# Action of Transition Metal Oxides on Composite Solid Propellants

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## Introduction

TRANSITION metal oxides (TMO) are known to promote the thermal decomposition (TD) of ammonium perchlorate (AP), deflagration of AP, AP-binder sandwich burning, and the combustion of AP-based composite solid propellants.[1] Many attempts have been made to understand how these catalysts effect decomposition and combustion but no clear-cut picture has emerged, particularly regarding composite solid propellants.

In order to understand the nature of catalyst action (in the presence of TMOs) on the combustion of propellants, two systems based upon polystyrene (PS) and carboxyl-terminated polybutadiene (CTPB) were chosen. The catalysts chosen were $Fe_2O_3$, $Ni_2O_3$, $MnO_2$, and $Co_2O_3$.

## Experimental

PS/AP propellant was prepared as describe in Ref. 2. Additives and AP were used at 1% (by weight) level of propellant and a particle size of 53-106 $\mu$m was maintained in all the compositions. Perchlorates and perchlorate amines of iron, nickel, manganese, and cobalt were prepared in the laboratory as described elsewhere.[3,4] A CTPB-based propellant (80% AP, 14.4% CTPB, 2% dioctyladipate, 1.8% MAPO, 1.4% epoxy (CIBA GY 252), 0.4% lecithin with and without 1% additive) was processed in the usual manner. Pellets of AP and AP with additives were made by pressing 20 g of the material at a pressure of 1500 kg/cm$^{-2}$. The pellets obtained were of 5 cm in diameter and 0.5 cm thick. These were cut carefully to yield strands (4 cm long and 0.5 cm thick). The strands were coated with a homogeneous mixture of araldite and $TiO_2$ and dried. Burning rate ($\dot{r}$) measurements were made at ambient pressure as described elsewhere.[5] $\dot{r}$ measurements at high pressure (60 atm) were carried out using a strand burner similar to that devised by Crawford.[6] CTPB strands 6 cm long and 0.5 cm in diameter were used for the $\dot{r}$ measurements. Polymer $\dot{r}$ and degradation were studied as described in Ref. 7. Isothermal thermogravimetry experiments were made on a homemade assembly[8] and a Perkin Elmer DSC 1B-TGS unit at temperatures of 280-360°C. A homemade differential thermal analysis (DTA) assembly was used in the present investigation[9] at a heating rate of 7°C/min$^{-1}$.

## Results and Discussion

DTA of AP shows phase transition at 240°C followed by two distinct exotherms corresponding to a diffusion-controlled and an electron-transfer process, respectively. In the presence of 1% TMO the DTA traces show that the second exotherm is sharpened and that the end temperature at which the decomposition terminates drops, indicating that the TMOs have a catalytic effect on the decomposition of AP. From the end temperature the order of the effectiveness of TMO was as follows:

$$Co_2O_3 > MNO_2 > Ni_2O_3 > Fe_2O_3$$

Detailed studies of AP + $MnO_2$ system reported earlier[9] show that $MnO_2$ facilitates the electron-transfer process since Mn ions were found to be present in the lattice of AP. This happens during the curing period of the propellant. Similar studies were made to detect the presence of metal ions in other TMO systems. Co was found to be present in the lattice, while Fe and Ni could not be detected. It was also observed from TG studies that the $E$ for the electron-transfer process is reduced in the presence of all TMOs, although the actual extent differs. Based upon these results, the order of activity of TMOs can now be explained. In those systems in which the metal ions enter the lattice, the facilitation of electron-transfer process is much greater ($Co_2O_3$ and $MnO_2$), and hence the TD of AP is enhanced to a greater extent compared to $Fe_2O_3$ and $Ni_2O_3$.

The next step was to examine the effect of TMOs on the $\dot{r}$ of AP (at 60 atm). It was found that $Co_2O_3$ and $Ni_2O_3$ containing AP do not sustain combustion at this pressure. The $\dot{r}$ of other systems followed the following order:

$$\dot{r}(AP + Fe_2O_3) > \dot{r}AP(\text{uncatalyzed}) > \dot{r}(AP + MnO_2)$$

These studies indicate that the TD and $\dot{r}$ of AP have no similarity. This may be because the highest temperature at which the AP decomposition was studied is around 400°C, while the temperature encountered during deflagration was much higher. Moreover, the formation of melt has been observed during the deflagration of AP and the nature of the action of the TMOs in the melt could be different than their effect on the TD of AP.

