Effect of Transition Metal Oxides on Decomposition and Deflagration of Composite Solid Propellant Systems: A Survey

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Introduction

TRANSITION metal oxides (TMO) like Fe_2O_3, CuO, MnO_2, $CuCr_2O_4$, etc., form a very popular group of catalysts for burning rate modification of composite solid propellants. Although it is well known that these oxides affect the decomposition characteristics of polymers[1] and oxidizers like ammonium perchlorate (AP)[2,3] and potassium perchlorate, (KP)[3] the exact mechanism of the effect on solid propellants is by no means clear even today. Much fragmentary literature is available on the effect of these oxides on propellant burning and decomposition, oxidizer burning and decomposition, and sandwich and condensed mixture combustion. It is the purpose of this review to bring the material together so that a comprehensive picture can be drawn of the mechanism of the action of these catalysts. It may be mentioned here that these oxides also catalyze hydrocarbon oxidation reactions[4] by inducing free radical decomposition of hydroperoxides (formed by the contact of oxidizer and hydrocarbon).

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Effect on Propellant Combustion

Pittman[5] has described a series of experiments designed to locate the site of catalyst action on AP and KP based carboxy terminated polybutadiene (CTPB) propellants and to elucidate its mechanism. From his experiments he concludes that catalysts Fe_2O_3 and n-butyl (bis) cyclo-pentadienyl iron (BBCI) do not act beneath the burning surface to enhance AP decomposition or to catalyze oxidizer-binder heterogeneous reactions. According to him, catalysts probably act in the gas phase by promoting the reaction rates of $HClO_4$.

Kishore and Sunitha[6] studied the mechanism for the action of TMO (CrO_3, Fe_2O_3, MnO_2, Cr_2O_3, CuO and Ni_2O_3) on the linear burning rate ($\dot{r}$) of PS/AP propellant. They found that these oxides promote an electron transfer process during the propellant decomposition which affects $\dot{r}$ in a similar fashion. They supported their mechanism on the basis of the linear dependence between the degree of increase in $\dot{r}$ with redox potentials of the oxides and also with the heats of reaction associated with the electron transfer process.

The possibility that a catalyst might measurably change the surface temperature of burning propellant was tested by Pauling and Smith.[7] They measured the surface temperature of a poly-isobutylene-AP propellant and found that it did not vary measurably with the addition of catalyst.

On the contrary, Pearson[8] concludes that the enhanced heat release between NH_3 and $HClO_4$ in the presence of catalyst particles on the surface of the propellant constitutes one route by which $\dot{r}$ is enhanced. He examined the action of copper chromate and copper chromite catalysts on the reaction between NH_3, isobutane, and ethylene on oxygen or $HClO_4$ at 400-420°C. The catalysts were effective at temperatures close to those prevailing on the propellant surface. According to him, the catalyst may also be effective in other ways, such as by promoting the reaction of $HClO_4$ with solid fuel or by modifying the pyrolysis mechanism of the solid fuel.

Inami et al.[9] have studied the kinetics of reactions at the interface of propellant representative gaseous fuels like propane, propylene, and NH_3 and AP containing catalysts like copper oxide and copper chromite, to elucidate the rate processes controlling solid propellant ignition and deflagration. They concluded that catalysts play the dual roles of accelerating the decomposition of AP and promoting the oxidation of the fuel by heterogenous reactions. These surface-catalyzed reactions yield a net exothermic heat release whose magnitude is a function of the partial pressure of

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gaseous fuel and the concentration of the copper chromite catalysts. Pearson and Sutton[10] have made a study of the ignition of solid fuels, similar to those used in solid propellants, with oxygen in the presence of copper chromate and other catalysts. Their investigations also suggest that the catalysts may have a dual role. It may not only catalyze $HClO_4$ decomposition but also promote ignition of solid fuels in oxygen. Thus, under practical ignition conditions in rocket motors, the $HClO_4$ derived from AP is the important oxidizer, and the catalysts are effective at least in part by catalyzing the decomposition of the $HClO_4$ to reactive species.

Copper chromite has been shown by Summerfield,[11] Stammler,[12] and Powling[13] to be an excellent catalyst for increasing composite propellant $\dot{r}$. According to them, the quantitative comparisons of relative catalytic effectiveness of various catalysts, in mechanistic terms, is difficult because the particle size and state of aggregration of each catalyst is different. Burnside[14] has recently investigated the effect of particle size and has given a correlation between Fe_2O_3 surface area and propellant $\dot{r}$. It was observed that variation of Fe_2O_3 specific surface area is more significant at high than at low oxidizer specific surfaces. The effectiveness of a given Fe_2O_3 at a fixed level increases as the oxidizer-specific surface increases. It was also found that catalytic activity is a function of pressure.

