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Thermal decomposition of sodium oxalate in the presence of V_2O_5. Mechanistic approach of sodium oxibronzes formation

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Abstract

The thermal decomposition of sodium oxalate in the presence of vanadium pentoxide in 1:2 molar ratio affords the vanadium bronze α'-NaV_2O_5. Complementary techniques such as thermogravimetry (TG), differential thermal analysis (DTA), gas analysis (GC), X-ray powder diffraction (XRD) and infrared spectroscopy (IR) were applied to provide information on the operative mechanism. A promotive effect of vanadium pentoxide on the decomposition of sodium oxalate takes place. Carbonate species and carbon monoxide could not be detected as intermediates during the decomposition which occurs over a wide range of temperatures, typically between 200 and 525°C. The progressive formation of $Na_xV_2O_5$ bronzes with x increasing up to unity with temperature leads us to propose that the carbon–carbon bond cleavage of the oxalate is promoted by electron transfer between the oxalate anion and the vanadium pentoxide matrix. Such behaviour is dependent on the redox potential of the metal ion initially present in the oxalate and of vanadium pentoxide.

INTRODUCTION

The thermal decomposition of oxalates is an old method for the preparation of catalysts [1–3]. Recently this method has been successfully applied to the low-temperature syntheses of oxides [4], spinel structures AB_2O_4 [5], bronzes $A_xB_yO_z$ [6], and superconductors YBa_2CuO_{7-x} [7–9]. Oxalates have also been used for in situ generation of a determined amount of carbon monoxide. Such a procedure allows the reduction of metal oxides to a given lower oxidation state [6]. The formation of bronzes by the

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oxalate method offers the desired compound in a one-pot synthesis. For example, α'-NaV_2O_5 and β-$Cu_{0.5}V_2O_5$ bronzes have been prepared by heating V_2O_5 respectively with $Na_2C_2O_4$ and CuC_2O_4 at 600 and 555°C under inert atmosphere [10]. An XRD study has shown that the formation of the β-$Cu_{0.5}V_2O_5$ phase occurs after copper oxalate decomposition into metallic copper. However in the case of α'-NaV_2O_5 formation, the identification of the reaction sequence was not straightforward. Intermediate $Na_xV_2O_5$ phases ($x < 1$) were identified with x increasing with the reaction temperature.

Although the thermal decomposition routes of oxalates are well documented and have been recently reviewed [11], to our knowledge, no data have been reported for the decomposition in the presence of vanadium pentoxide. The present paper reports a study on the thermal decomposition of $Na_2C_2O_4$ in the presence of V_2O_5 in order to approach the mechanism for α'-NaV_2O_5 formation. This study was carried out by thermogravimetry (TG), differential thermal analysis (DTA), gas analysis by gas chromatography (GC). The solids were characterized by IR spectroscopy and X-ray powder diffraction (XRD).

EXPERIMENTAL

Analytical techniques

The TG–DTA experiments were carried out with a Setaram TG–DTA92 thermoanalyzer equipped with a PC92 data station under a nitrogen flow (99.995%, Air Liquide) of 17 $cm^3 min^{-1}$ at a 3°C min^{-1} heating rate. The powdered samples (20–60 mg) were placed in a platinum crucible using as a reference an identical empty crucible (0.1 cm^3).

Gas phase measurements were performed in the apparatus used for α'-NaV_2O_5 synthesis (total volume 134 cm^3) by connecting a pressure gauge (JPB Tb234) and a six-port valve sampling of a GC to the three-way valve. The sample (400–1000 mg) was decomposed at a 3°C min^{-1} heating rate under static vacuum and the progress of the reaction was monitored by the pressure change in the closed system due to self-generated atmosphere. CO_2 and CO were analysed on a Carbosphere column placed in 120 MB Intersmat chromatograph equipped with a catharometer detector.

The IR spectra were recorded on a Perkin-Elmer spectrometer 983G coupled with a Perkin-Elmer series 3600 Data Station. KBr pellets were made with the residues after quenching at room temperature under the reaction atmosphere. The temperature values indicated on the spectra are those corresponding to the final temperature of the heat treatment.

The X-ray powder diffraction patterns were recorded at room temperature in air using Cu Kα radiation.

