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Effect of the first row transition metal cations on the mode of decomposition of ammonium nitrate supported on alumina–aluminum phosphate and the final products obtained

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Abstract

The mode of decomposition of ammonium nitrate in mixtures with 80% Al_2O_3 and 20% of first row transition metal oxides MOx (M = Mn, Cr, Fe, Co, Ni, Cu, Zn) and containing different amounts of phosphorus (Al:M:P = 100:20:18 and 100:20:144) has been examined under non-isothermal conditions in a thermogravimetric balance. Pure ammonium nitrate is decomposed endothermically while addition of Al_2O_3 shows a stabilizing action of this endo effect. Substitution of 20% of aluminum by a first row transition metal (M = Mn, Cr, Fe, Co, Ni, Cu and Zn) shows that zinc does not alter the route of decomposition while the rest show a tendency to decompose ammonium nitrate exothermically. The catalytic action of the cations toward such an exothermic route is Fe = Ni < Cu < Mn < Co < Cr, the last cations driving the decomposition to explosion. Addition of phosphorus to ratios P/(Al + M) = 0.15 (Al:M:P = 100:20:18) and 1.2 (Al:M:P = 100:20:144) leads to a gradual inhibition of the catalytic action of the transition metal cations towards exothermic explosion. The reasons controlling the catalytic action of the cations for the explosive decomposition of NH_4NO_3 are primarily related to electrochemical Gibbs free energy $\Delta G = -nFE$ of the process $M_{oxidized}/M_{reduced}$. On top of this the crystal field stabilization effect for each particular cation should be taken into account. The extent of exothermic decomposition of the ammonium nitrate seems to influence the specific surface area of the final product in a positive manner in the absence of phosphorus but in a negative manner in its presence. The reasons underlying this effect should be attributed to the stabilizing action of phosphorus on the decomposition route.

INTRODUCTION

Ammonium nitrate is a common fertilizer and a highly explosive compound. This combination of extensive use and dangerous properties has attracted the interest of many workers in the field [1–15] examining the potential instability of this material under thermal treatment.

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Apart from the temperature another factor which may facilicate such explosive reactions is the catalysts. In our case such catalysts are the chloride cations [16–18] and the transition elements [19–21]. Among the last group it has been recognized that the best catalyst is chromium cations, their action being due to the formation of bichromates [21,22] which suffer continuous cycles of the type bichromates–chromates–bichromates and so on until all the nitrate groups have been decomposed.

A particular point is that unstable systems is the admixture with chemical compounds which can act as stabilizers, or modifiers, to the action of the catalysts. Alumina is among such species, decreasing the threshold limits for explosive action of chromium from 1:3000 in pure mixtures of $Cr:NH_4NO_3$ [23] to 1:200:600 in mixture of $Cr:Al:NH_4NO_3$ [24]. Another element which also acts as an inhibitor to such an explosive action is phosphorus [25]. In that work the inhibiting action of phosphorus was studied in mixtures of $Al_2O_3:Cr_2O_3:P_2O_5$ and $Al_2O_3:Fe_2O_3:P_2O_5$ which in that case were prepared for use as heterogeneous catalysts. In this paper we study the mode of decomposition of ammonium nitrate supported on alumina by addition of 20% of the first row transition metal oxides MOx where M = Mn, Co, Ni, Cu and Zn. In the above systems we shall examine the stabilizing action of phosphorus added in amounts $P/(Al + M) = 0.15$ and 1.2 and the effect of the mode of decomposition on the specific surface areas of the final products.

