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Catalyst screening for ammonium nitrate oxidizer

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Abstract

The ammonium nitrate (AN) represents a cheap and chlorine-free alternative to ammonium perchlorate but it suffers from low reactivity. The literature is populated by a large number of papers regarding the catalysis of ammonium nitrate decomposition but data are quite inhomogeneous. In the frame of the GRAIL project an experimental campaign was conducted to scrutinize some environmentally-friendly burning rate catalysts, investigating their peculiar role in the decomposition of the oxidizing salt only. The present paper reports about the results obtained by characterizing mechanical mixes of AN with selected metal oxides under slow heating rate with DTA/TG technique.

Nomenclature

Acronyms

AC activated carbon

AN ammonium nitrate

CB carbon black

DTA differential thermal analysis

GAP glycidyl-azide polymer

HTPB hydroxyl-terminated polybutadiene

PSAN phase stabilized ammonium nitrate

TG thermogravimetry

GHS Hazards: Environmental

H410d very toxic to aquatic life with long-lasting effects

H411d toxic to aquatic life with long-lasting effects

GHS Hazards: Health

H302 harmful if swallowed

H304 may be fatal if swallowed and enters airways

H315 causes skin irritation

H319 causes serious eye irritation

H332 harmful if inhaled

H336 may cause drowsiness or dizziness

H351 suspected of causing cancer

H361d suspected of damaging the unborn child

H373 may cause damage to organs through prolonged or repeated exposure

GHS Hazards: Physical

H225d highly flammable liquid and vapor

Symbols

Δh_f^0 standard enthalpy of formation

D_{43} volume-weighted diameter

m_{final} final mass

$m_{initial}$ initial mass

R_d reactivity parameter

TG_{off} onset temperature

TG_{on} onset temperature

1. Introduction

1.1 The ammonium nitrate salt

Ammonium nitrate is a common quaternary ammonium salt, produced by industry for a variety of purposes, spanning from fertilizer to explosive ingredient. From a safety viewpoint, it is considered relatively stable at ambient temperature and pressure. In modern solid propellants, ammonium nitrate finds application in slow-burning compositions and has the advantage of gaseous and chlorine-free combustion products. This aspect enables the use of this oxidizer in eco-friendly propellants, non-corrosive gas-generators, automotive airbags, low-signature propellants (minimizing the secondary smoke).¹

The AN salt is reported to decompose into gaseous products, without leaving residues. The steady-state process under which AN becomes a gaseous product has been described, in an early paper by Feich and Hainer, as the merge of two distinct processes: an irreversible decomposition and a reversible dissociation (respectively, Eq. 1 and 2).²



The same authors underlined that the rate was observed to be strongly dependent on the pressure. At ambient conditions, the process is endothermic as the dissociative sublimation of the AN is absorbing the heat available for the decomposition. The observed rate is moderately slow. Once the pressure is incremented, the dissociation is repressed and an explosive rate of decomposition is attained. It seems that there is a quite non-homogeneous method of referring to the terms dissociation and decomposition and, probably, there is not a unified view in the process.

Even in more recent literature it is generally accepted that thermal decomposition is initiated by an endothermic proton transfer reaction (Eq. 2). Most of the proposed mechanisms assume, first, production of ammonia and nitric acid with a subsequent oxidation of NH_3 by the decomposition product of HNO_3 . This process leads to the formation of other oxidizing species like NO_2^+ thus explaining the production of N_2O and water. Specifically, water evaporation cools the flame.¹ A paper by Wood and Wise underlined that the degradation of the salt was an auto-catalytic liquid phase reaction. Observations were performed at moderate temperature (443 K to 553 K). The auto-catalysis effect was attributed to the nitric acid, generated during the dissociation of the salt. The initial reaction rate was observed to increment as the concentration of HNO_3 was incremented. The same set of experiments also demonstrated that the acid also causes an inhibition effect in the course of the reaction.³

