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α-CADMIUM METAVANADATE PREPARATION AT ROOM TEMPERATURE. PART I

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ABSTRACT

In this paper we propose a method of obtaining α-CdV_2O_6 at room temperature from equimolecular CdO–V_2O_5 mixtures kept in a water-saturated atmosphere. Characterization has been carried out by X-ray powder diffraction, infrared spectroscopy and TG analysis. These studies show the instability of α-CdV_2O_6 and its evolution with time at room temperature towards the β-form. We propose a α-CdV_2O_6 formation mechanism based on the acid–basic reactivity of V_2O_5 and CdO, which is considerably increased by a humid atmosphere.

INTRODUCTION

α-CdV_2O_6 is generally obtained by a dry method from an equimolecular mixture of CdO and V_2O_5, heated at 580°C for 24 or 48 h [1–3].

It has been identified during the thermal decomposition of hydrated cadmium decavanadates [4,5].

This compound has also been obtained in an aqueous solution [6–9], but mixed with other vanadates, in particular $Cd_2V_2O_7$.

Structural data of α-CdV_2O_6 and its allotropic transformation $\alpha \leftrightarrow \beta$ have been reported by Bouloux et al. [1,3]. The infrared spectrum has been given by Ulicka [5]. There is no preliminary work on preparing α-CdV_2O_6 at room temperature.

Given previous experiences with different oxides, e.g. CdO [10], our aim has been to obtain cadmium metavanadate at room temperature.

In this paper we show a method of obtaining α-CdV_2O_6 via reaction between the respective oxides, in a water-saturated atmosphere, at room temperature.

We also suggest a reaction mechanism based on the acid–basic character of both oxides.

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EXPERIMENTAL

Reagents

V_2O_5, Merck AR, purity > 99%; CdO, Riedel de Haën AG, heated for 2 h at 400°C to eliminate the impurities of CO_2 and H_2O; both have been identified as crystalline by X-ray powder diffraction.

Preparation of the samples

We prepared mechanical equimolecular mixtures of CdO–V_2O_5. Grain size < 0.05 mm. The contents of Cd and V were determined by complexometry and redox titration, respectively.

Samples of 1 g were kept in a water-saturated atmosphere at room temperature, for periods of 7.5 h, 1, 3, 6, 12, 21, 42, 60 and 134 days.

Apparatus

X-ray powder diffraction. Siemens D-500 diffractometer, graphite monochromator, K 805 generator, Cu $K\alpha_1$ radiation.

Infrared spectroscopy. Perkin-Elmer spectrophotometer 599 B from 4000 to 400 cm^{-1}, KBr tablets, concentration of samples 0.3%.

Thermal analysis (TG). Mettler TA 3000 analysis system with TC10TA processor. The weight of all samples was about 30 mg, heating rate 10°C min^{-1} in an air stream, alumina crucibles.

RESULTS AND DISCUSSION

X-ray powder diffraction analysis

From the study of the CdO–V_2O_5 (1 : 1 M) system at room temperature in a water-saturated atmosphere, α-CdV_2O_6 is found to be the reaction product, as is seen from the XRD data (Fig. 1).

The reaction between both oxides starts immediately. At 7.5 h, α-CdV_2O_6 is already apparent (curve b in Fig. 1). After 6 days, α-CdV_2O_6 is the only phase, with CdO as impurities (curve e). In the course of 12 to 60 days (curves f and g), there is no change on the X-ray diffractograms, only some very weak lines of β-CdV_2O_6 appear (allotropic high-temperature variety). After 134 days (curve h), the X-ray diffractogram shows a considerable increase in the β-CdV_2O_6 lines. This fact suggests that the α-metavanadate has been transformed into the β-form.