EXPERIMENTAL

The specimens used in the experiments (Table 1) contained the elements Al:M:P in ratios 100:20:X, where X = 0, 18 and 144, and were prepared

TABLE 1

Compositions of the samples prepared, their designations and their specific surface areas (ssa)

Sample composition	Designation	ssa ($m^2\ g^{-1}$)	Sample composition	designation	ssa ($m^2\ g^{-1}$)
$Al_0M_0P_0$ (AN)	AN [a]				
$Al_{100}Al_{20}P_0$ (AN)	Al-1	254	$Al_{100}Ni_{20}P_0$ (AN)	Ni-1	252
$Al_{100}Al_{20}P_{18}$ (AN)	Al-2	443	$Al_{100}Ni_{20}P_{18}$ (AN)	Ni-2	308
$Al_{100}Al_{20}P_{144}$ (AN)	Al-3	71	$Al_{100}Ni_{20}P_{144}$ (AN)	Ni-3	7.5
$Al_{100}Mn_{20}P_0$ (AN)	Mn-1	228	$Al_{100}Cu_{20}P_0$ (AN)	Cu-1	201
$Al_{100}Mn_{20}P_{18}$ (AN)	Mn-2	278	$Al_{100}Cu_{20}P_{18}$ (AN)	Cu-2	254
$Al_{100}Mn_{20}P_{144}$ (AN)	Mn-3	4	$Al_{100}Cu_{20}P_{144}$ (AN)	Cu-3	7
$Al_{100}Co_{20}P_0$ (AN)	Co-1	186	$Al_{100}Zn_{20}P_0$ (AN)	Zn-1	152
$Al_{100}Co_{20}P_{18}$ (AN)	Co-2	351	$Al_{100}Zn_{20}P_{18}$ (AN)	Zn-2	311
$Al_{100}Co_{20}P_{144}$ (AN)	Co-3	6	$Al_{100}Zn_{20}P_{144}$ (AN)	Zn-3	3

[a] Ammonium nitrate.

as follows. The calculated amounts of metal nitrates (Merck p.a.) and phosphoric acid (Ferakl p.a.) were dissolved in 100 ml distilled water and 1 M NH_3 (Ferak) solution was added dropwise to pH 9.5 with continuous stirring. The gel thus obtained was dried at 105 ° C for 24 h and the resulting solids ground in an agate mortar. The amount of NH_4NO_3 in the samples was considered to be equal to the nitrate cations added initially, the excess of ammonia, except the amount needed to neutralize the H_3PO_4, being evaporated during drying.

Those samples will be designated in the next as M-1, M-2 or M-3 where M = Mn, Co, Ni, Cu and Zn and the numbers correspond respectively to no amount of phosphorus, 18 atoms of phosphorus and 144 atoms of phosphorus added.

The specific surface area (s.s.a.) of the final solids, obtained after heating the initial samples at 600 ° C for 6 h, was determined using the multipoint B.E.T. method. Nitrogen adsorption took place at 77 K from N_2–He mixtures in a continuous flow Nelsen Eggerten apparatus connected with a Gow-Mac 150 gas chromatograph. The results are summarized in Table 1. The estimated level of error was $< 2\%$ in the high surface area samples with a tendency to increase with decreasing surface area.

The thermal analysis of the initially prepared samples took place in a Chyo-TRDA-3H thermal balance with simultaneous recording of temperature (T), thermogravimetry (TG), differential thermogravimetry (DTG) and differential thermal analysis (DTA) data. In all the analyses α-Al_2O_3 was used as a blank and took place at a heating rate of $1\,°C\,min^{-1}$ between 20 and 700 ° C with a nitrogen flow of $15\,l\,h^{-1}$. The amount of samples used in each analysis was 100 ± 1 mg.

RESULTS

Figure 1 illustrates the DTA curves for all the samples included in Table 1. As can be seen pure NH_4NO_3 (AN) is decomposed endothermically. The decomposition starts immediately after a strong endo peak due to its melting at about 176 ° C and is completed abruptly at 253 ° C where all AN has been exhausted. Addition of aluminum cations (sample Al-1) acts to inhibit this decomposition lowering its pace. Introduction of phosphorus into the system (samples Al-2 and 3) further inhibits the decomposition of AN, especially in the case of the Al-3 sample in which the melting point peak nearly disappears.

