Investigation of Metal Oxides as Catalysts for the Thermal Decomposition of Potassium Chlorate(VII)

Andrzej T. Wojewódka,[*] Roman Zakusylo, Viktor Kravets, Angela Romanchenko, Tomasz Jarosz

Silesian University of Technology,
ks. M. Strzody 7, 44-100 Gliwice, Poland
[*]*E-mail: Andrzej.Wojewodka@polsl.pl*

Abstract: The results of studies on the thermal decomposition of potassium chlorate(VII) (PP) and the catalytic effects of copper, iron, nickel, titanium, magnesium, chromium and manganese oxides on the process are presented in this paper. The investigated oxides are ranked according to the magnitude of their catalytic effect; of these, CuO and MnO_2 show the best catalytic performance. These oxides reduce the PP decomposition temperature from 919.3 K down to even 825.2 K. The share of the catalytic additive in the composition, required to achieve a desirable thermal decomposition profile, was found to be no more than 0.5 wt.%. The activation energy of the decomposition process was determined, using the modified Freeman and Carroll method for both neat PP and PP supplemented with MnO_2; the addition of the catalyst produced a 48.8% decrease in the activation energy of thermal decomposition.

Keywords: metal oxide catalysts, thermal decomposition, potassium perchlorate, manganese oxide, copper oxide, differential thermal analysis

1   Introduction

Potassium chlorate(VII) (PP) is one of the strongest oxidising agents used in pyrotechnic formulations for use in industrial blasting operations, including such precise applications as blasting decorative stone blocks [1, 2]. Explosive compositions based on PP typically exhibit low detonation speeds, heats of explosion and critical diameters of detonation; they also produce limited amounts of gaseous decomposition products [3]. These features are beneficial for use in the

"soft" breaking of decorative stone, as they contribute to improving the quality of the split blocks. The operational characteristics of such explosive compositions are directly determined by their thermal decomposition profiles and, as such, their components. The explosive decomposition of PP can be problematic in this respect, as it occurs and spreads with relative difficulty [4]. Consequently, finding and selecting appropriate catalysts for facilitating the explosive decomposition of PP-based compositions is a necessary and commercially motivated task.

Various metal oxides, such as MnO_2, MgO, Cr_2O_3, CuO, Fe_2O_3, NiO, TiO_2 and their combinations, can be used as catalysts for the thermal decomposition of PP [5]. A similar investigation was conducted by Ping *et al*. [6] for a composition using ammonium chlorate(VII), where a catalytic system composed of carbon nanotubes and copper particles was investigated. Later, Patil *et al*. [7] performed a similar investigation, using nano-copper and copper chromite as the catalytic system.

Interestingly, no quantitative studies of the catalytic reduction of the PP decomposition temperature have been published to date. Therefore, in this work we aimed to remedy this situation by studying the process of thermal decomposition of PP-based explosive compositions that contain a series of metal oxides. These oxides are thought to be catalysts for the PP decomposition reaction and we have investigated their catalytic potency by gauging their impact on the decomposition temperature and activation energy of the decomposition reaction.

The catalytic effects of metal oxides, with comparable surface areas, on the decomposition of PP were studied by thermogravimetric analysis [8]. The catalytic mechanism was discussed, based on the relative activity of the metal oxides. It was found that oxides containing transition metal cations with partially filled d-orbitals have the highest activities, oxides containing transition metal cations with completely empty valence d-orbitals are moderately active, and oxides containing metal cations with completely filled d-orbitals or noble gas configurations have the lowest activities. The report [9] presents the results of DSC studies of the phase transition, decomposition and melting of PP with various additives. It has been shown that even minor additions of metal oxides to PP cause changes in the thermochemical behaviour of the PP. Some investigations on the particle sizes and materials were carried out and the authors provided data for choosing the optimum component shares for achieving certain burning characteristics of hot-wire pyrotechnic devices.

2   Experimental

The preliminary preparation of compositions in the laboratory consisted of the following steps: drying, sieving and mixing. Moisture is of great importance in composite explosives, as it affects the clumping of the explosives, their efficiency and sensitivity to initiating stimuli.