Hartman[15] has studied the effect of several dopants on composite propellant burning rates. AP was doped with various foreign ions such as Fe^{+2}, Co^{+2}, Mn^{+2}, NO_3^{-1}, etc., by coprecipitation from an aqueous solution of the corresponding perchlorates or ammonium salts. Differential scanning calorimetry (DSC) was used to monitor the effect of dopants on the thermal decomposition of AP. Fe^{+2}, Co^{+2}, and Mn^{+2} had profound effects on the decomposition rate while NO_3^{-1}, $H_2PO_4^{-1}$, SO_4^{-2}, K^{+1}, and Ba^{+2} had little effect on the decomposition rate. The $\dot{r}$ of propellants containing doped or undoped AP were identical in most cases. He inferred that gas-phase processes rather than solid-phase are critical in controlling the burning rates.

Effect on the Combustion of Condensed Mixtures

Combustion of a condensed mixture could be considered similar to that of pure AP deflagration except that it contains fuels like polystyrene (PS), polymethylmethacrylate (PMMA), soot, sulphur, etc., in particulate form in a particular proportion. Thus, the difference of a condensed mixture from that of a composite propellant is in the mode of the processing of the two. Generally, the condensed mixture is prepared by compressing a mixture of fine polymodal fractions of oxidizer, fuel and catalyst (if any). For $\dot{r}$ measurements, cylindrical strands of the compressed mixture are used.

Arsh et al.[16] find that the combustion of powdered mixtures of excess AP with PMMA or PS confined under pressure (40 atm) is accelerated by 1-5% Fe_2O_3. Combustion is additionally accelerated by incorporating needles of copper as a heat conductor. Bobolev et al.[17] have investigated the mechanism of action of iron containing catalysts (Fe, Fe_2O_3, and ferrocene) on the combustion and decomposition of stoichiometric mixtures of AP and PMMA. The maximum increase of the $\dot{r}$ was observed with Fe_2O_3. They find that the catalysts influence both gas-phase and condensed-phase reactions.

Nikiforov and Bakhman[18] have studied the effect of 1 wt% Fe_2O_3 and/or inert fillers like NH_4Cl or $AlCl_3$ on the combustion of PS or PMMA with AP. When $AlCl_3$ or NH_4Cl were used as diluents along with Fe_2O_3, the effectiveness of Fe_2O_3 in chaining the $\dot{r}$ was considerably enhanced. They[19] also investigated the effect of Al on the efficiency of action of Fe_2O_3 (1%) catalyst. AP and KP were the oxidizers employed and PS and PMMA were the organic fuels. Addition of fine Al reduced the efficiency of the catalyst with excess oxidizer

and a large excess of organic fuel. In mixtures with a small excess of fuel, addition of fine Al increased the efficiency of the catalyst.

Bakhman et al.[20] have studied the catalytic effect of Fe_2O_3 on the $\dot{r}$ of various condensed mixtures. For AP-PMMA and AP-PS mixtures, the catalytic effectiveness (Z) decreased with increasing ambient temperature. AP based mixtures were more sensitive to catalysis by Fe_2O_3 than KP and $(CH_3)_4$ $NClO_4$ mixtures. When the catalyst content was increased, Z and $\dot{r}$ increased at small concentration of the catalyst, and when the catalyst concentration was large (1-5%), $\dot{r}$ was affected only slightly. They have proposed a diffusion controlled model taking into account the competition of catalytic and homogenous reactions.

The same school, on the basis of the results on AP-PMMA/Fe_2O_3 mixture,[21] found that the dependence $\dot{r}$ on the catalyst specific area was very small. There was strong catalyst agglomeration in the burning zone. Similar results were also obtained by Andrianova et al.[22] who have investigated the dependence of the combustion rate of mixture of AP and PMMA on the specific surface area of the added catalyst (1% Fe_2O_3 or 1% carbon black). The dependence of $\dot{r}$ on the surface was found to be slight. The catalyst action was explained by the fact that only the outside exposed surface affects the rate. Leipenskii et al.,[23] from their experiments on AP-PMMA mixtures with and without catalysts (Fe_2O_3 and ferrocene) at 5-60 atm, suggested that the combustion rate is affected only by the catalytic effect on the surface.

Avdyunin et al.[24] found that the catalytic activity of Fe_2O_3 in the combustion of mixtures of AP with PMMA, PS, sulphur, or carbon is at a maximum with 1-5% Fe_2O_3 and falls off markedly for mixtures containing 20-35% Fe_2O_3. Studies with mixtures of $(CH_3)_4$ $NClO_4$, in which NH_3 and $HClO_4$ are presumably absent, indicated that a single mechanism of catalysis cannot account for the effect of Fe_2O_3 on the $\dot{r}$ of the mixtures.