Substitution of 20% of aluminum by manganese (sample Mn-1) changes the endothermic decomposition to an exothermic one. It should be noted that this exothermic decomposition appears as a double peak, with maxima at 232 and 237 ° C instead of the 253 ° C of pure AN or 245 ° C of the Al-1 sample. This double peak might be due to the different oxidation states of manganese which can act as catalyst of different activity for the AN

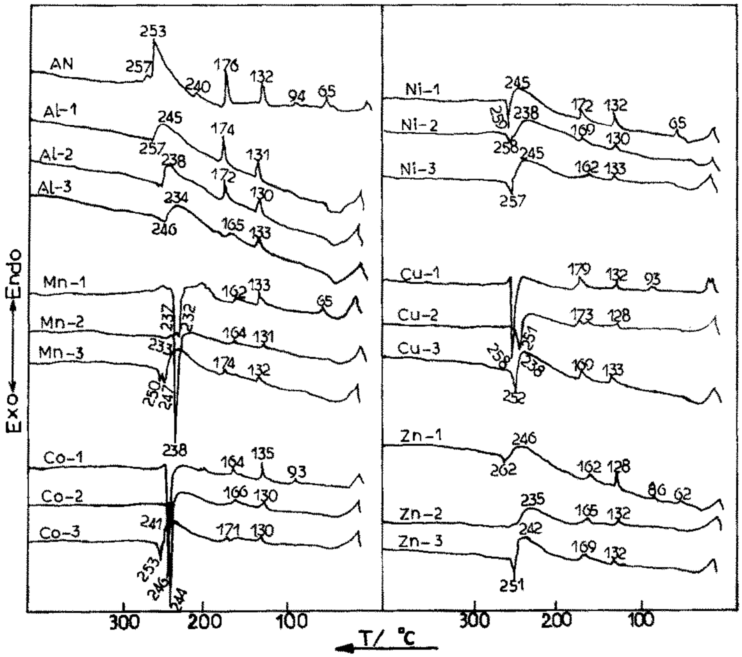

Fig. 1. DTA curves for the specimens of Table 1.

decomposition. Addition of phosphorus (sample Mn-2) in a ratio P/(Al + Mn) of 0.15 results in a very strong exothermic decomposition with a maximum at 238 ° C, i.e. near the upper temperature peak of sample Mn-1. Further addition of phosphorus to a P/(Al + Mn) ratio of 1.2 results in a supression of the exothermic decomposition and the system behaves similarly to the Al-1 sample with an initial smooth endo peak at 247–250 ° C.

The behavior of cobalt-containing samples is rather similar to those of manganese with the difference that no double peak appears at samples Co-1 and Co-3 and the exothermic decomposition of sample Co-1 is much sharper as compared to Mn-1. It should be stressed that in both manganese- and cobalt-containing samples excess addition of phosphorus results in a delayed decomposition and the maxima appear later (i.e. 246 ° C in sample Co-1 and 253 ° C in sample Co-3).

The behavior of nickel is rather different. Initial addition of nickel (sample Ni-1) leads to a small exothermic decomposition after the endothermic peak. Introduction of phosphorus in small amounts (sample Ni-1, P/(Al + Ni) = 0.15) inhibits both the endo and exo effect while excess addition of phosphorus (sample Ni-3, P/(Al + Ni) = 1.2) results in re-establishment of the thermal effects nearly to their initial form, i.e. that of sample Ni-1.

The behavior of the copper containing samples is similar to that of cobalt ones, although the activity of copper is less. Introduction of copper (sample Cu-1) results in an exothermic decomposition of AN. Further addition of phosphorus inhibits this exothermic decomposition and also gives rise to an endo effect just prior to the exothermic decomposition.