The $\dot{r}$ data of the propellant are presented in Table 1 and show the following order of effectiveness:

$$\dot{r} \text{ of (PS/AP + 1\% TMO)}: Ni_2O_3 \approx Fe_2O_3 > MnO_2 \approx Co_2O_3$$

**Table 1 $\dot{r}$ values of AP/CTPB and AP/PS propellant systems**

| Propellant system | TMO (1% wt) | Pressure | $\dot{r}$, cm/s |
|---|---|---|---|
| AP/CTPB (O/F = 4) | – | 60 atm | 0.95 ± 0.03 |
| | $Ni_2O_3$ | | 1.36 ± 0.05 |
| | $Fe_2O_3$ | | 1.09 ± 0.02 |
| | $MnO_2$ | | 1.05 ± 0.03 |
| | $Co_2O_3$ | | 1.05 ± 0.05 |
| AP/CTPB (O/F = 4) | – | Ambient | 0.108 ± 0.004 |
| | $Ni_2O_3$ | | 0.119 ± 0.001 |
| | $Fe_2O_3$ | | 0.120 ± 0.004 |
| | $MnO_2$ | | 0.109 ± 0.005 |
| | $Co_2O_3$ | | 0.110 ± 0.005 |
| AP/PS (O/F = 3) | – | Ambient | 0.095 ± 0.002 |
| | $Ni_2O_3$ | | 0.131 ± 0.005 |
| | $Fe_2O_3$ | | 0.128 ± 0.003 |
| | $MnO_2$ | | 0.114 ± 0.003 |
| | $Co_2O_3$ | | 0.109 ± 0.003 |
| | $Mn(ClO_4)_2$ | | 0.083 ± 0.003 |
| | $Co(ClO_4)_2$ | | 0.102 ± 0.002 |
| | $Ni(ClO_4)_2$ | | 0.097 ± 0.003 |
| | $Fe(ClO_4)_2$ [a] | | – |
| | $Mn(ClO_4)_2$ amine | | 0.108 ± 0.001 |
| | $Co(ClO_4)_2$ amine | | 0.096 ± 0.002 |
| | $Ni(ClO_4)_2$ amine | | 0.107 ± 0.002 |
| | $Fe(ClO_4)_2$ amine | | 0.120 ± 0.002 |

[a] AP/PS strands with $Fe(ClO_4)_2$ did not cure.

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Index categories: Fuels and Propellants, Properties of; Thermochemistry and Chemical Kinetics; Ablation, Pyrolysis, Thermal Decomposition and Degradation (including Referactories).

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and

$\dot{r}$ of (CTPB/AP + 1% TMO):

$$Ni_2O_3 \approx Fe_2O_3 > MnO_2 \approx Co_2O_3$$

$\dot{r}$ data were obtained at high pressures for CTPB propellants containing TMOs. Table 1 shows that the order of effectiveness of TMOs at 60 atm is the same as that observed at ambient pressures, which suggests that the basic mechanism of catalyst action is not affected by the pressure. However, for any particular oxide the effectiveness at higher pressures is not the same as that observed at lower pressures. The $\dot{r}$ data of PS/AP propellant could not be obtained at high pressures since the burning was very rapid, which may be due to the polymer melting along the side of the propellant strands. Two interesting features come into focus from a comparison of the $\dot{r}$ data of PS/AP and CTPB/AP propellants at ambient pressure: 1) the order of catalytic effectiveness is almost the same in both cases, which suggests the mechanism of catalyst action to be the same in both the cases; and 2) $Ni_2O_3$ appears to be as good a catalyst as $Fe_2O_3$ at both ambient and high pressures.

Studies of the AP/PS propellant containing TMO were carried out. The propellant was ignited during DTA studies (depending upon the sample mass and heating rate) and the ignition temperature was precisely recorded. The following order was found for the ignition temperatures of the PS/AP propellant containing TMOs:

$$Fe > CO > Ni > Mn$$

It is evident that the effectiveness of the propellant decomposition (leading to ignition) is diffferent than that of AP decomposition and $\dot{r}$. From the TD results of AP and the propellant and the deflagration rate of AP, it is not possible to shed any light on the mechanism of burning except that the TMOs catalyze AP decomposition via the electron-transfer mechanism.

Patil et al.[10] have shown that transition metal perchlorate amines (TMPA) are formed as intermediates during the decomposition of AP. Apart from this, the formation of metal perchlorates (TMP) can also take place. Thus, detailed investigations were carried out on $\dot{r}$ and TD of AP/PS propellants with 1% (by weight) of TMP and TMPA. Additionally, the studies were also done to find the effect of TMO and TMPA on the degradation and combustion of binder PS. PS + TMP could not be studied as they were imcompatible.

