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BEHAVIOUR OF $CdCO_3$-V_2O_5(1:1M)SYSTEM IN A SATURATED ATMOSPHERE OF WATER VAPOR AT DIFFERENT TEMPERATURES

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ABSTRACT

The behaviour of an equimolecular $CdCO_3$-V_2O_5system in a saturated atmosphere of water vapor has been studied at different temperatures.It was found by means of IR spectroscopy and X-ray data,that the β-$Cd(VO_3)_2$is obtained at 150°C.The beginning of reaction is stated for an increase of intensity of(001)X-ray line of V_2O_5.On the other hand,the adsorbed water molecules might cause the transformation crystalline⟶amorphous of V_2O_5,and an increase of acid properties at the V_2O_5surface.

INTRODUCTION

The high temperature(β)polimorph of cadmium metavanadate has been prepared by heating mixtures of different cadmium and vanadium compounds at temperatures between 650-800°C(1-4),or by heating the low temperature(α)polimorph at 750-800°C(5).Only Bouloux et al.,(6) have obtained it at 460°C by compression of α-$Cd(VO_3)_2$lattice under 3000bars pressure.Generally it is not obtained pure.

We can get it practically pure at 150°C from an equimolecular $CdCO_3$-V_2O_5mixture kept in a saturated atmosphere of water vapor during 24 hours.

The mixture evolution with the temperature has been studied too.At 50°C,the α-$Cd(VO_3)_2$is detected.This compound has been obtained by us in a previous paper (7).

EXPERIMENTAL PROCEDURES

Reagents: V_2O_5Merck a.r.with a purity > 99%.$CdCO_3$Riedel de Häen A.G.,both identified by X-ray and thermal analysis.

Preparation of samples.We prepared a mechanical mixture of $CdCO_3$-V_2O_5(1:1M).Grain size < 0.05 mm.Samples of 1g.were kept in a pressure reactor Phaxe 2005 of 100 ml.capacity,under a saturated atmosphere of water vapor during 24 h. This study has been carried out at the following temperatures: 50,75,100 and 150°C.

Techniques:X-ray powder diffraction.Siemens D500 equipped with K805 generator,graphite monochromater and Cu K_α radiation. Infrared

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<u>spectroscopy</u>: Perkin Elmer 599B. KBr tablets, 0.3% sample concentration. <u>Thermal analysis (TG-DSC)</u>: Mettler TA 3000 Analysis System with TC10TA Processor. The weight for all samples was about 30 mg., an heating rate of 10°C/min. and a N_2 stream.

RESULTS AND DISCUSSION

In Fig.1 we give the X-ray powder diffractograms of mixture $CdCO_3$-V_2O_5(1:1M) heated at different temperatures. We can see a progressive increment of α and β-$Cd(VO_3)_2$ depending on temperature. At 150°C the reaction is finished. At this temperature the β form is obtained with an insignificant amount of α-$Cd(VO_3)_2$.

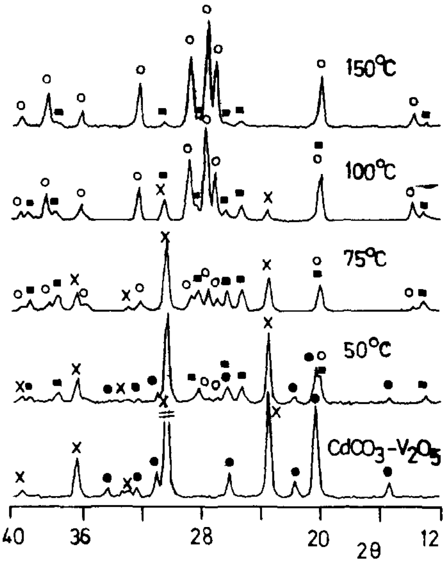

Fig.1 X-ray powder diffraction patterns

V_2O_5; $CdCO_3$; -$Cd(VO_3)_2$
-$Cd(VO_3)_2$

Fig.2 shows the IR spectra which are in agreement with the results above mentioned. When the temperature rises, the absorption bands of $CdCO_3$ and V_2O_5 decrease, and the $Cd(VO_3)_2$ ones increase. The respectively absorption bands are found at about:

$CdCO_3$:1320-1530, 860 and 720(cm^{-1})
V_2O_5:1020, 820 and 590-475(cm^{-1})(9)
$Cd(VO_3)_2$:550, 960 and 850(cm^{-1})(4)
$Cd(VO_3)_2$:515 and 890-830(cm^{-1})(4)

The results of thermal analysis are shown in Fig.3(TG) and Fig.4(DSC). The TG curves indicate between 25-100°C a weight loss corresponding to adsorbed water. In samples heated at 100 and 150°C (curves d,e) in which the β-$Cd(VO_3)_2$ is the main component, the amount of adsorbed water is minimum. Between 350-400°C, $CdCO_3$ decomposes. As we can see in curve (e), the amount of $CdCO_3$ is very small. This fact confirms the results obtained by X-ray and IR spectroscopy. In curve (c), at about 300°C a small weight loss is detected, very near to $CdCO_3$ decomposition, we think that it is due to loss of CO_2 proceding from labile $CO_3^{=}$. The DSC curves show between 25-100°C a first endothermic effect, due to loss of adsorbed water. A second endothermic peak appears with maximum between 392-433°C, which corresponds to $CdCO_3$ decomposition. About 300°C a shoul-