1.2 AN-based propellants

From a propellant combustion viewpoint, the use of AN must solve the problems of low burning rate, high pressure exponent, and problematic metal combustion. When compared to AP, the oxygen content of the nitrate ion (NO_3^-) is lower than the oxidizing capability of the perchlorate ion (ClO_4^-) ending up in lower gravimetric specific impulse. The density of the salt is lower as well (1.73 g cm^{-3} of AN vs. 1.95 g cm^{-3} of AP), thus compromising the volumetric specific impulse. Lower reaction kinetics is associated to the nitrogen oxide with respect to chlorine oxide, since liberation of oxygen from the nitrogen oxides requires higher temperature.^{4,5} Slower kinetics and lower combustion enthalpy with respect to AP-based propellants cause a cooler flame, located farther from the burning surface. Thus, the heat feedback from the flame to the surface is reduced. In addition to this aspect, hygroscopicity of AN attracts moisture which causes a further reduction of performance and, eventually, propellant degradation. The combustion of the binder and of the metal in AN-based propellants does not occur under efficient conditions. The reduced heat feedback does not enable the complete destruction of the binder which leaves a porous and solid carbonaceous structure.⁶ The metal (in general, aluminum) does not ignite easily and is trapped in the porous structure, causing the production of large agglomerates.⁷ The effect is more evident at lower pressure level since the monopropellant heat release of the ammonium nitrate is pressure-dependent and the flame is more stretched due to gas-phase density. The pressure dependence of combustion kinetics is considered the possible reason for the high ballistic exponent of the burning rate. In this respect, magnesium was observed to improve the burning features of AN-based propellants since the earlier ignition capability with respect to aluminum enables a heat release closer to the burning surface, despite the lower heat of combustion with respect to aluminum.⁴ In dual AP/AN compositions the progressive replacement of AP with AN leads to a reduction of burning rate and to a simultaneous increment of the PDL, which can result above the atmospheric pressure.⁸

1.3 Ammonium nitrate dissociation and decomposition

The AN is highly stable, featuring a high temperature of reaction onset (onset at 260 °C). However, the presence of other substances may turn the attitude into an explosive decomposition rate. A paper by Cagnina *et al.* mentions a list of accidents and of reportedly incompatible materials such as free ammonia, chlorine salts, powdered metals, acids, fuels, and few other components.⁹ Auto-ignition and explosion may take place due to the catalytic effects. An explosive behavior of AN can be induced by chlorine ions. Ammonium chloride was observed to trigger a violent reaction on heating of the samples. The fact was observed also for other chlorine-based salts such as calcium or iron (III) chlorides.⁹ Similar considerations have been done on finely powdered metals, organic compounds, or some sulfur-based additives.

Differential scanning calorimetry tests from 50 °C to 450 °C at 20 °C min⁻¹ were performed by Oxley *et al.* on several additives in different amount, from 3% up to 6% by mass. The position of the exothermic peak was mapped.¹⁰ The authors tested halides showing that they had a destabilizing effect on AN, with the exception of fluorides. They also reported chlorides to be the best in anticipating the maximum of the exothermic reaction, lowering it of about 70 °C. Vargeese and co-authors studied the reactivity of AN with copper oxide, titanium dioxide, and lithium fluoride by comparing the activation energy of the baseline and the mixture. They reported that titanium dioxide was not acting as a catalyst since no marked differences were appreciable in the activation energy, while lithium fluoride increased it. This last result is reasonable since the *LiF* powder is used as a burning rate retardant in ammonium perchlorate propellants.¹¹ Instead, copper oxide reduced the activation energy, demonstrating a catalytic effect on AN degradation. They concluded that auto-catalysis and the interaction of *Cu* species with the dissociative decomposition products of AN were responsible for the reduction of the activation energy barrier.

Kajiyama and co-authors tested different additives, hand-mixed with AN, including AN/AC, AN/CB, AN/*CuO*, AN/AC/*CuO*, and AN/CB/*CuO*. Copper oxide was included in the AN/AC/*CuO* and AN/CB/*CuO* mixtures at different concentrations (5, 10, and 25 wt.%).¹² DSC-TG tests under air atmosphere evidenced that the addition of *CuO* affected the thermal behavior, inducing an exothermic reaction at 240 °C. When mixed with carbon, a lower temperature exotherm was observed at 210 °C. The higher the amount of *CuO* generated, the more vigorous the exothermic peak. Possible cross effects among ingredients were not excluded. Iron (III) oxide with *NiO*-stabilized AN was tested by Carvalho *et al.* but no effect on the reactivity was reported, regardless the amount.¹³ The authors have shown that in a propellant environment the decomposition path of *Fe*₂*O*₃-coated PSAN(1% *NiO*) crystals was not altered with respect to the original, featured by the uncoated version. Rather, a positive effect was observed on the pyrolysis of the HTPB-IPDI binder.