Korobeinichev et al.[25,26] investigated the catalytic decomposition of AP and its mixture with PS by the application of dynamic mass spectrometry (MS) and thermogravimetry (TG). The catalyst employed was Fe_2O_3 and the investigations were carried out at 310-365°C. The decomposition reaction was of the zero order, and the decomposition rate was proportional to the catalyst concentration. The authors have presented and discussed a mathematical model for the process. The essential features of the proposed mechanism are as follows: 1) decomposition of AP: $NH_4ClO_4 \rightarrow NH_3 + HClO_4$, 2) diffusion of $HClO_4$ from AP particle surface through PS film and the simultaneous reaction of $HClO_4$ with PS.

a) At the first microstage the oxidative degradation of PS takes place giving rise to intermediate condensed-phase products AK:

$$HClO_4 + (C_8H_8)_n \rightarrow AK + 4C_8H_8 + 2CO_2 + HCl + \ldots$$
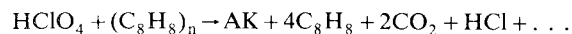
b) At the second microstage the interaction of $HClO_4$ with AK takes place. Diffusion coefficient of $HClO_4$ in the presence of AK is likely to be higher than that of $HClO_4$ diffusing into initial binder film. In the presence of Fe_2O_3, $HClO_4$ decomposes on FeO_3 forming products like Cl_2, NO_2, etc., which are less reactive than $HClO_4$ in the initiation of PS destruction.

Effect on Sandwich Propellant Combustion

Sandwich experiments provide a simplified picture of the combustion details of the complicated three-dimensional environment of composite propellants. A sandwich consists of alternate slabs of binder (or catalyst loaded binder) and slabs of either pure AP crystals or compressed pellet of AP. It has been conclusively proved that the form of AP slab does not alter the results as long as care is used in the manufacture of the pressed AP slabs.

Strahle et al. [27-30] have carried out a series of investigations on sandwiches prepared from AP disks and using CTPB and hydroxy terminated polybutadiene (HTPB) as binders. The catalysts were added by pressing into the disks, mixing with the binder, or by dissolving in CH_3OH and painting on the disk. The catalysts were Harshaw CuO 202 (82% CuO + 17% Cr_2O_3) and Fe_2O_3. There was no difference between the behavior of the two binders. Fe_2O_3 was as effective in catalyzing the interface processes over the entire pressure range, but the Harshaw catalyst was more effective in catalyzing the combustion of AP. Addition of the catalyst to the binder was found to have virtually no effect on $\dot{r}$. They also investigated the surface changes in the binder and the oxidizer. The oxidizer surface undergoes little change with pressure whereas the binder exhibits wrinkling on solidification.

Effect on AP Deflagration

The self-deflagration rate of AP at typical pressures is of the same order as the $\dot{r}$ of many AP-based propellants. Therefore, it is believed that AP deflagration may well be a controlling factor for propellant $\dot{r}$. AP undergoes self-sustained combustion only in certain pressure ranges, giving rise to pressure limits. No satisfactory explanation is available for the existence of nondeflagration pressure ranges. Generally, such range is found to be below a certain pressure level known as the low-pressure deflagration limit (LPL) and above a certain pressure level, the upper pressure deflagration limit (UPL). Of the two, the LPL has greater practical importance and has been the subject of many theoretical and experimental studies. An average value of 20 atm has been assiged to LPL at room temperature. LPL has been found to be very sensitive to catalysts and so also steady state $\dot{r}$ is markedly affect by the presence of catalysts.

Shidlovskii et al. [31] found that 3 wt% MnO_2, 5 wt% $KMnO_4$ lowers LPL. Friedman [32,33] and Shidlovskii et al. [31] have reported the orders of catalytic effectiveness for pure AP combustion as follows: copper chromite > Cu_2O > Fe_2O_3 > MnO_2 > Cr_2O_3. Glazkova [34] also found that combustion is catalyzed by Cr_2O_3.

Friedman et al. [32,35] found that 3 wt% of CuO, Cr_2O_3, Fe_2O_3, MnO_2 increase LPL, and copper chromite present in large quantity decreases the LPL while small quantity increases it. According to Friedman there are two processes which occur in the presence of catalysts: 1) increase in the radiative feedback to the surface and 2) increase in the radiative heat loss from the surface. Coupling the two shows that at low concentrations of the catalyst heat loss is dominant and heat feedback is less. At high concentrations catalysts catalyze the exothermic reactions and heat feedback outweighs the heat loss effects. He supported his argument with the fact that LPL decreases when radiative energy from external source is allowed to fall on the burning surface. Cohen Nir [36] found that Cu_2O sensitizes the deflagration of AP because it gives rise to exothermic reactions with products of AP decomposition.

Shadman-Yazdi and Petersen [37] have investigated the effect of $KMnO_4$, Fe_2O_3, CuO, and copper chromite on the pressure limits of combustion of AP. LPL in all of the cases increased with small additions of each catalyst and decreased at higher concentrations of the catalyst. The effect of catalysts depended strongly on the way they were distributed as well as their concentrations. The catalysts of smaller particle size were much more effective than larger particles. They believe the catalyst to act in both the condensed phase and gas phase.

