The influence of Mn, Co and Cu cations on the thermal decomposition of NH_4NO_3 in pure form and supported on alumina

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Abstract

The decomposition of ammonium nitrate has been studied thermogravimetrically in mixtures with varying amounts of metal cations M (where M is Mn, Co, Cu). The ratios studied were $NH_4NO_3:M = 30000:1$, 15000:1, 5000:1, 1500:1, 150:1, 25:1 and 10:1 in order to identify the threshold limits for the inversion from an endothermic to an exothermic decomposition. This transition takes place at $NH_4NO_3:M \approx 150:1$. Similar mixtures containing Al in ratios $NH_4NO_3:Al:M = 15000:5.1$, 500:165:1, 300:100:1, 150:50:1, 15:5:1 and 8:2:1 were also studied by DTA/DTG with respect to their thermochemical behaviour and the influence of the mode of decomposition on the final specific surface area (ssa, $m^2 g^{-1}$) of the remaining product. This was related to the fluctuation of temperature observed during the endo- and/or exothermic decomposition which reflects the mode of decomposition. Some mathematical expressions are derived expressing the relation between the produced ssa and the thermal fluctuation ΔT observed in the studied samples.

INTRODUCTION

Ammonium nitrate has attracted the attention of workers in different disciplines for a variety of reasons. Firstly, the intrinsic phase transitions of this solid [1] have been studied in the field of solid state physics in order to examine the details of such transformations [2–4]. Secondly, ammonium nitrate is a common fertilizer, often showing the unwanted phenomenon of agglomeration. It is believed that the phase transitions of the solid that take place near ambient temperatures (20–30°C) contribute to this. Therefore, researchers in fertilizer technology are very interested in methods which may help to prevent such phenomena [5–7]. Thirdly, ammonium nitrate is an explosive compound and because as noted above, it is produced in very large quantities, the conditions under which such disastrous effects can take place should be carefully scrutinized and scrupulously avoided [8–14]. There is a fourth area of interest which is indirectly related to the stability

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and the routes of decomposition of NH_4NO_3, namely the preparation of different metallic or oxidic catalysts [15]. In the normal preparation of catalytic solids, the nitrate salts of the chosen metals are dissolved in water and a mixture of metal hydroxides is then precipitated by the addition of ammonia. The gel thus obtained is then dried and fired at temperatures high enough to decompose the nitrates, including the ammonium salt, in order to obtain the mixture of oxides desired, which may or may not be subsequently reduced to the metals. But such a procedure, and especially the decompositon during the firing stage, can be drastically influenced by the nature of the cations in the mixture, which may alter not only the route of decomposition but also the final products.

In a recent work [16] describing the preparation of Al_2O_3/P_2O_5, $Al_2O_3/Cr_2O_3/P_2O_5$ and $Al_2O_3/Fe_2O_3/P_2/O_5$ catalysts by the nitrate route, it was observed by DTA/DTG that in the first and third catalysts, the NH_4NO_3 in the mixture decomposes via an endothermic route, while in the second case it decomposes exothermically. Furthermore for kinetic reasons, which are probably related to the readiness of Cr^{3+} to eliminate NH_4NO_3, Cr_2O_3 remains as an isolated phase in the final solid, a situation which is not observed with Fe^{3+}. In the past, the catalytic action of a number of different cations on the decomposition of NH_4NO_3 has been examined in detail [17–22]. Among the transition metals, chromium compounds are outstanding in their catalytic power for NH_4NO_3 decomposition. In a previous work [23], the threshold limit of Cr^{3+} ions, which reverses the endothermic decomposition to an explosive exothermic one, was determined to be Cr^{3+}: $NH_4NO_3 = 1:3000$. Furthermore it was shown [24] that the exothermic action of the cations is related to the electrochemical free energy $\Delta G = nFE^0$ of the process (metal cation oxidized)/(metal cation reduced). It also appeared that the presence or absence of an explosion has some influence on the specific surface area of the solids obtained [24]. For the above reasons we decided to study thermogravimetrically the threshold limits of the transition from endothermic to exothermic decomposition of NH_4NO_3 under the influence of increasing amounts of the cations Mn^{3+}, Co^{2+} and Cu^{2+}. The study, apart from the mixture of NH_4NO_3 with cations, also contains results for the action of the above cations in mixtures with Al^{3+} on the decomposition of NH_4NO_3. The cation Al^{3+} is inactive as a catalyst but it modifies the activity of the transition metals by inhibiting explosion. For the samples of mixtures of transition metal with Al^{3+}, we also became interested in the possible relationship between the mode of decomposition of the substrate and the final specific surface area of the remaining solids.

