pressure of 13440 lbs. The sandwiched sample was placed inside the chamber (Fig. 1) for the measurement of its electrical properties. The vacuum inside the chamber was maintained at 10⁻³ mm Hg. The temperature measurements of the sample were done with Pt/Pt, Rh (13%) thermocouple. The dc conductivity of the sample was measured with the help of an electronic volt-ohm meter.

The thermoelectric power measurements of the pellets (length 1.0 cm and area of cross section 1.839 cm²) of these two catalysts were made in a similar experimental set up as

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Index categories: Fuels and Propellants, Properties of; Combustion in Heterogeneous Media; Liquid Rocket Engines.

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described above. One end of the pellet was heated by an electric heater. The temperatures at the two ends and the potential difference across the pellet were measured.

Results and Discussion

Conductivity Measurements

From Fig. 2, it can be concluded that as the temperature is raised through 327° K, a jump in the conductivity is observed by an amount 0.138. Above the transition temperature, resistivity increases linearly with temperature and the behavior is metallic. Below transition temperature, conductivity increases exponentially with temperature.

Similar typical results have also been obtained in the case of ammonium dichromate, Fig. 2. The transition temperature in this case is found to be 339° K and the value of sudden rise in conductivity is 0.31.

This typical behavior can be explained on the basis of a model presented by Adler and Brooks.⁴ The supposition of the model is that the gap arises from either a crystalline distortion or antiferromagnetism. Since ammonium vanadate and ammonium dichromate are diamagnetic, the narrowing of the band gap in these cases may be due to crystalline distortion. It has also been shown that a narrow-band material whose structure is such that it would be expected to have a half-filled conduction band, can lower its ground state energy by a crystalline distortion. The conductivity measurement results indicate that these two catalysts are semiconductors and this knowledge further helps to study certain catalytic properties which are responsible for catalytic activity of semiconductors.

Thermoelectric Power Measurements

Different values of charge carrier concentrations at different temperatures in case of these catalysts have been calculated from Eqs. (1) and (2) and are plotted in Fig. 3.

$$n = 2UT^3/2 \exp - (E_c - E_0)/2KT \quad (1)$$

$$p = 2UT^3/2 \exp - E_f/2KT \quad (2)$$

From Fig. 3, the activation energies for the donor levels in case of ammonium vanadate and acceptor levels in case of ammonium dichromate have been calculated and are 0.05484 eV and 0.914 eV respectively. The band gaps in case of ammonium vanadate and ammonium dichromate have been calculated from Eq. 3, and their values are 1.371 eV and 1.5995 eV respectively.

$$N = p = n_i \approx 2UT^3/2 \exp - E_g/2KT \text{ particles/cm}^3 \quad (3)$$

For the initiation of the combustion reaction, the presence of chain carriers is an essential factor. Ammonium vanadate

Table 1 Mean free path of charge carriers of ammonium vanadate and ammonium dichromate

Temperature (°K)	Mean free path (cm)	
	ammonium vanadate	ammonium dichromate
343	0.2125×10^{-4}	0.2735×10^{-3}
338	0.2723×10^{-3}	0.3585×10^{-3}
333	0.2962×10^{-3}	0.4582×10^{-3}
328	0.3461×10^{-3}	0.5585×10^{-3}
323	0.3841×10^{-3}	0.9057×10^{-3}

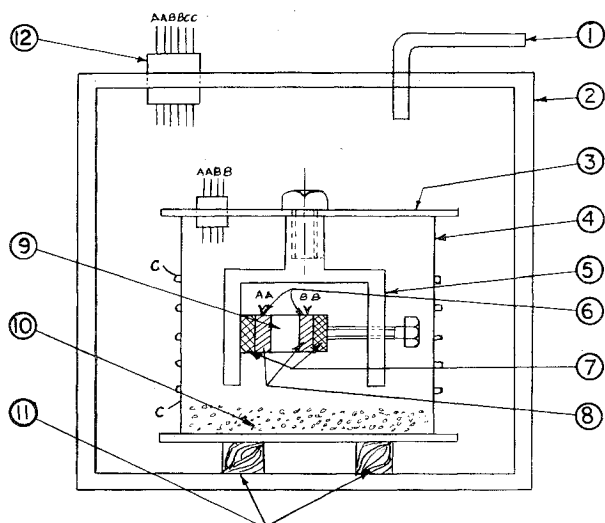


Fig. 1 Apparatus for conductivity measurement: 1) connection to vacuum pump; 2) vacuum chamber; 3) Asbestos sheet; 4) electric heater; 5) clamping device; 6) thermocouple wires; 7) Teflon sheet; 8) copper discs; 9) sample; 10) glass wool; 11) wooden block; 12) pipe filled with epoxy resin; AA) terminals of the first thermocouple wires; BB) terminals of the second thermocouple wires; CC) terminals of the wire heater.

