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PREPARATION OF V_2O_5 WITH AN ENHANCED DISPERSITY BY THERMAL DECOMPOSITION OF OXALATES AND PEROXIDES

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ABSTRACT

Samples of initially sintered V_2O_5 were dissolved in concentrated solutions of oxalic acid and hydrogen peroxide. Disperse V_2O_5 was synthesized by thermal decomposition of the intermediate dissolution products. Decomposition at different temperatures showed that with rising temperature the specific surface area passed through a maximum. The V_2O_5 formed during the decomposition of the intermediate oxalates had a five times larger specific surface area (55.0 m^2 g^{-1}) than that of V_2O_5 prepared by decomposition of the intermediate peroxide complex.

INTRODUCTION

Vanadium pentoxide is widely used for the preparation of numerous compounds of vanadium, ferrovanadium vanadium catalysts, luminophores and metallic vanadium. It is also a common component of catalysts for oxidation processes [1].

The reactivity of V_2O_5 and its catalytic activity depend on its dispersity and specific surface area. Two methods of preparation of disperse V_2O_5 by thermal decomposition of its oxalates and peroxides are considered in this paper. The aims of the investigation are to find the optimum conditions of dissolution of the initial V_2O_5 in oxalic acid and in a 30% hydrogen peroxide solution followed by thermal decomposition of the intermediate compounds obtained.

EXPERIMENTAL

The initial V_2O_5, the intermediate compounds and the final products were investigated by a series of physicochemical methods. The X-ray spectra were taken with a DRON-1 apparatus using Cu *Kα* radiation. The *IR* spectra were obtained in a KBr tablet using a Specord 75 IR apparatus, and the electron paramagnetic resonance (EPR) spectra were obtained using a JEOL 100 B instrument. The specific surface areas of the samples were determined by a modified BET method.

The initial material was V_2O_5 (AnalaR) sintered at 600 °C for 2 h. Its specific surface area was 3.5 m^2 g^{-1}. The vanadium pentoxide thus deactivated was dissolved in 30 w/v % solutions of oxalic acid and hydrogen peroxide.

Homogeneous solutions were obtained from stoichiometric oxalic acid/V_2O_5 ratios according to the reaction [2]

$$V_2O_5 + 4H_2C_2O_4 = H_2V_2O_2(C_2O_4)_3 + 2H_2O + 2CO_2$$

The necessary amount of oxalic acid was dissolved with stirring and heating of the solution at 70 °C. After the complete dissolution of the acid, the stoichiometric amount of V_2O_5 was added and the mixture was stirred until completely clear (5 h). The dissolution temperature was 70 °C and the pH value was 3.5. The sky-blue solution obtained was concentrated on a water bath and the residue was dried at 80 °C for 3 h.

The deactivated V_2O_5 was also dissolved in a weakly acidic 30% hydrogen peroxide solution. The mixture obtained was red [3–6]. The dissolution was an autocatalytic process, the accumulation of the reaction products leading to enhancement of the reaction rate. The reaction mixture was continuously stirred and cooled at a pH value of 5.5. By means of cryoscopic methods, dialysis, conductometry, spectrophotometry and pH determination, the red colour of the solution was found to be a result of the formation of a monomeric monoperoxy vanadate cation $(VO/O\text{–}O)^+$. The colour was stable in a moderately acidic medium. With an excess of acid, the monoperoxy vanadate cations condensed forming isopolyvanadate followed by the appearance of V_2O_5 and O_2. In a strongly acidic medium and, especially after heating of the solution, $VO(O\text{–}O)^+$ was reduced to VO_2^+ [7–9] and was transformed into a yellow oxodiperoxy cation $VO(O\text{–}O)_2$ in the presence of excess hydrogen peroxide [4,7–12].

The EPR method showed that in the $VO(O\text{–}O)^+$ cation, vanadium is tetravalent [13].