EXPERIMENTAL AND RESULTS

The samples used in the thermogravimetric experiments are listed in Table 1 and were prepared as follows. The calculated quantities of metal

TABLE 1

Composition of the samples prepared, their designation, the areas of the endothermic decomposition peak and the specific surface areas of the solids

Sample composition	Designation	Area of endo peak (mV K mg^{-1})			ssa (m^2 g^{-1})			Δ(exo − endo) (mV)		
		Mn	Co	Cu	Mn	Co	Cu	Mn	Co	Cu
NH$_4$NO$_3$ Pure	AN									
NH$_4$NO$_3$:M										
30000:1	M-1	7.57	5.81	4.27						
15000:1	M-2	7.91	6.90	4.79						
5000:1	M-3	8.68	5.61	5.19						
1500:1	M-4	6.92	5.06	5.03						
150:1	M-5	6.80	5.28	6.19						
25:1	M-6	3.49	2.65	2.53						
10:1	M-7	−3.65	−13.41	−4.32						
NH$_4$NO$_3$:Al:M										
15000:5000:1	AlM-1	1.99	3.24	4.72	248	234	265	9.4	9.8	15.7
500:165:1	AlM-2	3.11	1.50	5.59	273	288	286	7.5	12.7	19.6
300:100:1	AlM-3	2.96	5.36	5.29	277	243	266	12.4	17.2	16.7
150:50:1	AlM-4	3.77	1.24	4.96	271	309	221	29.6	17.6	17.7
15:5:1	AlM-5	1.92	1.88	2.53	238	242	173	39.2	49.0	43.3
8:2:1	AlM-6	−4.12	−4.01	−3.77	207	225	179	60.4	78.4	94.5

nitrates (Merk, p.a.) and NH$_4$NO$_3$ (Ferak p.a.) were dissolved in 100 ml of distilled water; 1 M ammonia (Ferak p.a.) solution was added dropwise up to pH 9.5 ± 0.1 with continuous stirring. The gel thus obtained was dried at 105°C for 24 h and the resulting solid was ground in an agate mortar. The amount of NH$_4$NO$_3$ in these samples was considered to be equal to that resulting from the nitrate anions added initially, the excess of ammonia being evaporated during drying.

The thermal analysis of the obtained solids took place in a Chyo-TRDA-3H thermal balance under non-isothermal conditions. Simultaneous recording of temperature (T), thermal gravimetry (TG), differential thermal gravimetry (DTG) and differential thermal analysis (DTA) took place. All the analyses were carried out with α-Al$_2$O$_3$ as a blank at a heating rate of 2 K min^{-1} under an air flow of 15 l h^{-1}. The resulting DTA curves are shown in Fig. 1 for the systems NH$_4$NO$_3$:M as well as for the systems NH$_4$NO$_3$:Al:M (where M is Mn, Co, Cu).