Different authors underlined the possible cross-interaction between some phase-stabilizing agents and AN dissociation. During their studies on AN phase stabilization, Oommen reported that *K*₂*Cr*₂*O*₇ produced a strong exothermic reaction at nearly 180 °C in both simple mixing or co-crystallization. The same positive effect was observed in propellants, leading to a decrement of the PDL pressure-deflagration-limit and an increment of the burning rate with respect to compositions based on pure AN. Nevertheless, high level of additive toxicity discourages its use. Synergetic interaction was also present for PSAN(1% *NiO*)-HTPB-IPDI propellants, demonstrated by a strong exothermic reaction located at about 500 K temperature. No evidence was mentioned about the potential phase stabilization of the iron oxide. In this respect, propellants containing iron (III) oxide featured a moderate increment of both pressure exponent and pre-exponential factor of the Vieille's law, when used in quantity in the order of 0.4-0.5%. Other evidences about the effectiveness of transition-metal oxides on catalytic decomposition of AN was reported by Zhao and co-authors.¹⁴ They claimed a rate increment of about 15 times but they did not release the composition of the catalyst. A joint thermal and decomposition effect was observed for PSAN stabilized with the co-crystallization of *CuO*, by both suppression of phase transition and enhanced decomposition kinetics. It is already known that the co-crystallization or the melt-mixing of ingredients is fundamental for the phase stabilization effect. Recent works on AN/*CuO* hand-mixes have demonstrated that catalytic action is absent without co-crystallization.¹² Low heating rate degradation analyses have been performed on AN-pyrite mixes both in nitrogen and air atmosphere.¹⁵ A large exothermic peak at nearly 200 °C was observed. A second exothermic peak was also present at 450 °C only under air condition, and was ascribed to possible oxidation of residual pyrite. The oxides contained in PSAN have shown to deliver beneficial effects on propellant combustion. Improvement of burning rate and decrement of the pressure exponent was reported for stabilization with nickel oxide (*NiO*), copper oxide (*CuO*), zinc oxide (*ZnO*).¹⁶ Similar tests have been conducted on titanium dioxide (*TiO*₂) but no influence has been observed.¹¹ Manganese dioxide (*MnO*₂) has been indicated as a catalyst for gas-generating compositions containing ammonium nitrate.¹⁷ The use in HTPB propellants improved the ignitability by lowering the PDL but, at the same time, the increment of *MnO*₂ caused an increased pressure exponent. Tests performed on AN-GAP propellants showed that MoVO catalysts (based on molybdenum/vanadium oxides) were effective in both burning rate tuning and in reduction of the pressure exponent.¹⁶

The effect of metal fuels on AN depends on the combustion properties of the metal itself. In AN-HTPB propellants, the use of aluminum is not efficient due to the low heat feedback and the reduced burning rate. Higher residence

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time, entrapment in the porous structure, and delayed ignition lead to an increment of the agglomerate size for standard micrometric Al powders. The application of ultrafine aluminum (about 100 nm) is capable of improving the combustion property of the final propellant.¹⁸ It is very likely that the improvement is not connected to a catalytic effect, rather, there is an incremented heat release close to the burning surface, thanks to a different metal fuel reactivity. Also the use of magnesium is beneficial from this viewpoint. As additive in AN/HTPB propellants, it delivers improved burning rate and reduced pressure exponent.^{4,19}

2. Experimental

The work presents the reactivity characterization of mechanical mixes containing ammonium nitrate and different oxides, under slow heating rate conditions. The additives were derived from the literature review and were added with a mass fraction of 1%. Simultaneous calorimetric and thermogravimetric traces have been recorded and analyzed. The interpretation of the results was mainly based on thermogravimetric traces, on which an index of reactivity was derived. The DTA signals were used to clarify some behaviors.

2.1 Materials

Ammonium nitrate A non stabilized ammonium nitrate has been supplied by Yara (Lot 14962-1-2). The particle size distribution, measured using laser diffraction and dry dispersion, is reported in Fig. 1. The powder is quite coarse and shows a monomodal feature, with span of 1.18 and a D_{43} of 384 μm .