Results on the $\dot{r}$ of AP/PS propellants with TMP and TMPA are presented in Table 1. It may be observed that perchlorates do not have much effect on $\dot{r}$ with the exception of Mn $(ClO_4)_2$ which shows a desensitizing effect. Therefore the results on the $\dot{r}$ of AP/PS propellants with TMOs could not be explained on the basis of the formation of perchlorates as intermediates. From Table 1 it may be seen that Fe, Ni, and Mn perchlorate amines (PA) sensitize the $\dot{r}$ of propellants, while Co PA appears to have no effect. TMPAs have the following order of effectiveness:

$$Fe\ PA > Mn\ PA > Ni\ PA > Co\ PA$$

This order is almost the same as that observed for TMO catalyzed propellants. In order to explain the above trend in the $\dot{r}$, the role of TMPA was examined on the binder combustion and degradation. Binder $\dot{r}$ was found to be slightly desensitized and degradation was desensitized to a greater extent in the presence of both TMO and TMPA. The results did not have any bearing with propellant $\dot{r}$. Thus, the effect of these additives on the combustion of the propellant could not be explained on the basis of the combustion of the binder alone.

An attempt was then made to understand the effect of TMPAs on the $\dot{r}$ of propellants based upon their effect on the TD of AP. Patil etal.[10] have shown that these compounds sensitize the TD of AP and the effectiveness of TMPAs on the TD of AP has the following trend.

$$Co\ PA > Mn\ PA > Ni\ PA > Fe\ PA$$

and the thermal stability of these amines is in the following order:

$$Fe\ PA > Ni\ PA > Mn\ PA > Co\ PA$$

The $\dot{r}$ data as well as the ignition temperature data (obtained from DTA) of the propellant containing TMPA have the same trend as that indicated by the stability of the amines, from which it may be inferred that during the combustion of propellants it is the stability of the amines which determine their effect on $\dot{r}$. This could be because at the temperatures encountered during combustion, which are quite high, only those compounds which are thermally more stable can act effectively. This appears to be quite sound since the formation and decomposition of TMPA is exothermic and therefore the chances of formation of this compound (which is more stable at higher temperatures) are greater and will release more heat in the propellant matrix. Therefore, the effect will be greater. Another observation made during these studies was the effect of Mn PA on the $\dot{r}$ of AP/PS propellants. From Table 1 it is evident that the $\dot{r}$ of the Mn PA catalyzed propellant is of the same order as the $\dot{r}$ of the Ni PA catalyzed propellant. Based upon this, $MnO_2$ would be expected to be just as effective a catalyst as $Ni_2O_3$; however this is not true. This could be perhaps due to the combined effect of Mn perchlorate and Mn PA on the $\dot{r}$.

In conclusion it may be stated that one of the ways by which TMOs act is through the formation of reactive TMPA intermediates as indicated by the correlation between thermal stability of TMPAs and $\dot{r}$ of the propellants containing TMOs and TMPAs.

## References


[1] Kishore, K. and Sunitha, M. R., "Effect of Transition Metal Oxides on Decomposition and Deflagration of Composite Solid Propellant Systems," *AIAA Journal*, Vol. 17, Oct. 1979, p. 1118.

[2] Kishore, K., Pai Verneker, V. R., and Prasad, G., "Effect of Storage Temperatures on the Mechanical Properties of the Composite Solid Propellants," *Combustion Science Technology*, Vol. 19, 1979, pp. 107-118.

[3] Schumacher, J. C., *Perchlorates, Their Properties, Manufacture and Uses*, Reinhold Publishing Corp., New York, 1960.

[4] Patil, K. C., Pai Vernecker, V. R., and Jain, S. R., "Metal Perchlorate Amines: Thermal and Infrared Studies," *Thermochimica Acta*, Vol. 15, 1976, p. 257.

[5] Kishore, K., Pai Verneker, V. R., and Sunitha, M. R., "Effect of Catalyst Concentration on Burning Rate of Composite Solid Propellants," *AIAA Journal*, Vol. 15, Nov. 1977, pp. 1649-1651.

[6] Crawford, B. L. Jr., Hugget, C., Daniels, F., and Wilfong, R. E., "Direct Measurement of Burning Rates of Propellant Powders," *Industrial and Engineering Chemistry, Analytical Edition*, Vol. 19, No. 9, 1947, p. 630.

[7] Kishore, K., "Polymer Flame Inhibition in Presence of Transition Metal Oxides," *Colloid and Polymer Science*, Vol. 257, No. 9, 1979, pp. 984-986.

[8] Kishore, K., Pai Verneker, V. R., Sunitha, M. R., and Prasad, G., "Contribution of Condensed Phase Reaction in the Combustion of Solid Rocket Fuels," *Fuel*, Vol. 56, July 1977, pp. 347-348.

[9] Kishore, K., Pai Verneker, V. R., and Sunitha, M. R., "Effect of Manganese Di-Oxide on the Thermal Decomposition of Ammonium Perchlorate," *Journal of Applied Chemistry and Biotechnology*, Vol. 27, 1977, pp. 415-422.

[10] Patil, K. C., Pai Verneker, V. R., and Jain S. R., "Role of Metal Perchlorate Amines on Ammonium Perchlorate Decomposition," *Combustion and Flame*, Vol. 25, 1975, p. 387.