We have measured the surface area of the exothermic peak from the DTA curves in Fig. 1. Then, from the heating rate (2 K min^{-1}), the DTA sensitivity of the thermobalance (mV) and the mass of the sample used (g), we can easily express the result in (mV K mg^{-1}). These results are given in Table 1. The table also gives the specific surface areas of the samples AlM-n (where M is Mn, Co, Cu) after heating for 3 h at 673 K. This last parameter
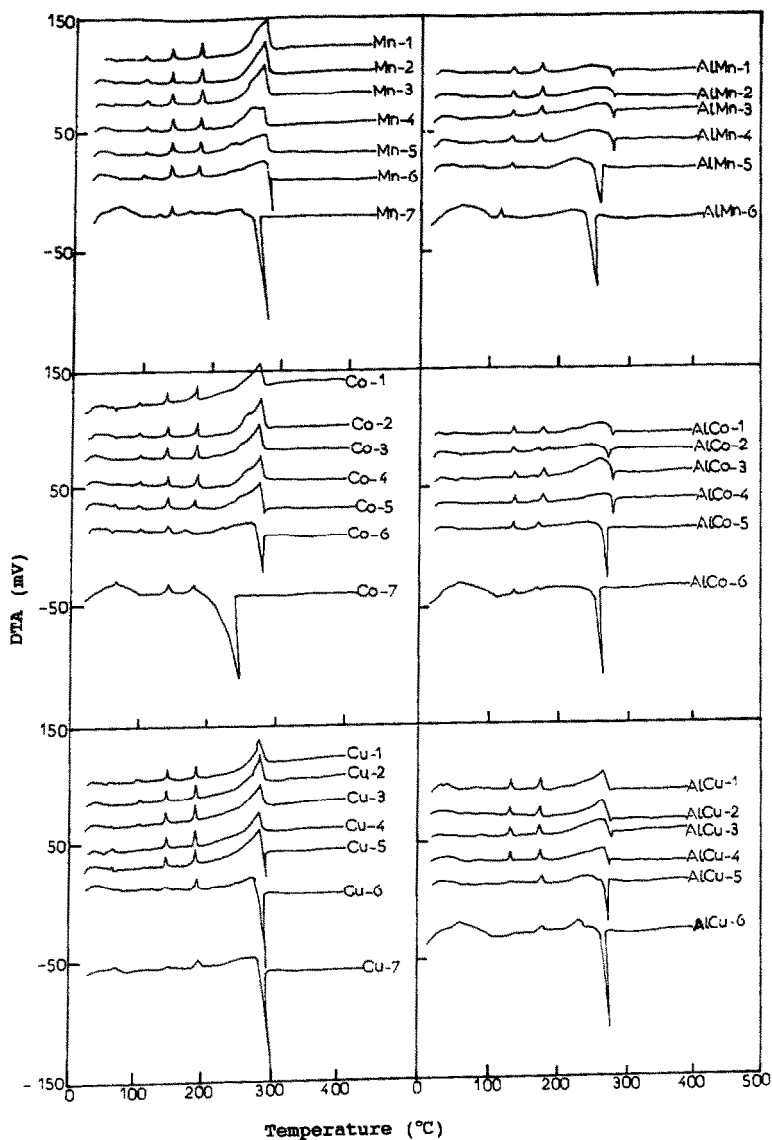
Fig. 1. DTA curves for the specimens M-*n* and AlM-*n* (where M is Mn, Co, Cu) of Table 1.

was checked in a Carlo Erba Sorpty 1750 single-point apparatus with N_2 adsorption at $T = 77$ K.

DISCUSSION

As can be seen from Fig. 1, the addition of cations of transition metals Mn, Co or Cu to NH_4NO_3 results in an inversion of the endothermic decomposition (samples M-*n* with $n > 4$) to an exothermic decomposition.
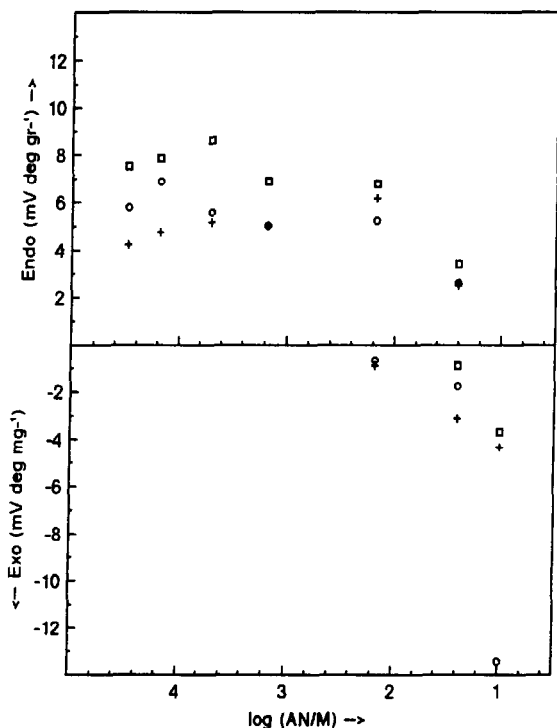
Fig. 2. Plots of the areas of the exothermic and endothermic DTA peaks, calculated as mV K g^{-1}, versus the logarithm of the ratio (ammonium nitrate/metal) log(AN/M): ($\square$), Mn; ($\bigcirc$), Co; (+), Cu.