RESULTS AND DISCUSSION

To elucidate the conditions of the thermal decomposition of the compounds formed after the dissolution, their differential thermal analysis (DTA) curves were obtained. The decomposition of the vanadium oxalate complex was found to proceed in several stages. Endothermic processes with peak maxima at 110, 200 and 250 °C and exothermic processes with peak maxima at 270 and 310 °C (Fig. 1) were observed.

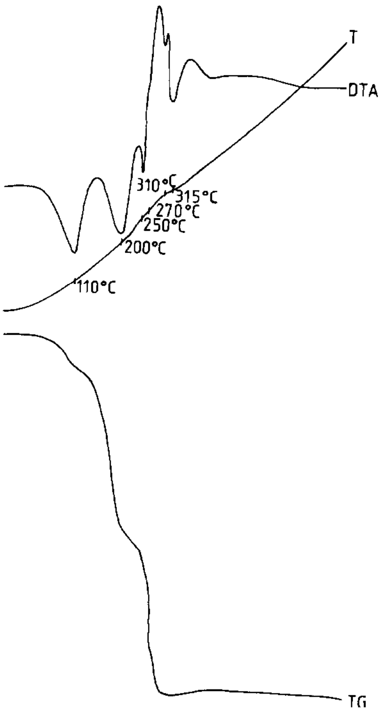

Fig. 1. DTA curve of the vanadium oxalate complex.

The DTA curve of the vanadium peroxide complex clearly inicates two processes: an endothermic process with a maximum at 120 °C and an exothermic process with a maximum at 400 °C (Fig. 2).

The data from derivatographic analysis were used to determine the temperature ranges of the isothermal decomposition of the precursors obtained from the two dissolutions.

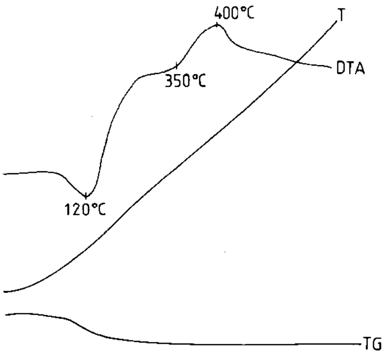

Fig. 2. DTA curve of the vanadium peroxide complex.

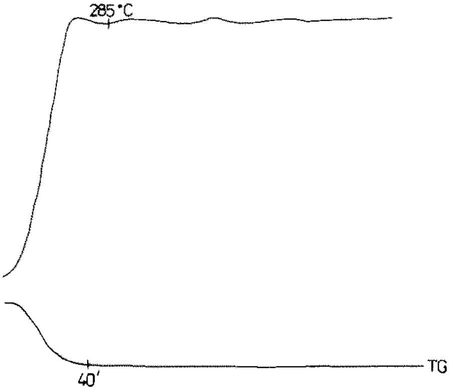

Fig. 3. TG curve obtained in an isothermal regime at 285 ° C.

The decompositions proceeded under static isothermal conditions in air for 3 h, the duration being determined by preliminary derivatographic investigations in an isothermal heating regime (Fig. 3).

The change in the specific surface area of the samples obtained at different temperatures of thermal decomposition is presented in Table 1.

Obviously, with both complexes, the curves illustrating the specific surface area change with the temperature of thermal decomposition and pass through a maximum which corresponds to the end of decomposition of the intermediate compounds to the final product V_2O_5.

After the temperature (300 ° C) which corresponds to the maximum of the specific surface area of the vanadium peroxide complex (7.0 m^2 g^{-1}), a decrease in surface area to 3.5 m^2 g^{-1} is observed at the final temperature of thermal decomposition (500 ° C). We are of the opinion that this decrease in the specific surface area is due to the recrystallization processes of the oxide

TABLE 1

Change in the specific surface area of the samples

Temperature (° C)	Specific surface area (m^2 g^{-1})	
	Vanadium oxalate complex	Vanadium peroxide complex
100	10.6	5.3
200	11.5	5.5
250	30.6	6.0
275	40.0	6.2
285	55.5	6.5
300	38.2	7.0
320	33.2	6.8
350	28.9	5.0
400	15.2	4.2
500	5.5	3.5