PP is only marginally hygroscopic, but is commonly contaminated with hygroscopic sodium chlorate(VII). Consequently, for use in explosives, the humidity of such an oxidising agent must be controlled and cannot exceed 0.2 wt.%. To ensure this, the batch of PP (Altaikhimprom) was dried at a temperature of 358 K for 3 h. Afterwards, the PP was sieved to exclude any grains larger than 100 μm. The purity grades and relevant regulations on the possible contaminants for PP and the metal oxides used are given in Table 1.

Table 1.   Purity grades and relevant regulations pertaining to contaminants present in the PP used and in the metal oxide samples

Chemical	Regulations	Purity grade[a]	Mass fraction of the main component [wt.%] (not less than)
$KClO_4$	TC 6-09-3801-76, TC 2147-471-05121441-2008	PFA	99.5
ZnO	STST 10262-73	CP	99.5
CaO	STST 8677-76	PFA	97.5
SiO_2	STST 9428-73	PFA	98
TiO_2	TC 13463-67-7	PFA	98
Fe_2O_3	TC 6-09-5346-87	P	98
Cr_2O_3	STST 2912-79	TECH	99
Cu_2O	TC 6-09-765-85	P	98
NiO	STST 4331-78	P	77
MgO	STST 4526-75	PFA	98
CuO	STST 16539-79	PFA	99
MnO_2	STST 4470-79	PFA	90

[a] PFA: pure for analysis; CP: chemically pure; P: pure; TECH: industrial (technical) purity.

Metal oxides, if necessary, were dried and rubbed through a sieve with an opening diameter of 50 μm. Mixtures containing 97 wt.%. of PP and 3 wt.% of one of the investigated oxides were prepared by mechanical mixing.

In this study we used differential thermal analysis (DTA) to follow the thermal decomposition of PP. Simultaneously, thermogravimetric (TG)

measurements were carried out, allowing changes in the mass of the sample to be recorded as a function of temperature [10]. The temperature scan rate used for the measurements was 10 K/min. Each sample had a mass of 200 mg and was heated from room temperature (20 °C, 65% relative humidity) to 700 °C in an open quartz vessel (volume of the vessel: 0.5 cm^3). The experimental uncertainty values of the instrument were: ±1 K, ±0.02 g and ±2.2 J/g respectively for temperature, mass sample change and enthalpy baseline stability.

The parameters of PP thermal decomposition were determined using a "Thermoscan-2" instrument (see «Аналитприбор», St. Petersburg, 2012).

3   Results

3.1 Differential thermal analysis of potassium chlorate(VII) decomposition

Neat PP, lacking any catalytic additives, was used as the base for comparing the catalytic effects of the various metal oxides investigated. The simultaneous TG/DTA analysis was carried out in air, at a heating speed of 10 K/min, with a sample mass of 200 mg. A sample of aluminium(III) oxide (α-Al$_2$O$_3$), which undergoes no changes in the temperature range of 288-1273 K, was used as the external reference material for these measurements.

The measurements were conducted in the temperature range of 293-973 K, with the results being obtained as graphical plots – thermograms. Due to the various processes taking place in the samples on heating, both endo- and exo-thermic peaks were observed on the thermograms. These peaks were annotated with the temperatures, at which they occurred (Figure 1), the corresponding transitions were identified and their enthalpies were calculated.

Following the DTA-TG investigation of neat PP, samples "contaminated" with each of the abovementioned metal oxides were tested under the same conditions. Sample thermograms, for neat PP and for PP containing 3 wt.% CuO, are shown in Figure 1.