Finally the introduction of zinc into the system (sample Zn-1) stabilizes it further as compared to sample Al-1. Addition of phosphorus (sample Zn-2) stabilizes the system even more, but excess of phosphorus seems to act catalytically towards exothermic decomposition. In that point the system behaves similarly to nickel containing samples.

DISCUSSION

The routes according to which the decomposition of ammonium nitrate can take place are

$$NH_4NO_3 \xrightarrow{T=150\,^\circ C} NH_3 + HNO_3 \qquad \Delta H = +176 \text{ kJ mol}^{-1} \qquad (1)$$

$$NH_4NO_3 \xrightarrow{T=400\text{–}500\,^\circ C} N_2O + 2H_2O \qquad \Delta H = -38 \text{ kJ mol}^{-1} \qquad (2)$$

$$NH_4NO_3 \xrightarrow{T=400\text{–}500\,^\circ C} N_2 + 2H_2O + 0.5O_2 \qquad \Delta H = -120 \text{ kJ mol}^{-1} \qquad (3)$$

Pure AN is decomposed according to route (1) and the same is also true for the Al-1 sample. The remaining cations appear to divert the route of decomposition to (3) according to the scheme

$$\text{Co} > \text{Mn} > \text{Cu} > \text{Ni} > \text{Zn} \qquad (4)$$

which holds for the samples with no addition of phosphorus (M-1). Small addition of phosphorus in ratio $P/(Al + M) = 0.15$ (samples M-2) inhibits this exo effect in the case of zinc, copper and nickel but seemingly not in the case of manganese and cobalt where the exo effect appears to be enhanced. Finally excess addition of phosphorus to ratio $P/(Al + M) = 1.2$ (samples $M = 3$) inhibits the exothermic decomposition in the case of manganese and cobalt as compared to samples M-2, but increases it in the case of nickel, copper and zinc. This last observation is not valid for aluminum where the addition of excess phosphorus does not alter the exothermic route.

In order to quantify the exothermic effect of decomposition as indicated in sequence (4) we calculated the surface areas of the exothermic peak in each thermograph of samples M-1 and M-2. The results are included in Table 2 which, apart from the samples examined in this work, also contains the samples $Al_{100}Cr_{20}P_0$ (Cr-1) and $Al_{100}Cr_{20}P_{18}$ (Cr-2) as well as the samples $Al_{100}Fe_{20}P_0$ (Fe-1) and $Al_{100}Fe_{20}P_{18}$ (Fe-2). The thermographs from these samples are cited in a previous publication [25]. The question arising now is which physicochemical quantity controls the diversion towards exothermic decomposition of AN.

TABLE 2

Samples prepared, areas of their exothermic peak, the standard electrochemical potential $E^{\ominus}$, the Gibbs free energy $-\Delta G$ for the indicated reduction, the difference in the crystal field stabilization energy $-\delta(\mathrm{CFSE})$ for the change of coordination from tetrahedral to octahedral and the sum $(-\Delta G)+(-\delta(\mathrm{CFSE}))$

Sample	Area exoth. peak (cm^2)	$E^{\ominus}$ (V)	$-\Delta G = nFE^{\ominus}$ (eV)	$-\delta$(CFSE) (eV) (tetr → oct)	$nFE^{\ominus} + \delta$(CFSE) (eV)
Al-1	0	–	–	0	0
Al-2	0	–	–	(Al^{3+}, d^0)	0
Mn-1	2.9	1.69	5.07	0.80	5.87
Mn-2	3.4	MnO_4, Mn^{4+}/Pt		Mn^{4+}, d^4	
Cr-1	5.3	1.36	8.17	1.71	9.88
Cr-2	5.9	Cr_2O_7, $2Cr^{3+}$/Pt		Cr^{3+}, d^3	
Fe-1	0.2	0.77	0.77	0.2	0.97
Fe-2	0.4	Fe^{3+}, Fe^{2+}/Pt		Fe^{2+}, d^6	
Co-1	2.3	1.81	1.81	0.7	2.51
Co-2	2.2	Co^{3+}, Co^{2+}/Pt		Co^{2+}, d^7	
Ni-1	0.5	0.49	0.49	0.9	1.39
Ni-2	0.4	Ni^{3+}, Ni^{2+}/Pt		Ni^{2+}, d^8	
Cu-1	2.4	0.15	0.15	0.00	0.15
Cu-2	0.8	Cu^{2+}, Cu^{+}/Pt		Cu^{1+}, d^{10}	
Cu-1	2.4	0.63	0.63	0.70	1.33
Cu-2	0.8	Cu^{3+}, Cu^{2+}/(?)		Cu^{2+}, d^9	
Zn-1	0.3	–	–	0	0
Zn-2	0.0	–	–	Zn^{2+}, d^{10}	0

