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WATER INSOLUBLE FORMS OF P_2O_5. THERMAL DECOMPOSITION OF Ca/II/ HYDROGENEPHOSPHATE

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ABSTRACT

Calcium hydrogenephosphate prepared in the forms of suspensions served us as model of one step in the production of the nitrogene-phosphor-kalium containing fertiliser /NPK/. They showed a lower thermal stability as their standard compound, prepared after literature. The mode of the preparation of both kinds of compounds determines their thermal decomposition and the physical properties. The products of such decomposition were controlled by IR spectra, also with regards to the change of their modification.

INTRODUCTION

In water insoluble forms of P_2O_5 are the compounds /1/ creating possible problems in the production of fertilizers. The compounds and suspensions prepared as models had to help to the elucidation of problems arousing during the step of the neutralisation with ammonia in the production.

MEASURING METHODS

Preparation. The model suspensions were prepared with proportion 6:5:2,56in mixing H_3PO_4, $Ca/NO_3/_2 .2 H_2O$ and HNO_3 and finally adding water that its content in total was 33,77% /2/. The suspensions were not the same as the suspensions present in natural way in the fertilizer production, we had to eliminate the secondary retrogradation of phosphorpentoxide during the neutralisation and mainly about its end. The calcium carbonate and fluoric acid was not added to the suspensions, the former affects the retrogradation of P_2O_5-creating its less easy assimilated forms, thus it degenerates the course of the second neutralisation and lowers the content of P_2O_5 soluble in water.

The standards known from the literature were prepared and controlled by IR spectra, thermal analysis and CHN analysis.

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Analysis. In the water soluble part of the suspensions, the free acids content was determined by alcalimetric titration, the ammonia content by distillation method. In the water insoluble part the P_2O_5 content was controlled by photoocolorimetric measurements /Carl Zeiss, Jena, MK6 /6/, calcium content by complexometric /Eriochromblack T/.

IR spectra /KBr disc/ were measured /IR Perkin Elmer 557/ after dilution 1:200 in samples gained from the water insoluble part of the suspensions.

Thermal analysis was made /Derivatograph OD 102/ in both types of compounds in analogous manner with rate of heating 6^0/min. in air/ /DTA:1/5; DTG:1/5/.

RESULT AND DISCUSSIONS

Thermal decomposition of the standards $CaHPO_4.2H_2O$ /1/ begins at 80°C. Till 218°C it looses 19,85%/T_{max} on DTA at 112°C/, this represents two molecules of crystallinic water/theoret.20,9%/. In temperature interval 358-462°C/T_{max} on DTA at 434°C/the loss of 5,3% is to be seen, what is equivalent to one molecule of H_2O/ theor 5,23%/.The thermal decomposition is after

$$CaHPO_4 \cdot 2H_2O \longrightarrow CaHPO_4 + 2\,H_2O$$

$$2\,CaHPO_4 \longrightarrow Ca_2P_2O_7 + H_2O$$

The standard $CaHPO_4$ begins to decompose at 464°C/T_{max} on DTA at 432°C/, the loss 6,7%/theor.6,62%/ is equivalent to one water molecule. At 500°C we could folow a slightly endothermic process without the loss of the mass, which after Wikholm/3/ represents a change of the $Ca_2P_2O_7$ to $Ca_2P_2O_7$ modification.

Seven samples of the model suspensions /2/ exhibited characteristic thermal decompositions /see Table 1/. The samples are without loss of mass till 290°C, what means no crystalinic water is present in samples. The weight loss /$\triangle$m/ in interval of temperatures T_1 - T_2 are in a rather good coincidence with the theoretical value /6,62%/ for the reaction of conversion from $CaHPO_4$ to $Ca_2P_2O_7$. The starting temperatures of the decomposition and the values T_{max} on the DTA curves are values different in the case of each individual sample and equally from the standard /T_{max} 432°C/. The experimentally observed T_{max} were between 333-358°C, but the measurements conditions were the same. The difference in the measured temperatures may be affected by the physical properties of

the particles present in the suspensions /grain size, the degree of cristalinity a.o./. The preparation mode of suspensions was analogous, but the reaction medium was gradually differenciated according to the actually achieved degree of the ammoniacalisation. Each sample aroused as a "mixture" of products from the neutralisation performed with ammonia during the infinitely little changes in the degree of the ammoniacalisation. Only in this manner we may explain the DTA maxima of each individual suspension lying together in 25°C broad interval of temperatures.

Table 1. Characteristics of the thermal decomposition of the water insoluble component in model suspension /2/.

Sample	D	$T_1 - T_2$/°C/	T_{max}/°C/	△m/%/
1	2,72	290 - 397	350	6,8
2	3,21	282 - 394	347	6,8
3	3,61	292 - 408	353	7,0
4	3,91	280 - 410	351	6,7
5	4,23	295 - 414	358	7,0
6	4,43	274 - 396	333	7,1
7	4,54	280 - 382	342	7,0

D ... achieved degree /2/ of neutralisation by ammonia

T_{max} .. temperature of the maxima on DTA curve

T_1-T_2.. temperatures interval for the lost of H_2O

The thermal stability of $CaHPO_4.2H_2O$, $CaHPO_4$ was studied by many authors/2-5/. All are unified, that during the thermal decomposition both compounds are dehydrated and that in the case of the former the cistallinic water is lost as the first. Both forms of phosphorpentoxide exhibit an analogous second step - their conversion to $Ca_2P_2O_7$ salt. The course of the dehydratation is very mild and strongly dependent on the partial pressure of the water vapors being present in the furnace atmosphere. The IR spectra showed coincidence /2/ with products of the decomposition.

CONCLUSIONS

The reaction conditions during the preparation of the model suspensions greatly affect their thermal decomposition. Their thermal stability was lowered, which fact may be of practical importance. The results of thermal analysis had shown the $CaHPO_4$ as the essential part of each suspension. This compound stays - as an in

water insoluble form of P_2O_5 - till the finalisation of the fertiliser its determinative component, with regard to the phosphor assimilation. These experiments may have therefore significance not only for better knowing the properties of the in water insoluble form of P_2O_5 also in the dependence of the degree ot the achieved ammoniacalisation, but also for the investigation of the dry part in the next steps ot the fertiliser production.

REFERENCES

1 A.Tovborg-Jensen,J.Rathler, Inorg.Synth.,Vol.IV, Mc Graw Hill, N.Y.1953
2 G.Čík,Thesis, Faculty of Sciences, P.J.Šafarik's University, Košice 1978
3 N.W-Wikholm,R.A.Blebe,J.S.Kittelberger,J.Phys.Chem, 798 /1975/853
4 G.Berend,A.Hegedüs, Thermochimica Acta,11,4/1975/367
5 E.I.Duff,J.Appl.Chem.a.Biotechnol.,21,8/1971/233