It is no less important to establish the smallest amount of the catalyst that needs to be introduced into PP in order to successfully modify the thermal decomposition profile, in turn augmenting the operational parameters of the explosive composition based on the PP-catalyst system. This was done in our previous work [11] for manganese(IV) oxide, MnO$_2$, which is a rather effective catalyst for PP decomposition. Similar results were obtained for the other metal oxides investigated in this work. Consequently, a metal oxide content of 0.5 wt.% or even 1.0 wt.% might be sufficient to investigate their effects on the

thermal decomposition of PP. However, due to our focus on the highest attainable performance for each investigated catalytic system, we chose to employ a large safety margin and used 3 wt.% metal oxide content for our measurements. This value was selected, as earlier work had established that increasing the catalyst content beyond 3 wt.% does not result in noticeable changes in the thermal decomposition profile of the composition.
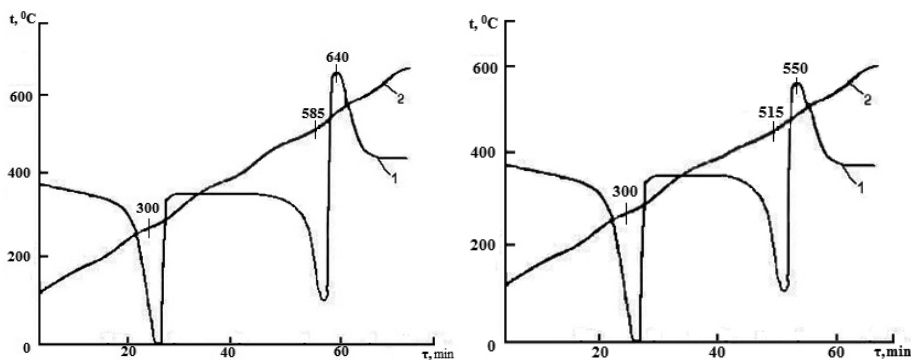

Figure 1. Thermograms of the decomposition of neat PP (left) and PP containing 3 wt.% copper(II) oxide (right). The DTA and temperature curves are labelled as curves 1 and 2 respectively

The temperature ranges, in which physical and chemical transitions take place for each of the investigated samples, are listed in Table 2, along with the calculated enthalpies of these processes. The different PP-metal oxide compositions have been arranged according to their decomposition onset temperatures, a parameter used as an initial, rough measure of the catalytic activity of the investigated oxide.

The abovementioned experiments, monitored by DTA-TG, revealed that once a catalyst had been introduced into PP, the thermal decomposition temperature decreased by up to 100 K in comparison to that of neat PP. The magnitude of this decrease appeared to stabilise at a metal oxide content of ~0.5 wt.%, and further increase of the catalyst content had no discernible effect on the thermal properties of the samples. Interestingly, it was necessary to use a relatively fine catalyst and care must be taken to ensure uniform distribution of the catalyst in the composition.

The data summarised in Table 2 is in line with what has been reported in the literature for these and similar oxides [8, 9]. The thermal decomposition parameters presented in Table 2 reveal that the PP phase transition from the β- to the α-structure occurs at temperatures around 573 K, with the addition of

Table 2. Key parameters found for the thermal decomposition of potassium chlorate(VII) and potassium chlorate(VII) mixed with 3 wt.% of each of the investigated metal oxides