Preparation of α'-NaV_2O_5 from $Na_2C_2O_4$ and V_2O_5

Commercial vanadium pentoxide (Merck) and anhydrous sodium oxalate (Prolabo) were used as received. A well-ground mixture of these two compounds in 2:1 molar ratio was put in a platinum crucible (total mass 1000 mg), then introduced into a quartz tube and inserted in a tubular furnace. The quartz tube was connected through a three-way valve to a vacuum pump (10^{-3} mbar) for 1 h to eliminate air, and then nitrogen was admitted. The standard heating was at a 3°C min^{-1} rate under nitrogen atmospheric pressure up to 650°C. This temperature was maintained for 10 h then the sample was cooled to room temperature within 4 h. This procedure allowed us to obtain pure well-crystallized α'-NaV_2O_5 as shown by the XRD technique [10] and elemental analysis for carbon, sodium and vanadium.

RESULTS AND DISCUSSION

α'-NaV_2O_5 synthesis

α'-NaV_2O_5 was obtained at 600°C, under nitrogen atmosphere, from a 2:1 mixture of vanadium pentoxide and sodium oxalate. Heating rates in the range 2–16°C min^{-1} and cooling rates of 3–16°C min^{-1} had no effect on the synthesis. XRD lines of pure α'-NaV_2O_5 phase were always observed. When nitrogen atmosphere was changed for vacuum (either static or dynamic), again pure α'-NaV_2O_5 was formed. The best crystallinity was obtained after maintaining a final temperature of 650°C for 10 h.

The TG curve resulting from heating a well-ground mixture of V_2O_5 and $Na_2C_2O_4$ in a 2:1 stoichiometry under nitrogen is reported in Fig. 1. The profile shows that the decomposition occurred smoothly in successive steps, not well resolved, over a wide range of temperature, typically between 200

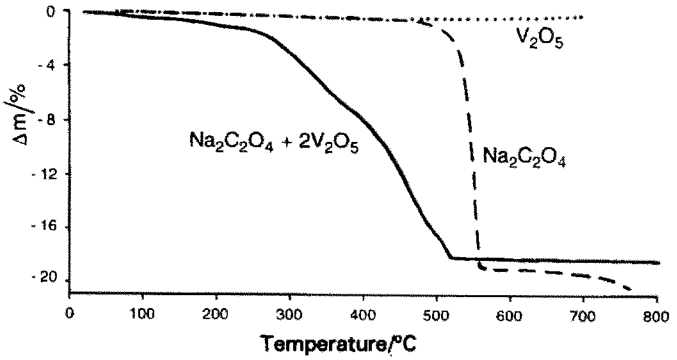

Fig. 1. TG traces of $Na_2C_2O_4 + 2V_2O_5$ (61.40 mg), $Na_2C_2O_4$ (18.48 mg) and V_2O_5 (24.37 mg): heating rate, 3°C min^{-1}; nitrogen flow rate, 17 cm^3 min^{-1}.

and 525°C. No residual carbon was found by elemental analysis in the resulting solid heated at 600°C. The total mass loss experimentally found (17.74%) corresponds to the one calculated (17.67%) for eqn. (1)

$$Na_2C_2O_4 + 2V_2O_5 \rightarrow 2NaV_2O_5 + 2CO_2 \qquad (1)$$

In an independent experiment, the GC analysis of the gas evolved showed a continuous production of CO_2 with trace amounts of CO at 550°C (≈0.1 vol.%). The quantitative analysis gave a total number of 2.0 mol of gas formed per mol of oxalate, in agreement with eqn. (1).

Comparison of the TG profiles obtained for the individual decompositions of $Na_2C_2O_4$ and V_2O_5 points out significant differences. Under the same experimental conditions, sodium oxalate started to decompose above 500°C with a maximum rate at 560°C (Fig. 1). The IR spectrum of the residue obtained at 650°C fitted with that of Na_2CO_3, in agreement with previous observations [12]. However the observed mass loss (18.29%) is lower than the calculated value of 20.89% for Na_2CO_3 formation. This discrepancy has been found to arise from the presence of carbon in the residue: 3.37% obtained by elemental analysis versus 3.29% calculated from the TG curve. When the decomposition was carried out up to 650°C for gas phase analysis, CO was identified in the temperature range of the mass loss. It was accompanied by a small quantity of CO_2 with a maximum concentration of 0.5 vol.% at 550°C. The identification of both carbon and