Shadman-Yazdi [38] has studied the effects of catalysts on the deflagration limits and the $\dot{r}$ of AP. LPL increased in all cases with small additions of each catalyst and decreased at higher concentrations. A theoretical model has been developed to explain the existence of pressure limits in the deflagration of AP. The effect of catalyts can be explained qualitatively by

this model. He [39] has also studied the ignition of pellets of AP containing different concentrations of catalyts like Fe_2O_3, CuO, and copper chromite under nitrogen pressure. From the results a two-step reaction model has been developed assuming the first step to be an exothermic reaction producing intermediate products and the second step to be an exothermic reaction leading to the final products. According to the model at low catalyst concentrations, the rate of the endothermic step is predominant and at higher catalyst concentration the rate of the exothermic step becomes predominant while LPL decreases.

Boggs et al. [40] have investigated the combustion of AP in the presence of various inorganic additives. The authors have also reviewed the investigations of others on this subject. In their investigations, they find that pellets with 2% CuO, Cu_2O do not sustain combustion while 8% CuO and Cu_2O show catalytic effects. In the decomposition of AP, CuO is the superior catalyst, whereas in the deflagration, Cu_2O is the better catalyst compared to CuO. 2% Fe_2O_3 increases the $\dot{r}$ of AP, whereas 8% Fe_2O_3 brings down the $\dot{r}$. The authors find that MnO_2 (both 2% and 8%) decreases the $\dot{r}$ at all pressures tested. Thus, MnO_2 is a strong positive catalyst for decomposition but a negative catalyst for deflagration. Cr_2O_3 (2% and 8%) was found to increase the $\dot{r}$. The decomposition and deflagration results differ because of widely differing conditions under which the data are obtained. The more pertinent differences between the two situations are as follows. 1) The temperature of the surface of the deflagrating solid is nearly 900 K while the highest decomposition studies are around 700 K and most of the studies are around 525 K. 2) In addition to the temperature gradient caused by the deflagration flame, there will be concentration gradients caused by inhomogeneities over the surface as well as by the presence of reactive chemical species in the flame. 3) The most striking difference (other than the flame) between the decomposition and deflagration is the presence of the liquid on the surface during deflagration.

Effect on the Decomposition of AP

Catalyzed thermal decomposition (TD) of AP has been studied extensively for the last several years. It is surprising that the exact mechanism of catalyst action is not clear even today. Oxides and other compounds of the transition metals are well-known catalysts of AP decomposition.

Before discussing the catalyzed decomposition of AP, it would be appropriate to summarize the literature on the decomposition of normal AP [41]. AP is stable at room temperature, and measurable decomposition starts only around 150°C. The phase transition from orthorhombic to cubic occurs around 240°. Under dynamic heating conditions the decompostion of AP is complete around 400°C. At temperatures above 450°C the TD of AP is very fast. After an induction period it shows a sudden rise in pressure which is often accompanied by a flash of light and rapid burning. This phenomenon is known as thermal explosion. The literature on decomposition may be categorized into four temperature ranges: two in the orthorhombic and two in the cubic region.

Studies on the decomposition of AP below 200°C are comparatively fewer than those carried out at higher temperatures primarily because the decomposition is extremely slow in this range. Recent studies [42] on TD and electric field effect have shown that activation energy (E) in the range of 140-190°C is around 15 Kcal mole^{-1} (which compares well with the E (20 Kcal mole^{-1}) obtained from electrical conduction studies [43]) and involves the charge carrying species such as H^+ or NH_4^+. Some other work also supports the proton-transfer mechanism in this range.

Between 200-250°C, the decomposition is characterized by a sigmoid curve with an induction period, an acceleratory region, and finally a deceleratory region. The E in this region has been found to be 30 Kcal mole^{-1}, and the decomposition goes only up to 30%. While most of the investigators believe

the decomposition to be a proton-transfer process, a few others argue that decomposition proceeds by the initial destruction of NH_4^+ interstitials.

Between 250-350°C, decomposition goes to 100 % although TG data show a break in the curve at 30% decomposition level. The decomposition curve for this range is characterized by a short induction period and the main reaction being deceleratory in nature. Two E values, 30 Kcal mole $^{-1}$ and 20 Kcal mole $^{-1}$, have been reported in this range. Two mechanisms based on a proton-transfer model and defect (Schottkey-type) structure have been proposed.

Above 350°C the decomposition exhibits a completely deceleratory curve and is associated with fastness and completion to 100%. Two E values, 30 Kcal mole $^{-1}$ and 60 Kcal mole $^{-1}$, have been reported for the decomposition, and the mechanism has been argued in terms of proton-transfer process, electron-transfer process, and Cl-O bond dissociation.