No.	Components	Polymorphic transition			Melting			Decomposition		
		Temperature band [K]	Δm^a [g]	ΔH [kJ/mol]	Temperature band [K]	Δm^a [g]	ΔH [kJ/mol]	Temperature band [K]	Δm^a [g]	ΔH [kJ/mol]
1	$KClO_4$	568.1-576.6	0.02	6.5	851.2-876.3	0.035	4.89	876.3-919.3	0.045	2.2
2	$KClO_4$, MnO_2	566.6-573.2	0.02	4.97	785.6-789.4	0.035	3.78	789.4-825.2	0.065	1.95
3	$KClO_4$, CuO	567.1-576.8	0.025	5.38	787.1-794.3	0.04	3.62	794.3-825.5	0.055	1.86
4	$KClO_4$, MgO	569.2-576.2	0.02	5.04	789.2-801.3	0.035	2.87	801.3-839.9	0.06	1.56
5	$KClO_4$, NiO	567.6-575.9	0.02	4.81	793.4-804.8	0.03	2.17	804.8-851.9	0.05	1.17
6	$KClO_4$, Cu_2O	568.2-578.2	0.02	5.01	795.7-805.5	0.04	2.42	805.5-875.6	0.058	1.81
7	$KClO_4$, Cr_2O_3	568.5-573.6	0.025	5.79	809.5-816.6	0.03	3.21	816.6-860.7	0.055	1.34
8	$KClO_4$, Fe_2O_3	567-576.3	0.02	4.59	819.7-832.2	0.04	1.99	832.2-874.4	0.055	1.68
9	$KClO_4$, SiO_2	569.2-576.8	0.02	4.63	801.4-844.3	0.03	3.45	844.3-893.4	0.05	1.75
10	$KClO_4$, CaO	568.3-577.6	0.02	4.48	829.3-845.4	0.03	3.29	845.4-894.5	0.045	1.62
11	$KClO_4$, TiO_2	567.7-575.8	0.025	4.68	832.4-856.3	0.025	2.54	856.3-895.2	0.05	1.12
12	$KClO_4$, ZnO	567.9-576.3	0.02	4.86	844.3-858.7	0.03	3.95	858.7-895.6	0.05	1.26

[a] change of sample mass in the indicated temperature range

the metal oxides having no significant effect on the process, in regard to what is observed for neat PP. Melting and decomposition of the samples supplemented with metal oxides occurs at lower temperatures than in the case of neat PP. This observed eutectic effect indicates interactions between PP and the investigated metal oxides, possibly offering a clue as to the mechanism of the catalytic activity in the PP thermal decomposition reaction.

An interesting observation was that, contrary to expectations, the d-block metal oxides are not necessarily the most active catalytic systems, with magnesium oxide showing the third lowest decomposition onset temperature. Similarly, the activity of silicon(IV) oxide is higher than would be expected; we had initially intended this compound to be a "blank sample", due to its excellent thermal stability and very low reactivity. Although its addition decreases the PP decomposition onset temperature by only 30 K, this effect is still more significant than the effects of titanium oxide and zinc oxide, both being d-block metal oxides. In light of these "irregularities", we can assert that the mechanism underlying the catalytic activity of metal oxides in the decomposition of PP is not solely dependent, if dependent at all, on interactions with d orbital electrons of a transition metal and is likely based on another phenomenon.

Another matter of interest is that copper(II) oxide appears to be a more efficient catalyst than copper(I) oxide, even though the latter would be expected to readily react with PP, at temperatures far lower than 803 K, undergoing oxidation to produce copper(II) oxide.

3.2 Determination of the activation energy using the modified Freeman and Carroll method

Due to the simultaneous DTA and TG measurements, the thermograms of the thermal decomposition of potassium chlorate(VII) presented in the earlier section can be used to provide an insight into the kinetics of the processes occurring in the samples.

The modified Freeman and Carroll method [12] is one of the most commonly used methods for determining the kinetic parameters of the thermal decomposition of pyrotechnic compositions, and is based on mathematical processing of the recorded thermograms. Other methods of analysis [13] can also be used to provide information about other parameters; these however are less common and, for the purpose of our investigation, are all but equivalent to the Freeman-Carroll (FC) method. The advantage of the FC method is that for a continuous study of kinetics in a wide range of temperatures, only a few data points are required. The main drawback of the method is that the decomposition rate is determined by calculating the slopes of tangents to the experimental

curve, which details changes in the mass of the sample during the decomposition process, significantly increasing the experimental uncertainty.

According to this method, for a certain decomposition rate of the condensed substance, PP in our case, at a temperature T, the following equation holds true at a given time:

$$P_T = \frac{dW}{dT} = \frac{Z}{q} \cdot e^{-\frac{E_A}{RT}} \cdot W^n, \tag{1}$$

where: P_T – decomposition rate of PP, mg/K; q – heating rate, K/min; Z – pre-exponential factor; W – mass of the sample consumed in the reaction, mg; n – order of the reaction; E_A – activation energy, J/mol·K; R – gas constant, 8.314 J/mol.