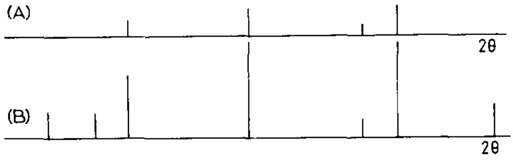

Fig. 4. Diagram of the vanadium peroxide complex (A) and pure V_2O_5 (B).

which are accompanied by heat evolution (Fig. 2) as well as to the sintering process.

According to physicochemical studies (X-ray phase analysis and IR spectroscopy) of the vanadium peroxide complex, the sample heat treated at 100 ° C (Fig. 4) contained V_2O_5.

The IR spectra (registered in a KBr tablet) of the initial vanadium peroxide complex before thermal treatment show intense peaks with maxima at 1014, 820 and 540 cm^{-1} which, according to refs. 14 and 15, characterize the vibrations of V_2O_5 and indicate the presence of the oxide in the sample. A low-intensity peak with a maximum at 907 cm^{-1} is also observed. It may be attributed to O–O stretching modes of the peroxide residue and indicates complete decomposition of all peroxide groups at this temperature (Fig. 5a). The sample with the maximum surface area, decomposed at 300 ° C (Fig. 5b), gives intense peaks characteristic of V_2O_5.

X-ray data (Fig. 4) on the initial vanadium peroxide complex and on the sample decomposed at 300 ° C are identical with those pure on V_2O_5.

Obviously, the intermediate vanadium peroxide complex decomposes to V_2O_5 at temperatures close to its drying temperature, which is in agreement with the data from the derivatographic analysis.

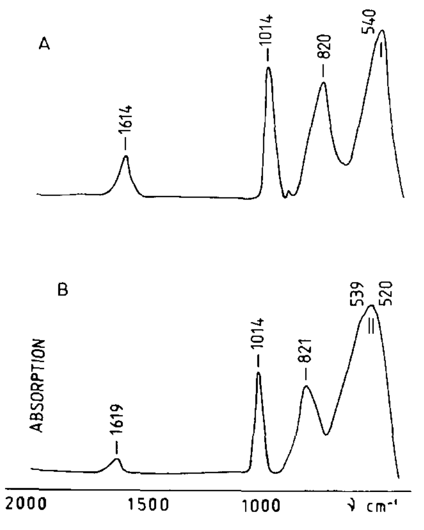

Fig. 5. IR spectra of vanadium peroxide complexes: A, initial complex; B, a complex calcined at 300 ° C.

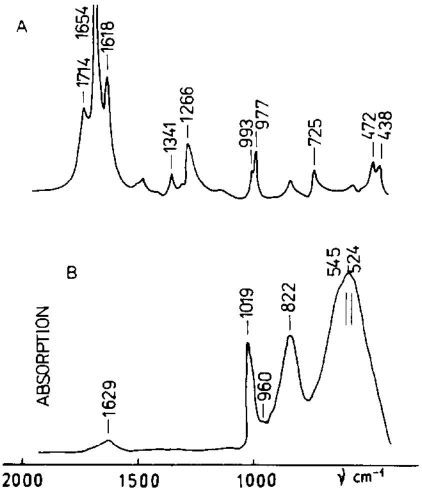

Fig. 6. IR spectra of vanadium oxalate complexes: A, initial complex; B, a complex calcined at 285 ° C.

The change in the specific surface area of the vanadium oxalate complex with temperature is analogous to the case of the vanadium peroxide complex. A maximum specific surface area (55.5 m^2 g^{-1}) is measured at a decomposition temperature of 285 ° C, after which the surface area decreases to 5.5 m^2 g^{-1} at 500 ° C, which is the final temperature of heat treatment. This is due to the same reasons as in the vanadium peroxide complex, i.e. recrystallization and sintering of the decomposition products.