In a somewhat similar study carried out some time ago [26] for the catalytic effect of metal oxides on the thermal decomposition of chlorates and perchlorates it was proposed that the main factor controlling the catalytic action was the difference $\delta(-\Delta H_f)_M$ between the heats of formation of the reduced and oxidized form of metal oxides calculated per metal atom. The oxides analyzed then, and correctly ordered in activity sequence according to $\delta(\Delta H_f)_M$, were $Cr_2O_3/CrO_3 > Fe_3O_4/Fe_2O_3 > Mn_2O_3/MnO_2 > CoO/Co_3O_4 > Cu_2O/CuO$ and Ti_2O_3/TiO_2. From this sequence the nickel oxide is suspiciously absent. Although according to $\delta(-\Delta H_f)_M$ data this material should be very active just after Cr_2O_3, in reality and for $KClO_3$ decomposition, it was much less active and falls just after CuO and before TiO_2 [26]. Exactly the same sequence of activity is observed in our results for the NH_4NO_3 decomposition, so we searched for another factor which might better explain the results.

In a previous publication [23] referring to Cr_2O_3 we noticed that the catalytic action of the metal ion is actually due to oxidation–reduction–oxidation ... cycles. Such a process should be related to the electrical work done per metal cation in the redox cycles. This work is the Gibbs free

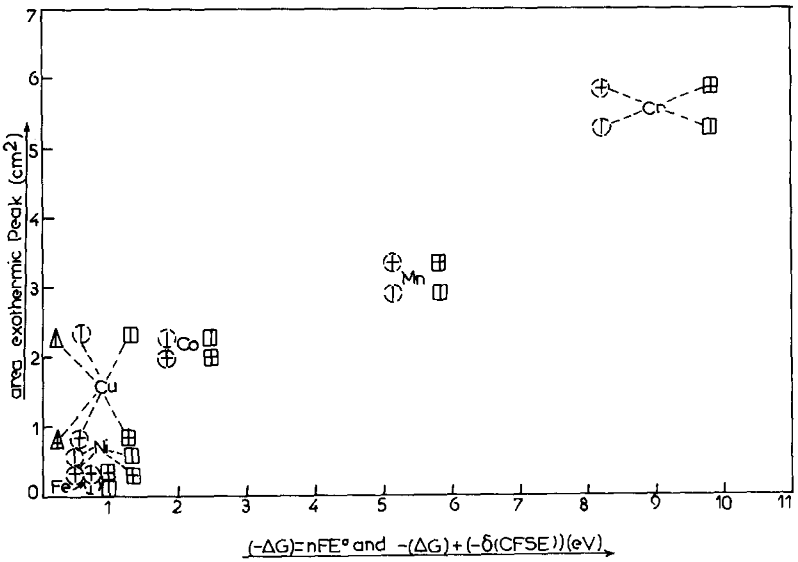

Fig. 2. Relationship between the area of the exothermic peak from Fig. 1 and the quantity $-\Delta G$ (○) and $-\Delta G+(-\delta(\mathrm{CFSE})$ (□) for samples 1 (⦶ and ◫) and 2 (⊕ and ⊞) of Table 1. Points △ and ▲ correspond to Cu^{2+}/Cu^{+} potential.