This equation can be transformed into a linear form in order to allow its use to determine the value of E_A based on the rate of decomposition:

$$log(P_t) = log\left(\frac{Z \cdot W^n}{q}\right) - \frac{E_A}{R} \cdot \frac{1}{T} \tag{2}$$

Using this equation, the activation energy of the thermal decomposition of PP was calculated using the changes in the mass of the sample (TG) observed in the temperature range corresponding to decomposition, until a constant sample mass was achieved, which signified the completion of the decomposition process. For this purpose, four points were chosen on this part of the curve and the temperature corresponding to each point was determined, as were the decomposition rates at each point. The dependence of $log(P_t)$ on $1/T$ was then plotted, allowing the activation energy to be calculated from the slope of the plot (Figure 2).

The relevant numerical data are listed in Table 3.

Table 3.   The values of the parameters used for defining the activation energy of the decomposition process of neat PP

No.	T_i [K]	$1/T_i$ [K^{-1}]	α_i [deg]	P_{Ti}	$P\tau_i$	$lgP\tau_i$
1	811	0.00123	34	0.67	6.7	0.82
2	841	0.00119	74	3.49	34.9	1.54
3	847	0.00118	79	5.14	51.4	1.71
4	851	0.00117	87	19.08	190.8	2.28

The following formulae were used for the calculations:

$$P_{Ti} = tg(\alpha), \tag{3}$$

where: P_{Ti} – temperature decomposition rate, mg/K; α_i – slope of the tangent to the thermogram at temperature T_i.

$$P\tau_i = P_{Ti} \cdot q, \tag{4}$$

where: $P\tau_i$ – rate of transformation, mg/min; q – heating rate, 10 K/min.

Then, knowing that $\log(P) = f(1/T)$, the slope of the curve can be used to calculate the activation energy, as indicated below and in Figure 2.
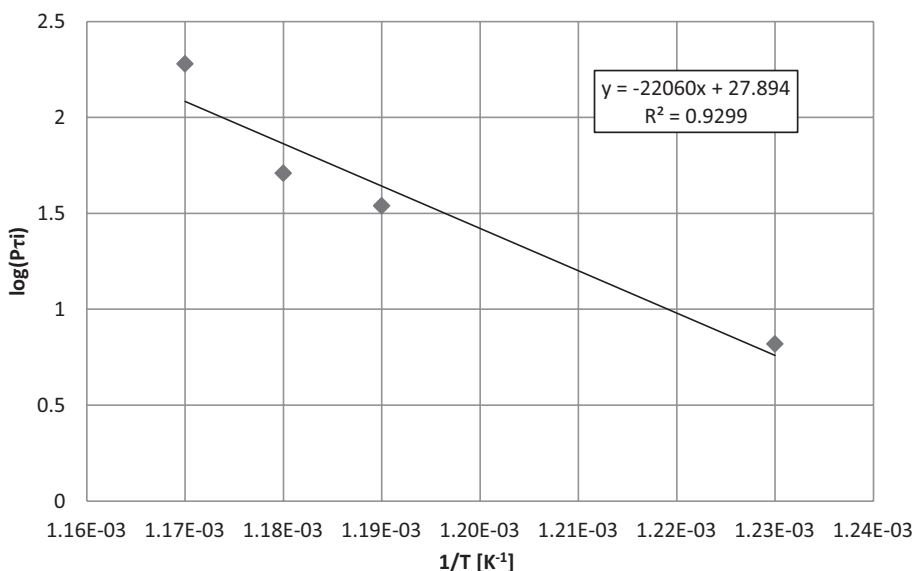

Figure 2.   The semi-logarithmic dependence of the change of PP decomposition rate on the inverse temperature plot

The value of the tangent of the β angle was extracted from the linear equation of the graphic dependence (using Equation 2, $y = \log(P_T)$, $a = -E_A/R$, $x = 1/T$, $b = \log(Z \cdot W^n/q)$, and knowing that for the graphical plot $tg(\beta) = -a$). Based on the given linear equation, the value for the data shown in Figure 2 was 87.4°, therefore:

$-a = tg\,\beta = 22060$ K
$-a = E_A/(2.303 \cdot R)$
$E_A = 422.4$ kJ/mol

The activation energies of the thermal decomposition of the explosive compositions consisting of 97 wt.% potassium chlorate(VII) and 3 wt.% of a metal oxide were subsequently determined using the same methodology for each of the investigated compounds. The relevant numerical values are listed in Table 4.