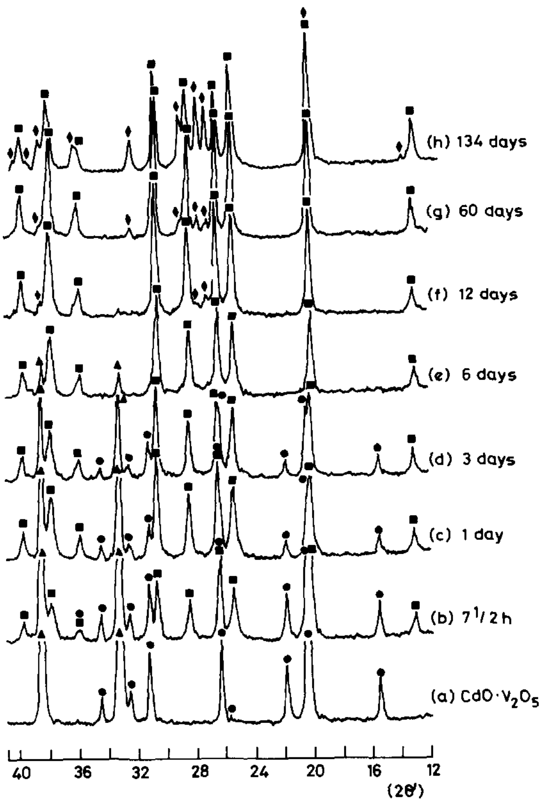

Fig. 1. X-ray diffraction patterns of CdO–V_2O_5 mixtures treated in a humid atmosphere at 25 °C for different times: (●) V_2O_5; (▲) CdO; (■) α-CdV_2O_6; (◆) β-CdV_2O_6.

The $\alpha \leftrightarrow \beta$ transformation of cadmium metavanadate has been studied by Bouloux et al., by heating α-CdV_2O_6 at 650 °C for 6 h at normal pressure [1] or at 460 °C and 3000 bars pressure [3].

Infrared spectroscopic analysis

IR analyses of the samples confirm the above X-ray results.

In Fig. 2 we give the IR spectra in the region 1200–400 cm^{-1}. As it can be seen, the absorption bands at 860, 950 and 540 cm^{-1} for α-CdV_2O_6 (according to Ulicka [5]), increase in intensity with time. On the contrary, the V_2O_5 absorption bands at 1020 cm^{-1} corresponding to V≡O vibrations, 820 cm^{-1} to νOV_2 and 590–475 cm^{-1} to νOV_3 and δOV_2 (according to Gilson et al. [11]), decrease in intensity. These are not present on curve d.

Thermal analysis (TG)

Figure 3 shows the TG curve of the CdO–V_2O_5 mixture kept for 3 days in a humid atmosphere. The TG curves of other samples are identical in shape.

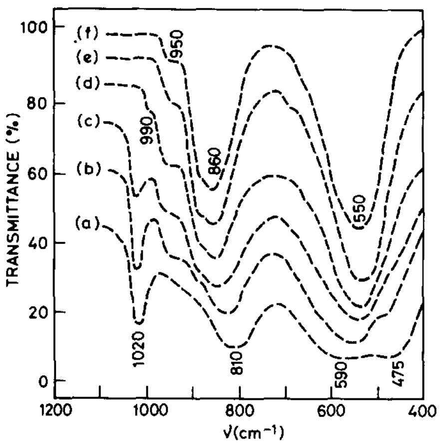

Fig. 2. IR spectra of CdO–V_2O_5 mixtures treated in a humid atmosphere at 25 °C for different times: (a) CdO–V_2O_5 without treatment; (b) $7\frac{1}{2}$h; (c) 1 day; (d) 6 days; (e) 12 days; (f) 134 days.

As it can be seen, there is a continuous weight loss from 25 to 600 °C, with an inflection at about 200 °C.

Since the reaction is not complete in this sample, free V_2O_5 exists, and considering the lamellar structure of V_2O_5 we think that water molecules can easily be intercalated into its layers. According to Abello et al. [15], when the number of water molecules in amorphous V_2O_5 is ~ 0.6, as it is in the present case, the vanadium atoms are coordinated to water molecules by V–OH_2 bonds, therefore, removal of these water molecules during heating occurs at higher temperatures than that of water not bonded to V_2O_5.

The two said weight losses (Fig. 3) may be due to the volatilization of adsorbed H_2O molecules (25–200 °C) and to the removal of H_2O more strongly bonded to V_2O_5 (200–600 °C), respectively.

Table 1 presents the TG data obtained from the thermal analysis of all mixtures.

The amount of water superficially adsorbed (25–200 °C) increases until the reaction has finished (12 days), and starts decreasing later. The amount of water more strongly bonded to V_2O_5 (200–600 °C) is less than the

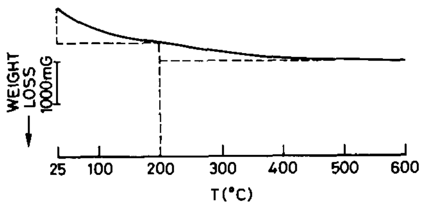

Fig. 3. TG curve of CdO–V_2O_5 mixture treated for 3 days in a humid atmosphere.