energy $(-\Delta G)$ of the system given in such cases by

$$(-\Delta G) = nFE^{\ominus} \tag{5}$$

where n is the number of transferred electrons, F is the Faraday constant and $E^{\ominus}$ the standard electron potential of the corresponding metal. In Table 2 we have calculated the $(-\Delta G)$ values for the corresponding reactions of metal oxides. In Fig. 2 we have plotted the area (cm^2) at the exothermic peak versus $(-\Delta G)$ and as can be seen there is a quite striking correlation. Nevertheless some discrepancies are apparent. One is the inverse order of nickel and iron oxides. Another is the abnormally high activity of copper oxide in contrast to its low $(-\Delta G)$ value, if the ΔG values are taken for the system Cu^{2+}/Cu^{+}. Nevertheless copper can also appear at oxidation state 3+ [27] which is very probable in our experiments in the hot melt of nitrates. We notice the Cu^{3+} has attracted enormous interest from people working in very diverse fields such as copper-containing ceramic superconductors [28] as well as copper-containing metalloenzymes [29] or systems imitating the active centers of such enzymes [30]. We notice that Demazeau et al. [28] obtained Cu^{3+} in $LaCuO_3$ perovskite by adding some $KClO_3$ as explosive in the mixture of CuO and La_2O_5 under pressure. Hence it is quite probable that in our case Cu^{3+} is formed. If the value of $(-\Delta G) = nFE$ is calculated according to the system Cu^{3+}/Cu^{2+} [29] then the high activity of copper is better justified (see Fig. 2).

The observation that the quantity $nFE^{\ominus} = -\Delta G$ is related to the exothermicity of the process might originate as follows. The critical step for the decomposition of NH_4NO_3, during which the catalytic action of metal cations is necessary, is the decomposition of nitrates. It is at this stage that the action of chromium for example has been evaluated as critical [21–23] and it is expected that the same should happen with the rest of cations. This decomposition may imply different parallel reactions but the most important one should be the reduction of nitrogen of nitrates to elementary N_2. This reaction could proceed according to the scheme

$$NO_3^- + 6H^+ + 5e^- \rightarrow 0.5N_2 + H_2O \tag{6}$$

The electrons necessary for reaction (6) could be taken from the metal cations which are then oxidized to a higher oxidation state

$$\frac{5}{n}M^{m+} \rightarrow \frac{5}{n}M^{(m+n)+} + 5e^- \tag{7}$$

or summarizing

$$NO_3^- + 6H^+ + \frac{5}{n}M^{m+} \rightarrow 0.5N_2 + H_2O + \frac{5}{n}M^{(m+n)+} \tag{8}$$

The equilibrium constant K of reaction (8) is related to its Gibbs free energy ΔG via the well known relation

$$\Delta G = -RT \ln K = -RT \ln \frac{\alpha_{N_2}^{1/2} \alpha_{H_2O} \alpha^{5/n}_{M^{(m+n)+}/M^{m+}}}{\alpha_{NO_3^-} \alpha^6_{H^+} \alpha^{5/n}_{M^{m+}}} \tag{9}$$

where α_i is the activity coefficient of i species. Considering that the entropic effects are small in comparison to $-\Delta H$, $((-\Delta H) \gg T\Delta S)$, then eqn. (9) is written

$$-\Delta H = RT \ln \frac{\alpha_{N_2}^{1/2} \alpha_{H_2O}}{\alpha_{NO_3^-} \alpha^6_{H^+}} + RT \ln \frac{\alpha_{M^{(m+n)+}}}{\alpha_{M^{m+}}} \tag{10}$$