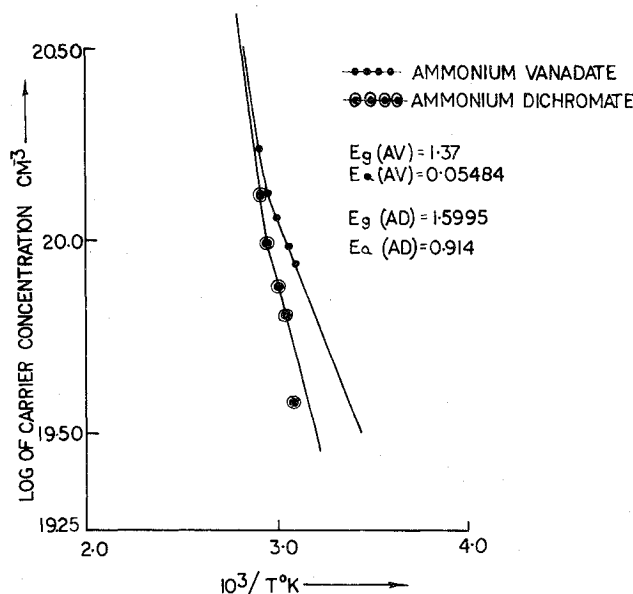


Fig. 2 Temperature dependence of specific conductivity.

can provide chain carriers by exciton formation easier than ammonium dichromate, because the energy required for the exciton formation in case of ammonium vanadate is much less than that required for ammonium dichromate. Since the rate of reaction is proportional to the number of collisions taking place per second, the rate of collision would be high if the concentration of the reactants are high and their mean free path is small. The relation (4) developed by Aigrain and Dugas^{5,6} for charge carrier concentration and the number of species adsorbed on the surface of semiconductor catalyst indicates that the higher the charge carrier concentration, the higher the concentration of the adsorbed species.

$$N_f = \left[\frac{k}{2\pi e} n_0 V_f \right]^{1/2} \quad (4)$$

Figure 3 shows that the charge carrier concentration in case of ammonium vanadate is higher at all temperatures than in case of ammonium dichromate. Further the values of mean free path of the charge carriers, calculated from Eq. (5), indicate that at each temperature the mean free path in case of

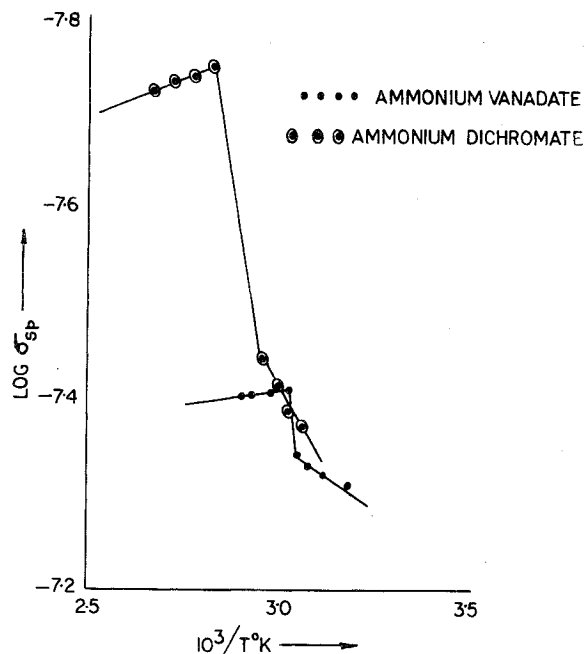


Fig. 3 Variation of charge carrier concentration with temperature.

ammonium vanadate is shorter than in case of ammonium dichromate (Table 1).

$$l = \left[\frac{2KmT}{n_0 e^2} \right]^{1/2} \quad (5)$$

These observations suggest that the higher the concentration and mobility⁶ of the charge carrier of the catalyst, the higher the catalytic activity to expedite surface reaction rates. These conclusions help to explain the higher activity of ammonium vanadate over ammonium dichromate in reducing the ignition delay of the present hybrid propellant system.

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Improved Determination of Apogee Motor Pointing

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Introduction

THE first two geosynchronous communications satellites of Telesat Canada (ANIK I, ANIK II)¹ experienced

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