The IR spectra (Fig. 6a) of the initial vanadium oxalate complex prior to calcination show intense lines with maxima at 1618, 1654 and 1714 cm^{-1} which characterize $\nu_{C=O}$ and indicate the presence of $C_2O_4^{2-}$ ions. In addition, bands with maxima at 1266 and 1341 cm^{-1} are observed, which, according to ref. 16, are characteristic of oxalate–vanadate complexes [15]. A doublet at 977 and 993 cm^{-1} appears in the region of the *V*=O stretching modes. Most probably the band at 977 cm^{-1} characterizes the *V*=O bond in the oxalate complex, whereas the less intense band at 993 cm^{-1} is indicative of the presence of a V_2O_5 phase. The latter assumption is confirmed by the

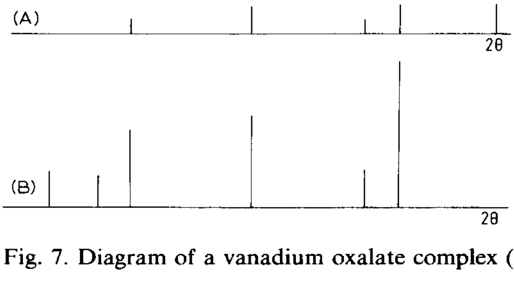

Fig. 7. Diagram of a vanadium oxalate complex (A) and pure V_2O_5 (B).

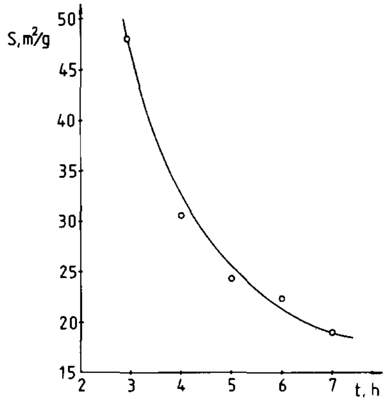

Fig. 8. Sintering curve of vanadium oxalate complexes in an isothermal regime at 285 ° C.

low-intensity peak at 842 cm^{-1} which is also typical of V_2O_5. With the sample heat treated at 285 ° C (Fig. 6c), all bands characteristic of oxalates disappear and bands of V_2O_5 are discernible.

X-ray studies of the intermediate compounds obtained during the thermal decomposition process of the vanadium oxalate complex showed the presence of a V_2O_5 phase in the sample heated at 100 ° C (Fig. 7), which is in agreement with the IR spectra (Fig. 6a). However, the incompletely decomposed vanadium oxalate complex was prevailing. The peaks of the sample decomposed at 285 ° C also showed a decrease in intensity compared with those of the model sample owing to the lower degree of crystallinity and the enhanced despersity of the sample.

Electron microscopy studies of V_2O_5 obtained by thermal decomposition at 285 ° C for 3 h showed that this compound consisted of spherical particles forming aggregates. The prevailing particle size ranged from 250–500 Å.

The EPR spectra showed that during the thermal decomposition of the vanadium oxalate complex, an intermediate compound with a *g* factor of 1.993 was formed in the case of the sample prepared by thermal decomposition at 250 ° C. The initial vanadium oxalate complex (before calcination) and the final product of V_2O_5 had the same *g* factor (2.014).

The large specific surface area of V_2O_5 obtained by thermal decomposition of the oxalate complex determines its easy sintering at relatively low temperatures. Figure 8 presents a typical sintering curve in an isothermal regime at 285 ° C.

CONCLUSION

This study shows that V_2O_5 with a relatively high despersity (a specific surface area of 50 m^2 g^{-1}) may be obtained by decomposition of a vanadium oxalate complex. It is established that V_2O_5 with a smaller specific surface area (7.0 m^2 g^{-1}) may be prepared by thermal decomposition of the vanadium peroxide complex.

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