The mechanism of the catalyzed decomposition of AP has been mostly explained on the basis of the proposed mechanism of the normal AP. Mostly, the catalyst action has been viewed via the facilitation of proton-transfer or electron-transfer processes.

Korobeinichev et al.[44] have made a study of the catalyzed TD of $HClO_4$ mass-spectrometrically in a flow reactor under nonisothermal conditions. The degree of activity of different catalysts was found to decrease in the following order: $Co_2O_3 > MnO_2 > CuO > Fe_2O_3 > CuCr_2O_4 > Al_2O_3 > SiO_2$. Shmagin and Shidlovskii[45] have studied the effect of some metal oxides on the composition of the products of the TD of AP. They also find that MnO_2 and Co_2O_3 are the most effective in increasing the decomposition rate of AP. Hermoni and Salmon[46] found that in the presence of MnO_2, CoO, Co_2O_3, Ni_2O_3, and Cr_2O_3 low-temperature decomposition of AP goes to completion. They also studied the TD of AP in the presence of MnO_2, Ni_2O_3, MgO, and Co_3O_4 (mixture of cobalt oxides). From their investigations they find that both gas-phase and condensed-phase reactions are influenced. In the presence of these catalysts the rate of TD increases and ignition delay decreases as the particle size of AP is increased. This suggests that these catalysts influence solid-state reactions. On the other hand, there is a change in the distribution of the gaseous products which suggests that gas-phase reactions have been influenced. Baldyreva et al.[47] have studied the effect of dispersity and surface area of NiO and CuO additives on the low-temperature decomposition of AP. These and other metal oxides such as Co_3O_4, Cr_2O_3, ZnO, MnO_2, and Fe_2O_3 are believed to enhance the gas-phase reactions.

Jacobs and Kureishy[48] found that Cu_2O exerts a pronounced catalytic effect on the decomposition and ignition of AP. Direct measurements of self-heating confirmed that the explosion is thermal in origin and that it can proceed either by the decomposition of AP, which is accelerated by the heat evolved from the oxidation of Cu_2O, or that the TD of AP is catalyzed by Cu_2O. Kuratani[49] has compared the effect of a number of metal oxides and drawn the following conclusions: 1) Cu_2O, CuO, and ZnO catalyze both the low-temperature and high-temperature reaction, 2) copper chromite catalyzes mainly the high-temperature reaction, 3) NiO and Cr_2O_3 promote mainly the low-temperature reaction, 4) Al_2O_3, TiO, and V_2O_5 are ineffective in both temperature regions. Burcat and Carmon[50] have investigated the TD of AP in the presence of Cr_2O_3 to determine the reaction mechanism. Two major simultaneous decomposition routes compete in the decomposition of AP. The first route is analogous to the decomposition of KP and is expected to give products like O_2 and NH_4Cl. The other decomposition route results in the formation of O_2, N_2 and other condensible gases. Levy et al.[51] have studied the catalytic TD of AP by coupling the techniques of DTA and the analysis of the

evolved gases. The catalysts employed were Fe_2O_3, ZnO, and Cr_2O_3. The authors found that only Fe_2O_3 remained unchanged. Its catalytic action has been explained on the basis of reactions between gaseous products. Waesche and Wenograd[52] have studied the effect of different additives on the TD of AP. They find that 2% and 5% by weight of copper chromite and Fe_2O_3 catalyze the decomposition of AP.

Korobeinichev et al.[53] have studied the pyrolytic decomposition of AP using a time of flight mass spectrometer. They find that in the presence of 5% Fe_2O_3 the gas-phase composition changes and they believe the additives catalyze the gas-phase reactions.

Kishore et al.[54] studied the effect of TMO (Fe_2O_3, Co_2O_3, and MnO_2) catalyst concentration on the $\dot{r}$ rate of composite solid propellant. They found that the TD of the AP containing these oxides and corresponding propellant $\dot{r}$ showa saturating effect at 1% of the catalyst. The behavior of the AP decomposition and propellant behavior was similar.

Bircumshaw and Newman[55,56] proposed the mechanism for action of transition metal oxides on AP decomposition. They associated the effectiveness to the ease with which the oxides could provide a bridge in an electron-transfer mechanism:

$$Mn^{4+} + ClO_4^- \rightarrow Mn^{3+} + ClO_4^\circ$$

$$Mn^3 + NH_4^+ \rightarrow Mn^{4+} + NH_4^\circ$$
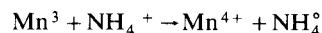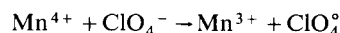
Particularly extensive studies of the decomposition of catalyzed AP have been made by Kuratani[49] and Solymosi et al.[57-62] Kuritani[49] proposed that only the p-type of the TMO were effective in the catalysis of the electron-transfer reactions and the oxides of the n-type were ineffective, although the behavior of ZnO was anomolous. Solymosi and Dobo[60] have studied the TD of AP in the presence of the low concentration (1%) of different impurities (electron donors such as Cl^-, Br^-, I^- and proton donors such as Ag^+, Cu^{2+}, Fe^{3+}). Detailed kinetic measurements were made at 200°-400°C and 260°-330°C. The E below 240°C was 28 Kcal mole $^{-1}$ with 1% Ag, 25 Kcal mole $^{-1}$ with 1% Cu, 30 Kcal mole $^{-1}$ with 5% Cu, 34 Kcal mole $^{-1}$ with 1% Fe, and 29 Kcal mole $^{-1}$ with 5% Fe $(ClO_4)_3$ in agreement with values corresponding to an electron-transfer mechanism. The effect of impurities is explained in terms of electron-transfer mechanism.

Solymosi and Revesz[63] have studied the action of Fe_2O_3 in catalyzing the various stages of the decomposition of AP. They find that Fe_2O_3 has very little effect at 210-240°C but shows pronounced activity for it at 245-270°C and is effective at higher temperatures also. From an analysis of their kinetic data they conclude that Fe_2O_3 facilitates the transfer of the electrons from anion to cation in the rate controlling step of the reaction.

Kishore et al.[64] studied the TD of powdered AP catalyzed by MnO_2. They found that MnO_2 sensitizes the TD of AP, and the E for catalyzed AP was found to be 30 Kcal mole $^{-1}$ throughout the low- and high-temperature regions, whereas uncatalyzed AP gives two E, 20 Kcal mole $^{-1}$ in the low-temperature region (280-320°C) and 60 Kcal mole $^{-1}$ in the high-temperatures region (350-390°C). They explained this behavior of catalyzed AP on the basis of an electron-transfer process. They observed that the effectiveness of MnO_2 in the TD further increases on preheating the sample at 50°C for two weeks: Mn^{2+} ions entered the AP lattice during the process of preheating.

The products of AP decomposition in the presence of various catalysts, especially with copper chromite, have been studied by Rosser et al.[65] They found that the products of decomposition were different from those of pure AP decomposition. They suggested an electron-transfer process in the presence of catalyst. The reaction mechanism proposed for the uncatalyzed decomposition involves the adsorption of

the dissociation products NH_3 and $HClO_4$, self-protonation of $HClO_4$ to yield the intermediate ClO_3^+, and oxidation of NH_3 by ClO_3^+. The reaction mechanism proposed for the catalyzed decomposition involves the formation of the free radicals NH_4^o and ClO_4^o, decomposition of the radicals to NH_3 and oxides of Cl_2, and subsequent oxidation of NH_3.

According to Jacobs and Russel Jones,[66,67] copper chromite alters the low-temperature reaction rate only slightly but accelerates the high-temperature reaction considerably. CuO is even more effective. This acceleration is associated with a change in the E value from 30 to 48 Kcal/mole. They propose the primary step in the presence of catalyst to be same as dissociation to NH_3 and $HClO_4$. Since the rate of the catalyzed reaction exceeds the sublimation rate at the same pressure, they proposed that $HClO_4$ migrates to the catalyst surface by surface diffusion and there decomposes heterogeneously. Subsequent steps involve the oxidation of NH_3. Support for this mechanism comes from recent work by Boldyreva et al.,[47] who have shown that NiO, ZnO, Cr_2O_3, Co_3O_4, and CuO can catalyze the decomposition of AP. In these experiments the $HClO_4$ molecules must diffuse to the catalyst through the vapor phase before decomposing heterogeneously on the oxide. The rate controlling step is believed to be $HClO_4$ decomposition. Galwey and Jacobs[68] have studied the effect of MnO_2 on the TD of AP at low temperatures. The formation of a $+ve$ hole was thought to be the initial step, and the catalytic action of the oxide was believed to be due to the extension of the average lifetime of a $+ve$ hole by the manganese ion of the oxide.

Pellet[69] has developed and applied a pulsed ruby laser mass-spectrometry technique to study the heterogenous AP decomposition. He has studied the AP decomposition in the presence of copper chromite, Fe_2O_3, and MnO_2. The gaseous products in the presence of these additives indicated a predominance of heterogenous reactions. He also believes that the primary step is a proton-transfer dissociation of AP into NH_3 and $HClO_4$. Adsorbed $HClO_4$ later undergoes rapid heterogeneous decomposition. Keenan[70] has studied the low-temperature TD of AP and also its catalysis by copper ion. The low-temperature TD of AP is initiated by a single-stage nucleation process at a lattice defect site on the surface of the crystal. The author suggests that the catalysis occurs through the formation of amine complexes which tie up the NH_3 on the crystal surface and thereby, prevent the reversal of the proton-transfer reaction. Santacesaria et al.[71,72] have investigated the TD of AP in the presence of MnO_2, CuO, and Cu_2O. MnO_2 strongly promotes the perchlorate decomposition and modifies the reaction kinetics. CuO and Cu_2O catalyze the decomposition of AP at high temperatures but not at low temperatures. Proton transfer is believed to be the fundamental reaction step.