This inversion of the thermal effect is gradual with increasing amounts of cations and the turning point seems to be around sample M-5 where $NH_4NO_3:M = 150:1$. Some small differences are apparent for the three cations. Thus, for example, copper produces a more sharp exothermic decomposition; this is also true in the case of manganese. However, cobalt produces a less violent decomposition, although it occurs at lower temperatures than with Mn and Cu. The transition point from the endo- to the exothermic decomposition is depicted in Fig. 2. In this figure the area of the endo- or exothermic peak, expressed in mV K mg^{-1}, has been drawn as a function of log(moles NH_4NO_3/moles M^{n+}). Although some scattering of the data is apparent, it can be seen that a decrease in the endothermic peaks is apparent after sample $n = 4$ ($NH_4NO_3:M = 1500:1$). From sample $n = 5$ ($NH_4NO_3:M = 150:1$), the exo-effect starts to become apparent. In the sample $n = 6$ ($NH_4NO_3:M = 25:1$), the endo-effects cease to be apparent while they become stronger and are the only ones present at sample $n = 7$ ($NH_4NO_3:M = 10:1$).

The situation with the samples AlM-n (where M is Mn, Co, Cu, $n = 1, 2, 3, 4, 5, 6$) shows some similarities and differences as compared to
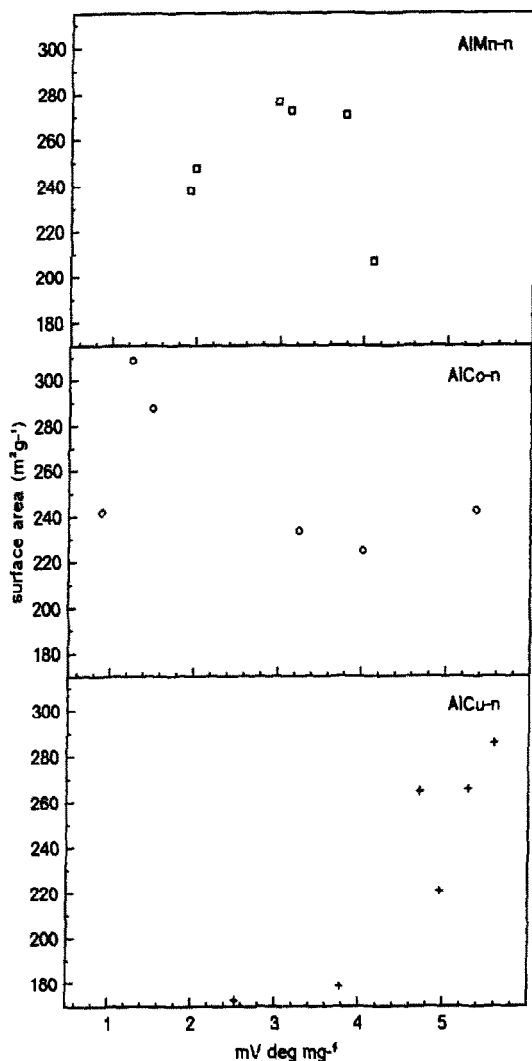
Fig. 3. Evolution of the specific area of the residue of samples AlM-n (where M is Mn, Co, Cu) as a function of the intensity of the endothermic peak calculated in mV K mg^{-1}.

the samples without Al (Fig. 1). A first point is that the introduction of Al in the ratio NH_4NO_3:Al = 3:1 diminishes the endothermic decomposition of ammonium nitrate, producing a rather thermally neutral decomposition. But the next increment of the transition metal cations results in a exothermic decomposition.