TABLE 1

T(°C)	ΔH(J/100mg.)	Content in 100 mg of mixture $CdCO_3$(mg.)	 H_2O(mg.)
25	25.7 ± 0.2	49.3 ± 0.3	0.7 ± 0.1
50	17.6 ± 0.3	32.2 ± 0.2	4.7 ± 0.1
75	9.7 ± 0.4	17.9 ± 0.5	3.9 ± 0.1
100	1.8 ± 0.1	2.9 ± 0.2	2.2 ± 0.1
150	——	1.1 ± 0.5	0.95± 0.05

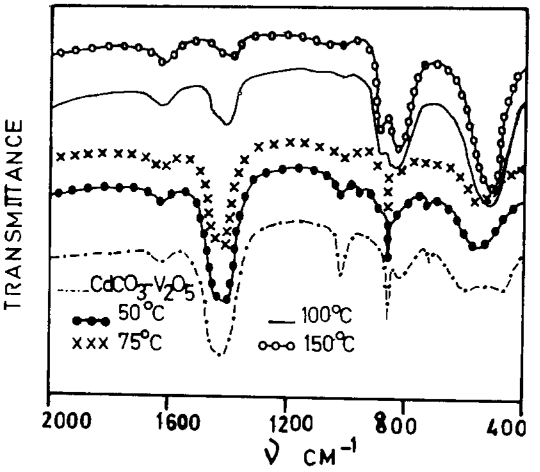

Fig.2 IR absorption spectra of $CdCO_3$-V_2O_5mixtures

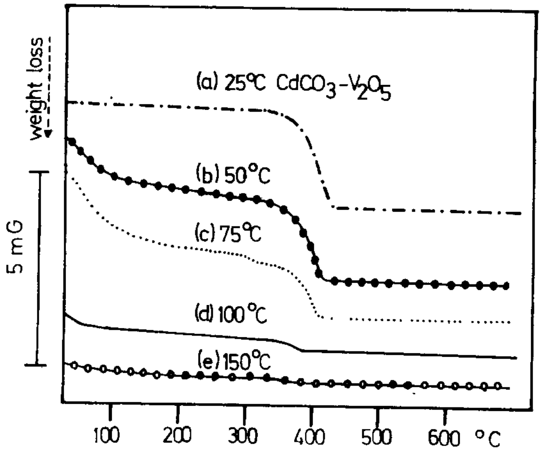

Fig.3 TG curves of $CdCO_3$-V_2O_5

der is detected in curve(b), and a weak endothermic peak (curve c)which correspond to decomposition of $CO_3^=$ more labile.In curve(c)we can see a shoulder between 140-175°C which becomes a peak in curve(e).According to(2)this last peak correspond to α - β transition.On the other hand,it is assigned for Livage(10)or Abello(11)to loss of water molecules more strongly bounded to amorphous V_2O_5.

The TG data and enthalpy of $CdCO_3$decomposition are given in Table 1.

Fig.5 shows the reaction evolution of $CdCO_3$-V_2O_5mixture with the temperature. It has been made from thermal analysis (TG-DSC) and X-ray data.This last ones has been got by semicuantitative measure of areas on the following peaks:3.78Å for $CdCO_3$,3.52Å forαCd$(VO_3)_2$ and 3.30Å for β-Cd$(VO_3)_2$. This graphic shows the good agreement between the results

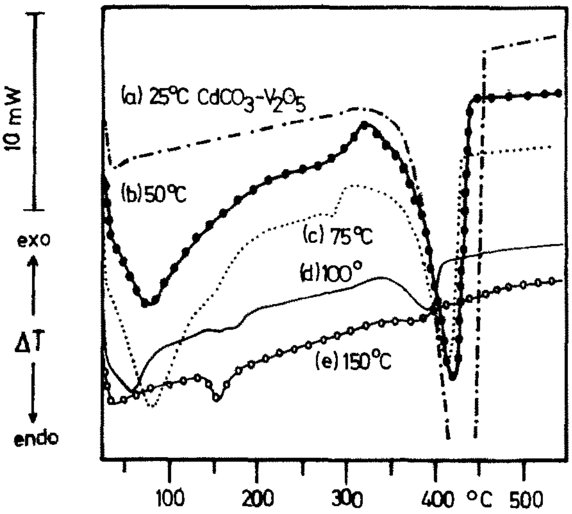

Fig.4 DSC curves of $CdCO_3$-V_2O_5 mixtures

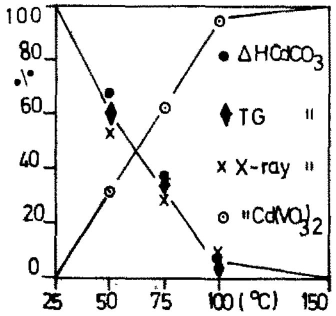

Fig.5 Variation of $CdCO_3$ and $Cd(VO_3)_2$ percentages in function of temperature during the thermal teatment of $CdCO_3$-V_2O_5 mixture.

obtained by the different techniques employed.

Finally, we propose the following mechanism for the reaction studied by us:

$$V_2O_5(s) + CdCO_3(s) + H_2O(g) \longrightarrow H_2(VO_3)_2(s) + CdCO_3(s) \longrightarrow Cd(VO_3)_2(s) + CO_2(g) + H_2O(g)$$

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