Logachev et al.[73] have discussed the mechanism of catalytic decomposition of AP. The catalysts considered were Co_2O_3, MnO_2, CuO, Cr_2O_3, NiO, Cu_2O, V_2O_5, and Fe_2O_3. The important features of the mechanism of catalysis are the contact of the catalyst with AP, particularly coverage of the AP crystals by the catalyst particles, and the diffusion of ClO_4^- anions to the surface of AP. Nagaishi et al.[74] have investigated the TD of AP in the presence of various metal oxide like Cu_2O, CuO, Cr_2O_3, and V_2O_5. The catalyst activity was in the following order: $Cu_2O \rangle CuO \rangle Cr_2O_3 \rangle V_2O_5$.

The rate determining step in CuO and Cr_2O_3 catalysis seems to be the TD of ClO_4^- via the rupture of a Cl-O bond. V_2O_5 has no activity at low temperatures and its activity at high temperatures may be due to its capability of oxidizing NH_3.

The Russian work up to 1966 on solid propellant studies dealing with studies on catalytic effects and additives is summarized from Ref. 75 as follows:

An investigation of the effects of Cu, Mn, Co, Fe, and Ni salts and oxides on the TD of AP showed that copper com-

pounds are most effective in increasing the $\dot{r}$ of the propellant. In another study it was found that Cu, Mn, Co, and Zn carbonates, oxalates, and chlorides accelerate the AP decomposition while Fe, Cr, V, and Ni compounds have an inhibiting effect. The effect of NiO, Cu_2O, ZnO, and CdO on decomposition of KP and AP showed that the decomposition rate can be varied in the desired direction by using such additives. Their effect can be evaluated from their electronic work function.

Effect on the Decomposition of KP

TD of KP has been extensively studied and has been reviewed[3] also. The mechanism proposed involves basically the breaking of the Cl-O bond:

$$KClO_4 \rightarrow KClO_3 + O \qquad (1)$$
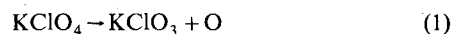
which is followed by the decomposition of the chlorate in the following manner:

$$KClO_3 \rightarrow \frac{3}{4}KClO_4 + \frac{1}{4}KCl \qquad (2)$$
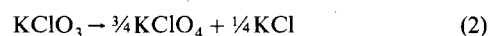
The experimental data are complicated by the fusion that occurs during the decomposition of KP. Reaction (1) is believed to be the rate determining step, and the observed E is in good agreement with the bond dissociation energy of the Cl-O bond (64.3 KCal $mole^{-1}$). However, a few other investigators report a lower E for KP decomposition.

Otto and Fry[76] studied the TD of KP in the presence of Fe_2O_3. They proposed a first-order reaction and ruled out the formation of chlorate. Markowitz and Boryta[77] investigated the TD of KP in the presence of MnO_2. They suggested that MnO_2 acts as a catalyst by abstracting atomic oxygen from the perchlorate, perhaps by the formation of some transient peroxide derivative. Udupa[78,79] has studied the effect of CrO_3 on the TD of the KP and $KClO_3$. Chemical, x-ray, and IR analysis indicate that 1:1 molar ratios of both systems give $K_2Cr_2O_7$ as the decomposition product.

Rudloff and Freeman[80] investigated the effect of different metal oxides (Cu_2O, CoO, NiO, CuO, MgO, Al_2O_3, ZnO, TiO_2, and Fe_2O_3) on the TD of KP and $KClO_3$. All oxides were mixed such that the mole ratio corresponds to a ratio of the one oxide cation to five potassium cations. From their investigations the authors conclude that transition metal oxides were the most reactive catalysts. This was attributed to the p-semiconductive nature of these oxides. Except with Fe_2O_3 the apparent n-semiconductive oxides were less active. Electrical conductivity measurements on some selected oxides indicated the catalytic activity to be electrical in nature. They have suggested that the mechanism involves charge transfer, at least part of which is ionic in nature.

Il'in and Khorunzhii[81-84] have carried out several investigations on TD of KP with and without 1% MnO_2. The increased rate of reaction has been related to an increase of the reaction zones due to the distribution of the reactive nuclei, slow cracking of the crystals, and the catalytic influence of the reaction products. They conclude that surface diffusion and diffusion at the crystal grain boundaries play an essential role in controlling the decomposition rate.