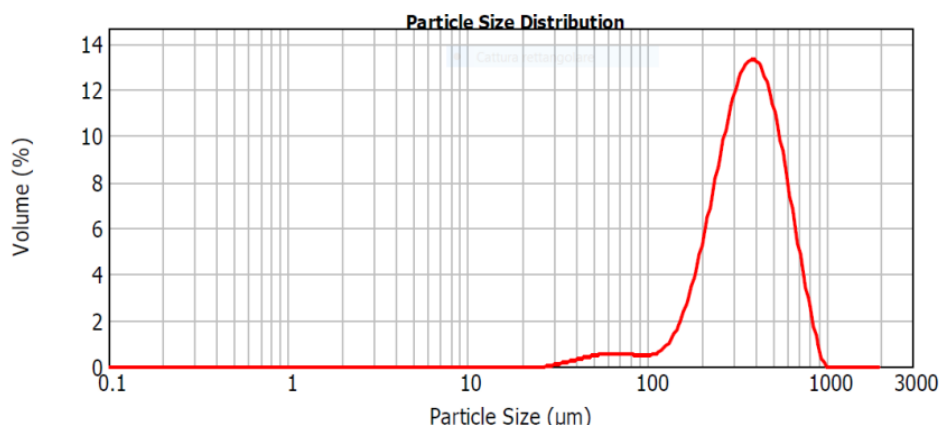


Figure 1: Ammonium nitrate: particle size distribution

Additives The oxide additives were selected following a criterion of low toxicity level to human beings (main criterion) and reduced environmental risk (second-level criterion). The list of the materials is reported in Table 1, including the relevant labels from the Globally Harmonized System of Classification and Labeling of Chemicals (GHS).²⁰ Table 2 reports the information on batch, purity, nominal size, and supplier.

Additive	Hazard types		
	Physical	Health	Environmental
Fe ₂ O ₃	None	None	None
Fe ₃ O ₄	H225	H304-H315-H336-H361d-H373	H411
MoVO	n.a.	n.a.	n.a.
Cu ₂ O	None	H302-H319-H332	H410
Cr ₂ O ₃	None	None	None
MnO	None	None	None
ZnO	None	None	H410

Table 1: Toxicity levels of the selected additives with GHS classification: physical, human and environment hazard.

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Additive (Purity%)	Supplier (Lot no.)	Melting temperature °C	Δh_f^0 kJ mol ⁻¹	Nominal Size µm
Fe_2O_3 (n.a.)	Propulsion-grade ¹	1565	-825.50	0.3
Nanocat (n.a.) ²	Mach I (n.a.)	1565	-825.50	0.005
Fe_3O_4 (>98)	Sigma Aldrich (MKBK2270V)	1538	-1118.4	<0.05
$Fe_2O_3 \cdot H_2O$ (98)	Strem Chemicals (250793-S)	>1000	-	<0.05
MoVO ($V_6Mo_{15}O_{60}$) (n.a.)	ICT (n.a.)	n.a.	n.a.	n.a.
MnO_2 (90+)	Sigma Aldrich (03502EB)	535	-520.00	< 10
Cu_2O (97)	Sigma Aldrich (MKBJ5694V)	1336	-168.60	< 5
Cr_2O_3 (99)	Alfa Aesar (D26Z027)	2435	-1139.7	n.a.
ZnO (>99)	Sigma Aldrich (BCBF0714V)	1975	-348.0	n.a.

Table 2: Additives characteristics

2.2 Methodology

The samples have been homogenized by mechanical mixing at low intensity, ensuring the absence of oxidizer particle fragmentation. Reactivity tests have been conducted on a TG/DTA apparatus STA 449 F5 Jupiter by *Netzsch*. Sample mass was fixed to 15 mg and purging gas was Argon flowing at 70 mL min⁻¹. At least two runs have been executed per sample to verify the repeatability. The heating rate was fixed to 10 K min⁻¹.