Table 4.   Values of the activation energy of the thermal decomposition of PP calculated for PP supplemented with 3 wt.% of an oxide catalyst

No.	Components	Activation energy, E_A [kJ/mol]
1	$KClO_4$	422.6
2	$KClO_4$, MnO_2	216.3
3	$KClO_4$, CuO	227.6
4	$KClO_4$, MgO	241.5
5	$KClO_4$, NiO	254.5
6	$KClO_4$, Cu_2O	257.6
7	$KClO_4$, Cr_2O_3	278.6
8	$KClO_4$, Fe_2O_3	291.3
9	$KClO_4$, TiO_2	318.7
10	$KClO_4$, SiO_2	326.3
11	$KClO_4$, CaO	329.8
12	$KClO_4$, ZnO	398.7

4   Summary and Conclusions

In summary, all of the investigated systems showed different levels of catalytic activity towards the process. Our findings are generally in line with those reported in the literature and, particularly for Fe_2O_3, with the results of Jinn-Shing Lee and Chung-King Hsua [9]. Our earlier studies have also confirmed that only marginal changes in the thermal features of the process occur above a catalyst content of approx. 0.5 wt.%., making it an optimal threshold in terms of cost-efficiency.

Based on the acquired DTA-TG data, the metal oxide catalysts were ranked in terms of their impact on the thermal decomposition of potassium chlorate(VII). Starting with MnO_2 as the most active catalyst, the order is as follows: MnO_2, CuO, MgO, NiO, Cu_2O, Cr_2O_3, Fe_2O_3, SiO_2, CaO, TiO_2 and ZnO. In terms of activation energy, a similar order was found, differing in the fact that the activation energy of the composition containing titanium(IV) oxide was lower than that of silicon(IV) oxide, but the sequence of oxide activity was otherwise the same. This sequence should be compared with the electron configurations

of the metal (or metalloid, in the case of SiO_2) atom of each of the investigated oxides, as given in Table 5 below.

Table 5. Electron configuration of the metal and metalloid atoms present in the investigated oxides

No.	Oxide	Core atom electron configuration (shortened)	Number of d orbital electrons (paired/unpaired)
1	MnO_2	[Ar] $3d^3$	0/3
2	CuO	[Ar] $3d^9$	8/1
3	MgO	[Ne]	0/0
4	NiO	[Ar] $3d^8$	6/2
5	Cu_2O	[Ar] $3d^{10}$	10/0
6	Cr_2O_3	[Ar] $3d^3$	0/3
7	Fe_2O_3	[Ar] $3d^5$	0/5
8	TiO_2	[Ar]	0/0
9	SiO_2	[Ne]	0/0
10	CaO	[Ar]	0/0
11	ZnO	[Ar] $3d^{10}$	10/0

Interestingly, in both types of evaluation, oxides of metals that have no d electrons or orbitals were found to be at least comparable in catalytic activity to the oxides of d-block metals. This evidence is not directly contrary to the aforementioned supposition that the presence of atoms with partially filled d-orbitals helps catalyse the decomposition of PP, but it demonstrates that systems, which, on the basis of Lee and Hsua's work [9], would not be expected to act as catalysts of PP decomposition, exhibit noticeable catalytic activity in that process. As such, we postulate that another mechanism, apart from d orbital interaction, underlies the results obtained. Although further investigation will be required to verify this, we suspect that the thermal features of the individual metal oxides are a significant factor, as the decomposition temperatures often coincide with the temperatures of their polymorphic or even phase transitions (as in the case of MnO_2, whose melting point is at ≈808 K).

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