Because both N_2 and H_2O are volatile their concentration in the melt should be minute. In contrast the concentrations of NO_3 and H^+ should be high and rather steady up to the final stages of decomposition. Therefore

$$\Delta H = B + nF(E^{\ominus} - E)_{M^{(m+n)+}/M^{m+}} \tag{11}$$

where B is constant and equal to $-RT \ln(\alpha_{NO_3^-} - \alpha^6_{H^+})$ and E and $E^{\ominus}$ are the electrode potential and the standard electrode potential respectively of the $M^{(m+n)+}/M^{m+}$ pair. If the reactants are at their equilibrium concentration as might expected then $E_{M^{(m+n)+}/M^{m+}} = 0$ and

$$-\Delta H = B + nFE^{\ominus}_{M^{(m+n)+}/M^{m+}} \tag{12}$$

Relationship (12) justifies the relation observed in Fig. 2 between the area of the exothermic peak and $nFE^{\ominus}$, if B is small and around zero.

A further correction to both discrepancies noticed above in Fig. 2 relative to the inverse order of nickel and iron oxides as well as to the abnormally high value of copper oxide could probably be attempted by taking into account the differences δ(CFSE) in the crystal field stabilization energies (CFSE) during change of coordination of the metal cation. The influence of CFSE on catalytic problems was proposed some time ago and is acknowledged by many authors [31]. Thus in Table 2 we have also tabulated the changes in crystal field stabilization energy δ(CFSE) for the transformation of the corresponding cations from tetrahedral to octahedral structure, the relevant values being taken from ref. 32. The sum $nFE^{\ominus}+$ CFSE $=(-\Delta G)+$ CFSE is also depicted in Fig. 2. As can be seen the picture is rather improved, not only relative to the order of activity of nickel and iron, but also with regard to the high activity of copper. Thus the main factor controlling the decomposition of nitrates to N_2 and O_2 seems to be the extent of the spontaneity of the step, metal ion(oxidized) → metal ion(reduced), as it is quantified by the values of $(-\Delta G)$. Indeed the metal ions should exist at their higher oxidation state in the nitrate melt and in order to act as catalysts should suffer reduction and subsequent redox cycles. It is exactly the readiness of reduction which is given by $(-\Delta G)$ and should be the slow and rate determining step of the process. On top of such electrochemical reasons the crystal field effect should be taken into account. Such effects might contribute from 10% (for example in chromium) to 50% (in copper) of the final energy driving the decomposition. The physical basis for this effect is that the spontaneity of the transition, tetrahedral → octahedral, as quantified by the values of $-\delta$(CFSE) in Table 2, is important during decomposition of nitrates to nitrogen and oxygen. The last species might increase the coordination of the reduced cation in a spontaneous way, and this cation might in turn be oxidized by electron transfer to oxygen species which are subsequently reduced to O_2 gas.

Another point for discussion is that of the active cations (Mn, Co) in which addition of phosphorus to small amounts (samples-2) increases the exo effects while excess of phosphorus (samples-3) inhibits the exothermic decomposition. On the contrary for the non-active cations (Ni, Cu, Zn) initial addition of phosphorus (samples-2) decreases the exo effect but excess of phosphorus (samples-3) increases it. It seems that somehow phosphoric cations act as promoters of reaction (3) in Mn-2 and Co-2 samples or reaction (3) or (2) in samples Ni-3, Cu-3 and Zn-3. It should also be noted that such a promotion effect is not observed in the case of aluminum samples. Nevertheless it might be that the phosphates in certain combinations with transition metal ions, depending on the specific action of the last, may promote the decomposition of nitrates, probably via redox cycles of themselves to different oxidation states of phosphorus.