Two reactivity parameters have been selected: the onset of the dissociation and the parameter R_d , derived from the TG trace and mapping how rapid is the reaction.

$$R_d = \frac{m_{final} - m_{initial}}{TG_{off} - TG_{on}} \quad \text{mg } ^\circ\text{C}^{-1} \quad (3)$$

3. Results and discussion

3.1 Iron Oxides

Four different iron oxides additives have been tested, as the literature did not always agree on the role of this ingredient. The behavior of the mixes were compared with the raw AN Yara under the same heating process. The identification codes of the runs are:

- Id 25 - Fe_2O_3 Propulsion grade powder;
- Id 26 - Fe_2O_3 Nanocat Mach I;
- Id 27 - Fe_2O_3 Mono-hydrate;
- Id 29 - Fe_3O_4 .

Sample id	TG_{on} , °C I-II (Mean)	TG_{off} , °C I-II (Mean)	R_d , mg °C ⁻¹ I-II (Mean)
AN-Yara	262.2-260.1 (261.1)	308.6-305.7 (307.1)	0.3424-0.3228 (0.3326)
id 25	259.9-258.3 (259.1)	304.9-304.9 (304.9)	0.3287-0.3212 (0.3249)
id 26	261.3-258.3 (259.8)	295.5-295.3 (295.4)	0.4386-0.4143 (0.4264)
id 27	253.9-261.7 (257.8)	304.3-304.1 (304.2)	0.2958-0.3533 (0.3245)
id 29	266.7-267.9 (267.3)	302.7-303.2 (302.9)	0.4230-0.4224 (0.4227)

Table 3: TG onsets, offsets and rates of decomposition of tested iron oxides.

¹Supplier not disclosed²Nanocat is assumed to be Fe_2O_3 only

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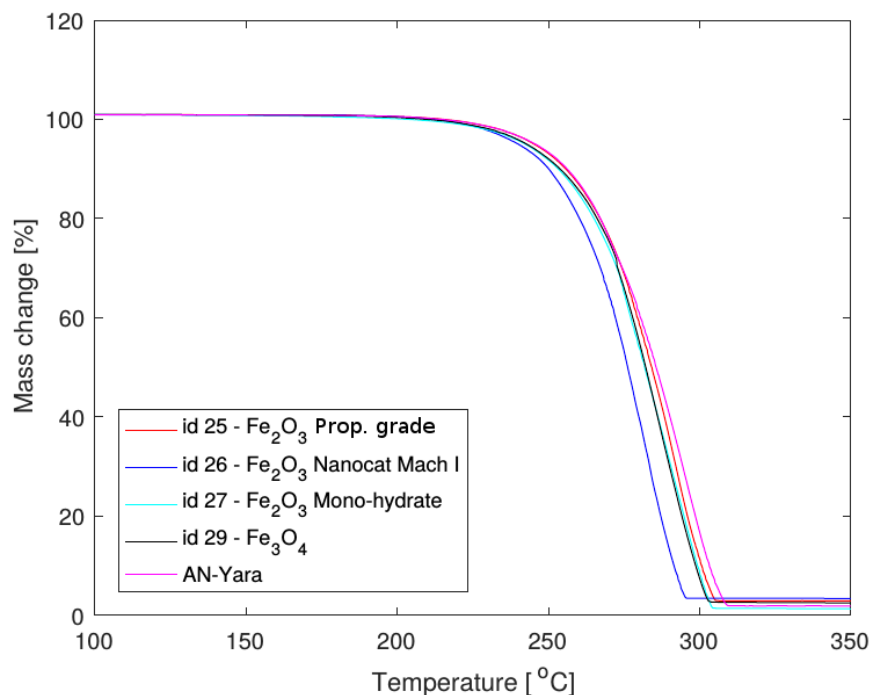


Figure 2: TG traces of tested iron oxides.

Nanocat Mach I and propulsion-grade Fe_2O_3 are the most effective in promoting the decomposition, suggested by an onset anticipation at 259.8°C and 259.1°C respectively. Possible effects are present for the Mono-hydrate form, having the mean onset at 257.8°C . A marked onset delay is observed in the case of Fe_3O_4 , for which the onset is set at 267.3°C .

All of the iron oxides have a positive effect on the offset, with most of them going from 305.0°C down to 303.1°C . The most interesting is anyway the Nanocat Mach I, for which the offset is at 295.4°C , having an anticipation of 11.7°C with respect to the raw AN. A possible explanation for this strong effectiveness may be the small particle size of the additive, since the catalytic effect should be enhanced by the high specific surface.