TABLE 1

TG data

Samples	Wt. loss, mmol H_2O per V_2O_5	
	25–200 °C	200–600 °C
$CdO-V_2O_5$	0	0
7.5 h	0.2	0.2
1 day	0.3	0.2
3 days	0.5	0.3
6 days	1.0	0.5
12 days	1.8	0.5
21 days	1.2	0.5
42 days	1.0	0.5
60 days	1.0	0.5
134 days	1.0	0.5

humidity water, and it remains constant (0.5 mmol per CdV_2O_6) when the reaction has finished (between 12 and 134 days). This fact suggests that the strongly bonded water remains irreversibly incorporated in CdV_2O_6 during the reaction process.

Numerous studies, nowadays, are carried out on the reactivity of amorphous V_2O_5 with water [12–20]. All of these agree with a number of possible linkages between the water molecules intercalated, mainly, into the basal 4.4 Å spacing.

On the other hand, a fundamental difference is established between the behaviour of amorphous and crystalline V_2O_5 in water: the amorphous one dissolves in water, whereas the crystalline one does not.

We have verified that the V_2O_5 employed in our reaction (crystalline, according to XRD data), dissolves in water, the higher the quantum number, the smaller the particle size. Therefore, it does not surprise us, in the present experimental conditions, that the behaviour of the V_2O_5 is similar to that of amorphous V_2O_5.

Reaction mechanism

Referring to the reaction mechanism, we think it deals with an acid–basic reactivity between V_2O_5 and CdO oxides, which is considerably increased by the humidity of the atmosphere. So, V_2O_5 transforms into metavanadic acid:

$$V_2O_5 + H_2O \rightleftharpoons H_2V_2O_6$$

According to this mechanism, it would bring two kinds of water molecules into play. One kind would be superficially adsorbed on the mixture and the other would be more strongly bonded to V_2O_5. The inflection at 200 °C on the TG curve (Fig. 3) seems to confirm this fact.

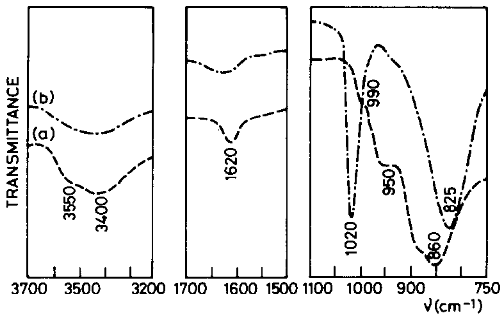

Fig. 4. IR spectra of: (a) CdO–V_2O_5 mixture treated for 6 days in a humid atmosphere; (b) V_2O_5 without treatment.

Figure 4 shows the IR spectrum of crystalline V_2O_5 (curve b) and that of the CdO–V_2O_5 mixture kept for 6 days in a humid atmosphere (curve a). In the latter, in the 3700–3200 cm^{-1} region, an asymmetric band appears with a shoulder at 3550 cm^{-1}, which could be associated (according to Abello and Lucazeau [20]) with V–OH_2 bonds. The δHOH vibration absorption band of water molecules that are not perturbed by H-bonding, appears at 1620 cm^{-1}. A shoulder also appears at 995 cm^{-1}, which could be associated (according to Abello et al. [15]) with the fixation of water molecules on the V_2O_5 skeleton.

Water interaction with V_2O_5 has also been studied by XRD. So, in Fig. 5 (curve b) a considerable intensity increase of the basal 4.4 Å (001) spacing is observed, which is due to the orientation effects produced by the polar water molecules.

Finally, we propose the following reaction mechanism:

$$V_2O_5 + H_2O + CdO \rightarrow H_2V_2O_6 + CdO \rightarrow CdV_2O_6 + H_2O$$

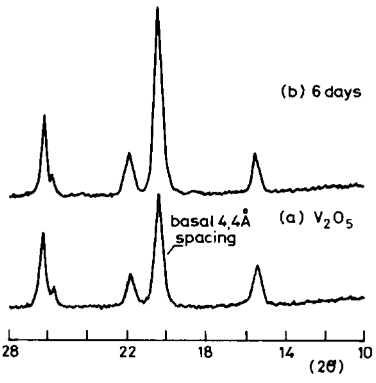

Fig. 5. X-ray diffraction patterns of: (a) V_2O_5 without treatment; (b) V_2O_5 treated for 6 days.

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