Thermochimica Acta, 52 (1982) 359–361
Elsevier Scientific Publishing Company, Amsterdam—Printed in The Netherlands

Note

CHARACTERIZATION OF THE THERMAL DECOMPOSITION PRODUCTS OF THE RARE EARTH DECAVANADATES

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(Received 20 July 1981)

As part of a research program dealing with the study of physicochemical properties of rare earth vanadates, we have now investigated the thermal behaviour of the corresponding decavanadates.

Although DTA/TGA measurements for most of the hydrated rare earth decavanadates have been carried out some time ago [1], nothing is known about the nature and characteristics of the decomposition residues. On the other hand, earlier conclusions about the composition of these residues [2] are dubious and need further confirmation.

Therefore, the main purpose of the present study was to obtain a definitive and unambiguous characterization of these pyrolysis products.

EXPERIMENTAL

All the investigated samples were prepared according to the method of Jahr and Preuss [3] by reaction of decavanadic acid and the corresponding lanthanide acetates, followed by a slow evaporation of the resulting solutions (see also [4]).

According to the known DTA/TGA data [1] the samples were gradually heated in two stages in a crucible furnace in air, at temperatures of 350° and 500°C, for one hour at each stage.

The fired products collected at the stated temperatures were submitted to infrared and X-Ray diffraction analysis. IR Spectra were recorded on a Perkin Elmer 457 instrument using the KBr pellet technique; X-Ray powder patterns were obtained on a Philips PW 1010 diffractometer, using Ni filtered Cu–K_α radiation.

RESULTS AND DISCUSSION

According to a previous crystallographic study [4] the hydrated rare earth decavanadates belong to four different structural groups: the 22-hydrates of La and Ce belong to the monoclinic space group $P2_1/n$ with $Z=2$; the 26-hydrates of Pr, Nd and Sm are also monoclinic, space group $P2_1/a$ and $Z=2$; the 24-hydrates of Eu, Gd, Tb, Dy, Ho and Er are triclinic, space group $P\bar{1}$ and $Z=1$ whereas the

24-hydrates of Tm, Yb and Lu also belong to the same triclinic space group but with $Z=2$.

In order to make a systematic study we have selected one or two compounds of each group (La, Nd, Sm, Eu, Er, Tm, Lu) and investigated their decomposition residues.

In most cases, the fired residues collected after the thermal treatment at 350°C show poorly defined X-ray diffraction diagrams, but by heating them later at 500°C better resolved diffractograms can be obtained, due to a better crystallinity of the products which originally are probably partially amorphous.

An especially interesting aspect of the investigated series is the possibility that structural differences could influence the decomposition mechanisms and yield different pyrolysis products in each case. Nevertheless, the X-ray powder patterns, as well as the IR spectra recorded for all phases obtained under the same experimental conditions, are very characteristic and similar in their main features: they reveal clearly the presence of V_2O_5 and the corresponding rare earth orthovanadate.

Consequently, the thermal decomposition occurs, in all cases, according to the following schema:

$$Ln_2V_{10}O_{28} \cdot n\ H_2O \rightarrow Ln_2V_{10}O_{28} + n\ H_2O \qquad (1)$$

$$Ln_2V_{10}O_{28} \rightarrow 4\ V_2O_5 + 2\ LnVO_4 \qquad (2)$$

The dehydration occurs in two or three well defined stages [1]. This is related to the well known fact that different types of water molecules are present in these structures, some of which are more tightly bonded to the cations than others. On the other hand, it is also admitted that the water molecules play an important role in the stabilization of these crystal lattices [5].

In order to confirm additionally the proposed stoichiometry for the final decomposition residues, synthetic mixtures of V_2O_5 and $LnVO_4$ in the molar ratio 2:1 were prepared and analyzed also by means of IR spectroscopy and X-ray diffractometry.

The results of these measurements are totally coincident with those obtained from the thermal decomposition residues. An example is shown in Fig. 1. The better definition of the X-ray peaks in the case of the synthetic mixture is simply a consequence of the better crystallinity of this sample.

For $La_2V_{10}O_{28}$, Ropp and Carroll [2] have previously reported a mixture of V_2O_5, $LaVO_4$ and V_4O_7 as the final decomposition products. This proposal appears unsustainable in the light of the present results and, on the other hand, the formation of V_4O_7 during the thermal decomposition in air is totally unacceptable because, as it is known [6], the formation of this mixed oxide requires very drastic reducing conditions. The reduction of part of the vanadium(V) to a mixture of vanadium(IV) and vanadium(III) under the present experimental conditions can, consequently, be totally excluded.

The only difference in the case of the lanthanum decavanadate, in comparison with that of the other rare earth decavanadates, is that the generated $LaVO_4$ is monoclinic whereas all the other orthovanadates are tetragonal [7,8]. The fact that some of the diffraction peaks of $LaVO_4$ coincide nearly with those of V_4O_7 has probably led to the erroneous results mentioned.

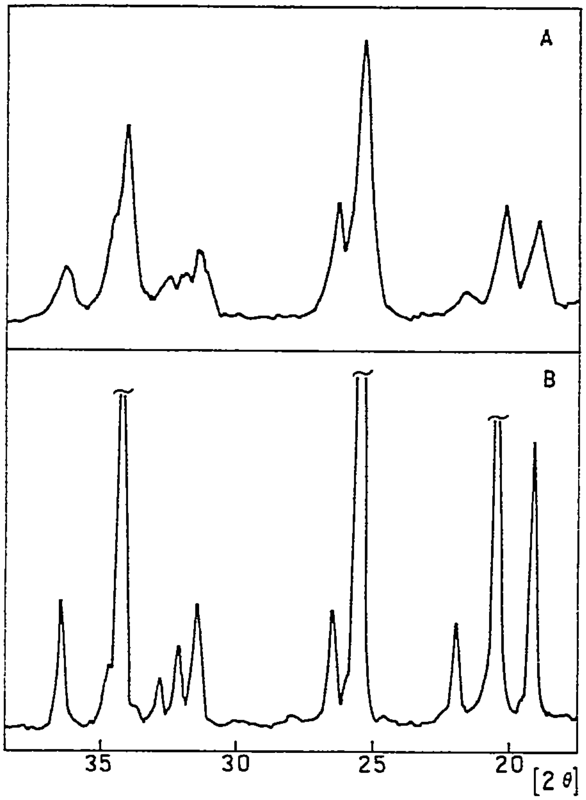

Fig 1 X-Ray powder diagrams of the pyrolysis residue of $Tm_2V_{10}O_{28}$ 24 H_2O (A) and of a 2 1 synthetic mixture of V_2O_5 $TmVO_4$ (B)

ACKNOWLEDGEMENTS

This research program is supported by SECYT, CONICET and CIC-Provincia de Buenos Aires.

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