Furuichi et al.[85,86] have studied the effect of Fe_2O_3 on the TD of KP. During the TD, Cl^{+7} is reduced to Cl^{+5} and O^{2-} is oxidized to O_2. It was, therefore, assumed that decomposition involves an electron-transfer process. In Fe_2O_3, the donor center is provided by the excess of Fe^{+2} which ionizes to Fe^{+3} to give the conduction electrons. This leads to the promotion of decomposition of KP as shown by the equation

$$2e^-(oxide) + ClO_4^- \rightarrow O^{2-}(oxide)$$

$$+ ClO_3^- \rightarrow \frac{1}{2}O_2 + ClO_3^- + 2e^-(oxide)$$
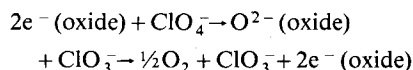
The same authors have also investigated the effect of 12 metal oxides on the TD of KP. They have proposed the following

modified mechanism considering both electron transfer between oxide and perchlorate ion and the abstraction of atomic oxygen from the perchlorate ion by the oxide:

n-Type Semiconductive Oxide

$$2e^- (oxide) + ClO_4^- \rightarrow O^{2-} (oxide)$$

$$+ ClO_3^- \rightarrow \tfrac{1}{2}O_2 + ClO_3^- + 2e^- (oxide)$$
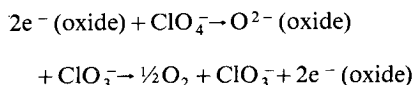
where $e_{(oxide)}^-$ is the electron of the conduction band of the oxide and O^{2-} is the oxygen abstracted by the oxide.

p-type Semiconducting Oxide

$$+_{oxide} + ClO_4^- \rightarrow O_{oxide} + ClO_3 \rightarrow \tfrac{1}{2}O_2 + ClO_3^- + +_{oxide}$$
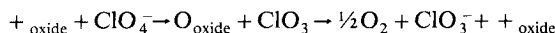
where $+_{oxide}$ is the $+ve$ hole of valence band of oxide, O_{oxide} is the oxygen atom abstracted by the oxide, and ClO_3 is a radical.

Conclusions

A literature survey has revealed that copper chromite and Fe_2O_3 are most effective catalysts amongst TMO on composite propellant, KP, AP-polymer condensed mixture, and AP-polymer sandwich combustion. TMO have also been found generally to sensitize the thermal decomposition of AP and KP. In spite of the voluminous literature on these aspects, the mechanism of decomposition and combustion in presence of TMO is a matter of controversy even today. Investigators have differed on the location of catalyst action during combustion. TMO may affect 1) gas phase, 2) subsurface condensed phase, and 3) surface condensed phase separately or all of them simultaneously. According to the location, the mechanism of action has been discussed in the past. In decomposition it is generally believed that TMO may promote either a proton-transfer process or an electron-transfer process, but the odds may be in favor of an electron-transfer mechanism. Recently, our laboratory has shown that TMO act through an electron-transfer mechanism even during propellant combustion. The argument has been supported by the fact that catalyst effectiveness is related to the redox potential of oxides and also with the energy associated with the electron-transfer process. Apart from this, the action has also been explained on the basis of semiconducting properties of TMO and a charge-transfer mechanism. Many Russian workers have related the TMO activity on decomposition to their electronic work function.

Boggs et al.[40] have recently pointed up the marked difference in catalyst behavior in AP decomposition vs behavior in propellants. More work is needed to be done to throw more light on this aspect. Recently[42] in this laboratory it has been observed that Fe_2O_3, Co_2O_3, Ni_2O_3, and MnO_2 catalyze the decomposition of AP and corresponding AP/PS and AP/CTPB propellants via the promotion of the electron-transfer process. Although the redox potential of metal ions to that of $\dot{r}$ gave a good correlation supporting the preceding mechanism, it was found that E for AP + catalyst decomposition and redox potential (and also the $\dot{r}$ of propellants) behave in an opposite direction. But a correlation was found between ΔE (energy required for the electron to go from valence band to conduction band – energy required for the electron to go from metal ions to valence band and conduction band) and the $\dot{r}$ fo the propellant, supporting that oxidizer decomposition plays a significant role in propellant combustion. Among the oxides of Fe, mostly the red oxide has been used as a catalyst and not the black iron oxide. It may be interesting to investigate the comparative behavior of these oxides in view of the specific surface area difference in Fe content and electrical conductivity. Apart from this the following aspects need to be investigated to give a clearer

picture of the process: 1) effect of TMO as a function of pressure; 2) effect of particle size of TMO on combustion and decomposition; 3) effect of mixture ratio on the effectiveness of catalyst; 4) effect of initial temperature on the effectiveness of catalyst; 5) concentration of catalyst has been found to affect LPL and deflagration rate in opposite directions in AP deflagration—why? 6) presence of metal like aluminum affects the effectiveness of the catalyst—why?

There is no adequate model to explain the effect of TMO on decomposition and combustion, although some qualitative predictions have been made in the past on the basis of models. An effort in this direction is also needed.

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