One final point to comment upon is the relation observed between the

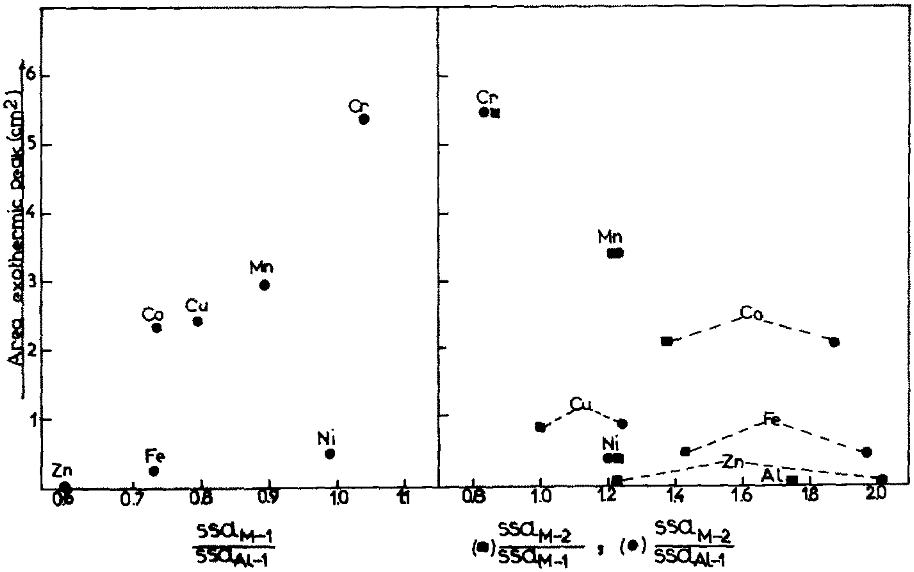

Fig. 3. Relationship between the area of the exothermic peak and the specific surface area (ssa) of the corresponding specimens normalized over the Al-1 or M-1 species.

catalytic activity of the different cations towards NH_4NO_3 decomposition and the desintering action of phosphorus observed in those samples as is estimated from the changes of the corresponding specific surface areas (ssa), after the final heating, normalized over the ssa of Al-1 samples or the s.s.a. of M-1 solids [33]. Such an effect is shown in Fig. 3 in which the exothermicity of the decomposition is compared to the ratios $ssa_{M\text{-}1}/ssa_{Al\text{-}1}$ as well as $ssa_{M\text{-}2}/ssa_{M\text{-}1}$ and $ssa_{M-2}/ssa_{Al\text{-}1}$ where $ssa_{Al\text{-}1}$ means the specific surface area of the Al-1 sample while $ssa_{M\text{-}1}$ is the specific surface area of the M-1 sample. As discussed in detail in ref. 33 those ratios describe the sintering action of metal cations (ratio $ssa_{M\text{-}1}/ssa_{Al\text{-}1}$) over that of aluminum or the combination of sintering action of metal cations and the de-sintering action of phosphorus (ratios $ssa_{M\text{-}1}/ssa_{Al\text{-}1}$ and $ssa_{M\text{-}2}/ssa_{Al\text{-}1}$). The comparison of exothermicity with $ssa_{M\text{-}1}/ssa_{Al\text{-}1}$ samples does not actually include the action of phosphorus since samples-1 do not contain phosphorus (Table 1). On the contrary the comparison of exothermic decomposition with $ssa_{M\text{-}2}/ssa_{M\text{-}1}$ or $ssa_{M\text{-}2}/ssa_{Al\text{-}1}$ contains the action of phosphorus.

From Fig. 3 it seems that, with the exception of nickel, at no phosphorus addition there is a tendency for the explosive decomposition of NH_4NO_3 to increase the ssa relative to the Al-1 sample. On the contrary with phosphorus addition the explosive decomposition decreases the ssa as compared to Al-1 or M-1 samples, with the notable exception of nickel and copper. It seems that in the last case the non-violent removal of gases from the pores of the solid permits the reservation of its porosity and therefore of its high surface area. On the contrary the explosive decomposition in the absence of phosphorus destroys the high surface area probably through local increase of temperature and sintering of the solids. It might be imagined that the action of phosphate salts formed onto and into solids act as reinforcing nets diminishing the breaking of the porous structure.

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