An attempt to correlate the area of the endo- or exothermic peak relative to the AlM-n samples, with the specific surface area being determined by the BET one-point method (Table 1), is unsuccessful: as shown in Fig. 3 no correlation is apparent between the endothermicity of the decomposition and the surface area produced in the final product. Nevertheless a
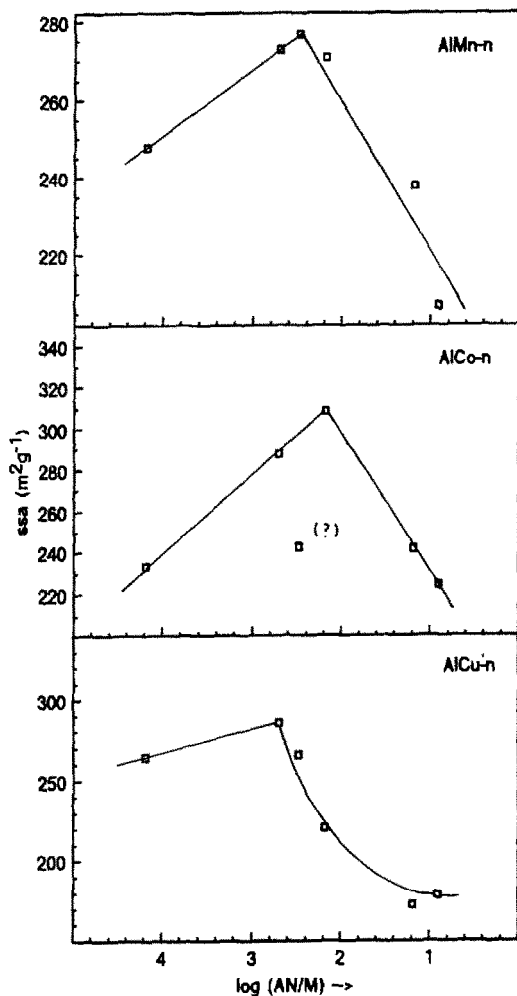
Fig. 4. Relationship between the specific surface areas of the samples AlM-n versus the logarithm of the ratio (ammonium nitrate/metal), log(AN/M).

meaningful relationship is produced if we draw the specific surface area of the solids as a function of the logarithm of the ratio (moles NH_4NO_3/moles M) as shown in Fig. 4. From this figure we observe generally that as the ratio (NH_4NO_3:M) decreases, the ssa initially increases and thereafter drops. Nevertheless the behaviour of each system is different. Thus for AlM-n, the ssa increases almost linearly from sample $n = 1$ up to $n = 3$ and thereafter drops up to sample $n = 6$, also linearly. The behaviour of AlCo-n solids is rather similar with the maximum ssa appearing at $n = 4$ while sample $n = 3$ shows an ssa abnormally low and out of trend. Samples AlCu-n show an increment of ssa from $n = 1$ to $n = 2$ and a drop thereafter up to $n = 5$, while sample AlCu-6 shows a stabilization of ssa.

CONCLUSIONS

In searching of a factor, or a group of factors, which might be critical in controlling the ssa, after a detailed examination of the results and several trials and correlations, the following conclusions could be made.

(i) The ssa appears low when there is a strong exothermic peak during decomposition of the precursor.

(ii) The above condition does not explain all the cases where a low ssa appears. Thus, for example, sample AlCo-3 shows low ssa but the precursor decomposed endothermically. But in that case the endo-peak was more intense, as judged by its height, as compared to the neighbouring samples AlCo-2 and AlCo-4.

(iii) Thus a critical factor in the final ssa produced seems to be the violence of the explosion (mV), which actually reflects the total temperature increment in the sample examined. In Fig. 5 we have plotted the logarithm of the specific surface areas of the samples AlM-n (where M is Mn, Co, Cu) versus the total difference in millivolts between the maxima points of the endothermic and exothermic peaks. The correlation observed is indeed persuasive. It is clear that the higher the values of $\Delta(mV)$ the smaller the ssa produced. It is known that the precursor NH_4NO_3 can be decomposed either endothermically or exothermically

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \qquad \Delta H = -176 \text{ kJ mol}^{-1} \qquad (1)$$

$$NH_4NO_3 \rightarrow N_2 + 2H_2O + 0.5O_2 \qquad \Delta H = -120 \text{ kJ mol}^{-1} \qquad (2)$$

It seems, therefore, that if either of these decompositions proceeds quickly, the result is a destruction of the fine porosity of the remaining solid and, as a result, the ssa appears low. In contrast, if the elimination of NH_4NO_3 takes place smoothly then the porosity of the solids remains intact and this results in higher surface areas. In such cases the rate of heating should be of paramount importance for the final result.