The decomposition rates are then evaluated for every samples; the analysis of these parameters show that also in decomposing the gaseous product the Nanocat is the best of all the iron oxides; the high reactivity of the Fe_3O_4 is probably due to the fact that is a combination of FeO and Fe_2O_3 that reacts and recombines, thus forming very small molecules, enlarging the specific surface, with the advantage explained for the Nanocat.

For all the samples the residual mass is more or less 2%, in agreement with the 1% additive loaded, suggesting that those additives are acting as a catalyst, since they have not been decomposed. The trend of the DTA curve is more or less the same for all the tested iron oxides, with an horizontal part probably due to some minor endothermic reactions. Different results arises when Nanocat is considered since it avoids the flat part of the curve; a stronger exothermic reaction may be the cause of this different trend and also of the violent descent.

3.2 Other Oxides

Other oxides have been mechanically mixed and tested. The reference identification code is:

- Id 28 - MoVO ;
- Id 32 - MnO ;
- Id 35 - Cu_2O ;
- Id 37 - Cr_2O_3 ;
- Id 51 - ZnO .

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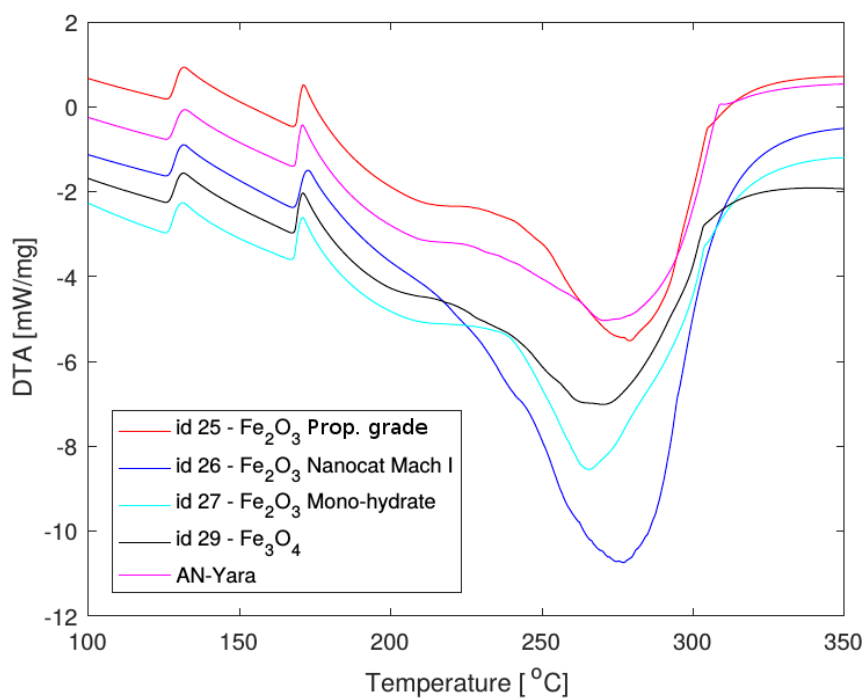


Figure 3: DTA traces of tested iron oxides.