Although a detailed mathematical description of the results cited in Fig. 5 requires further accumulation and scrutinization of data, it seems that, depending on the cation, the relationship between ssa and $\Delta(mV)$ is either linear, as in the case of the AlMn-n and AlCo-n samples, or parabolic, as in the case of the AlCu-n solids. In the first case we have

$$\log(\text{ssa}) = a - b(\Delta(mV)) \qquad (3)$$

which for AlMn-n becomes

$$\log(\text{ssa}) = 2.451 - 0.00194(\Delta(mV))$$

with a correlation coefficient $r = 0.844$ which is better than the 99% significance level.
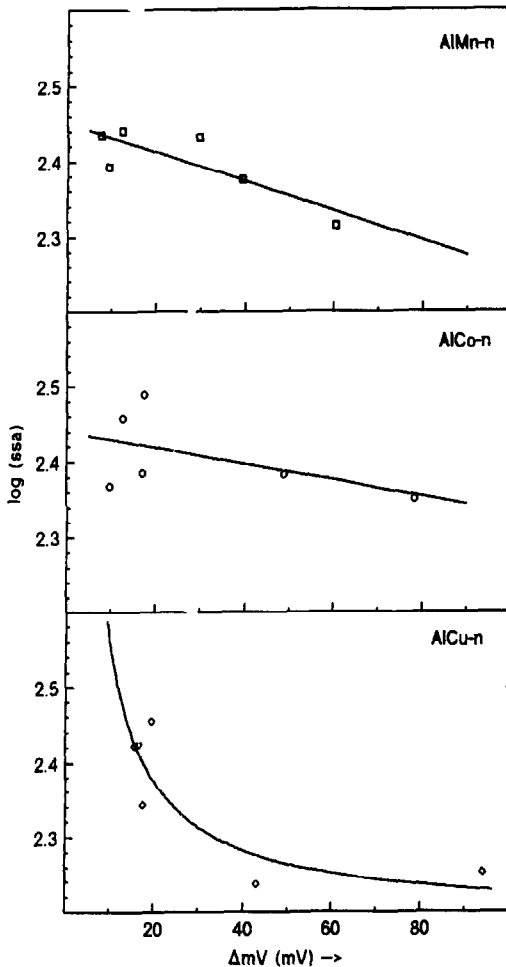
Fig. 5. Plots of the logarithm of the specific surface areas of the samples AlM-*n* versus the total difference in millivolts between the maxima points of the endothermic and exothermic peaks.

For AlCo-*n* eqn. (3) becomes

$$\log(\text{ssa}) = 2.440 - 0.00107(\Delta(\text{mV}))$$

with a correlation coefficient $r = 0.907$ which is better than the 99% significance level. In the case of AlCu-*n* the relationship observed is

$$\log(\text{ssa}) = 3.710/(\Delta(\text{mV})) + 2.19 \tag{4}$$

with a correlation coefficient $r = 0.860$ which is better than the 99% significance level. Because the mV values actually reflect a change in the temperature then $\Delta(\text{mV}) \propto \Delta T$ and relationships (3) and (4) can be written

respectively in the forms

$$ssa = A/10^{b(\Delta T)} = A10^{-b(\Delta T)} \tag{5}$$

where $A = 10^a$ and

$$ssa = -10^{c(\Delta T)} \tag{6}$$

These relationships actually express the degree of sintering of the surface and are of a form similar to the relationships expressing the sintering of metallic particles as a function of time at fixed temperature [25]. Nevertheless, a detailed formal mathematical description of the problem requires the accumulation of further and more extensive data.

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