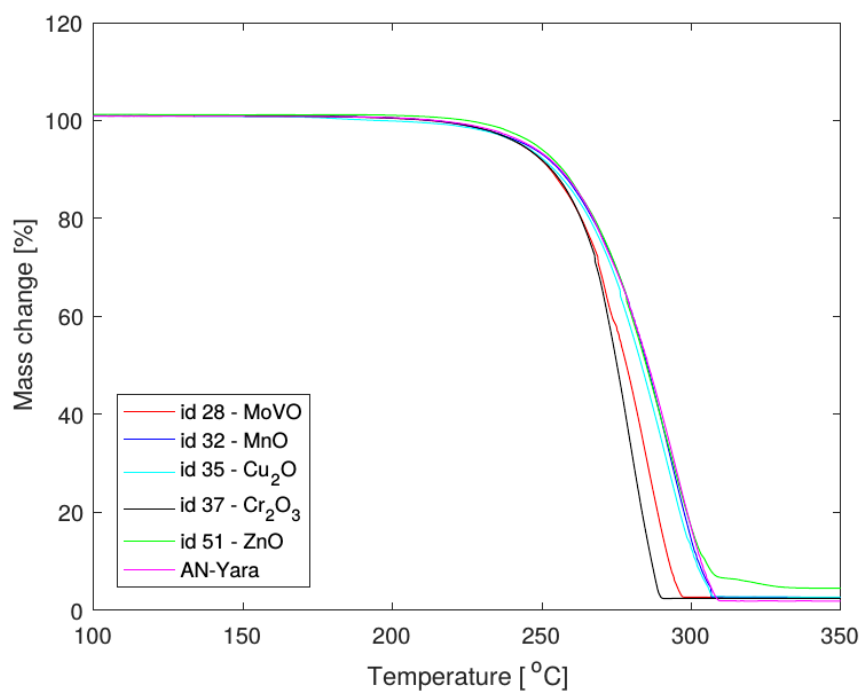


Figure 4: TG traces of tested oxides.

CATALYST SCREENING FOR AMMONIUM NITRATE OXIDIZER

Sample id	TG_{on} , °C I-II (Mean)	TG_{off} , °C I-II (Mean)	R_d , mg °C ⁻¹ I-II (Mean)
AN-Yara	262.2-260.1 (261.1)	308.6-305.7 (307.1)	0.3424-0.3228 (0.3326)
id 28	262.8-262.8 (262.8)	295.3-295.4 (295.3)	0.4581-0.4587 (0.4584)
id 32	261.1-270.1 (265.6)	306.7-305.9 (306.3)	0.3318-0.4170 (0.3744)
id 35	269.8-269.5 (269.6)	306.8-305.5 (306.1)	0.4038-0.4128 (0.4083)
id 37	263.5-263.3 (263.4)	289.4-287.6 (288.5)	0.5791-0.6185 (0.5988)
id 51	270.2-271.2 (270.7)	308.0-307.8 (307.9)	0.3878-0.3907 (0.3892)

Table 4: TG onsets, offsets and rates of decomposition of tested oxides.

The TG trace shows a delay of the starting of the decomposition for all the oxides; in particular MoVO and chromium have a small effect while manganese, copper and in particular zinc oxides strongly delay it. Considering the offset, small effects are produced by copper oxide and manganese one. Significant effect is produced by MoVO which has the offset at 295.3 °C while for sure the strongest one is obtained by Cr_2O_3 , anticipating it at 287.6 °C. The worst effect is produced by zinc oxide, delaying the end of the decomposition with respect to the reference. The decomposition rates are then evaluated for every sample, showing that MoVO and Cr_2O_3 are the most effective in decomposing the gaseous phase. Also in this case the residual mass is more or less 2% showing that the oxides have not been decomposed.

4. Final remarks

The results obtained so far demonstrate that iron oxide can have an important role in the decomposition of the ammonium nitrate. This is in contrast with some information found in the literature. The effect seems to be sensitive to the size of the ingredient, as Nanocat performed best among the tested materials (onset anticipation and increment of dissociation rate). From the analysis of the other oxides no one produced an anticipation of the starting onset. On the contrary some marked delays have been obtained with zinc, copper and manganese oxides. If the rate of decomposition is considered, the MoVO is a good candidate along with the chromium oxide. It should be noted that, in some cases, the scattering of the experimental data required more than two tests for reproducibility. The test-to-test variability was ascribed to the mechanical mixing. Even though the procedure was carefully optimized, the difference of particle size among the additives and between additive and oxidizer sometimes impaired uniform dispersion. As a matter of fact, the tested materials did not deliver an effectively rapid decomposition. The thermogravimetric curves showed an improved decrement rate but the variation was smooth. Also the DTA traces did not show rapid exothermic releases. It is very likely that the additives tested in this paper accelerate the sole dissociative sublimation due to proton transfer, represented by Eq. 2. Decomposition events are not evident, even though some clues of feeble heat release in the test crucible is recorded. The test of the components demonstrated the possibility to enhance the dissociation rate of ammonium nitrate using environmentally friendly additives, even though large effects are not attained. In the future tests will be carried on by incrementing the amount of the catalyst level and by carrying experiments on relevant propellants.

5. Acknowledgment

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