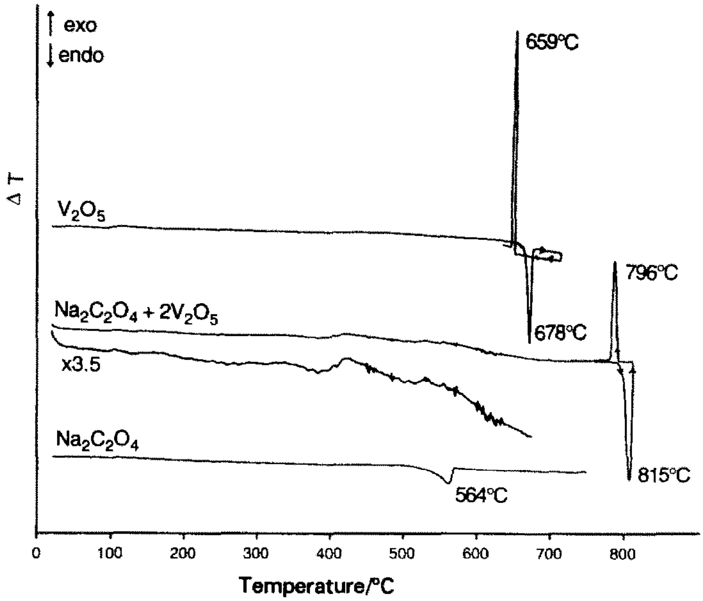

Fig. 2. DTA traces of $Na_2C_2O_4 + 2V_2O_5$ (61.40 mg), $Na_2C_2O_4$ (18.48 mg) and V_2O_5 (24.37 mg): heating rate, 3°C min^{-1}; nitrogen flow rate, 17 cm^3 min^{-1}.

CO_2 indicates the occurrence of Boudouard's reaction ($2CO \rightarrow CO_2 + C$) which slows down as more surface carbon is formed [13]. The total amount of evolved gas corresponds to 0.98 mol per mol of oxalate. A second mass loss started at 700°C up to 860°C and is relevant to the decomposition of Na_2CO_3 into Na_2O [14]. Under nitrogen atmosphere, vanadium pentoxide did not exhibit a significant mass loss up to 725°C (Fig. 1). These results show unambiguously that the presence of vanadium pentoxide leads to a promoting effect on the decomposition of sodium oxalate for the formation of α'-NaV_2O_5.

The DTA traces are also of interest (Fig. 2). Decomposition of sodium oxalate into the corresponding carbonate gave, as expected, an endothermic peak centred at 564°C. However, in the presence of V_2O_5 no significant peaks could be detected below 800°C. The lack of discernable peaks on the DTA trace is attributed to overlapping of endo- and exothermic processes. The endothermic peak observed at 815°C corresponds to the melting of α'-NaV_2O_5. The DTA profile of V_2O_5 exhibits only one endothermic peak at 678°C due to melting.

Mechanism approach for α'-NaV_2O_5 formation

The formation of α'-NaV_2O_5 involves a redox reaction consisting of the oxidation of the oxalate anion with the concommitant reduction of vanadium (5+). The titration of V^{5+} and V^{4+} ions [15] in the α'-NaV_2O_5 samples gave the composition $[V_{1.00}]^{5+}[V_{0.98}]^{4+}$, in agreement with the expected ratio $V^{5+}:V^{4+} = 1$. Therefore, the reaction stoichiometry implies that sodium oxalate provides one electron per V_2O_5 unit. The first step of the decomposition of oxalates has been suggested to originate from the homolytic C–C bond cleavage [16]

$$C_2O_4^{2-} \rightarrow 2CO_2^{-\cdot} \qquad (2)$$

Then the radical-anion $CO_2^{-\cdot}$ can act as an electron transfer reagent

$$2CO_2^{-\cdot} \rightarrow 2CO_2 + 2e^- \qquad (3)$$

or through dismutation can provide CO which will be the reducing species

$$2CO_2^{-\cdot} \rightarrow [OCOCO_2]^{2-} \rightarrow CO_3^{2-} + CO \qquad (4)$$

Both steps (3) and (4) have been recently confirmed by electrochemical techniques [17].

In the present study, if CO is the reducing species for the formation of α'-NaV_2O_5, the following sequence of reactions should take place:

$$Na_2C_2O_4 \rightarrow Na_2CO_3 + CO \qquad (5)$$

$$Na_2CO_3 + V_2O_5 \rightarrow 2NaVO_3 + CO_2 \qquad (6)$$

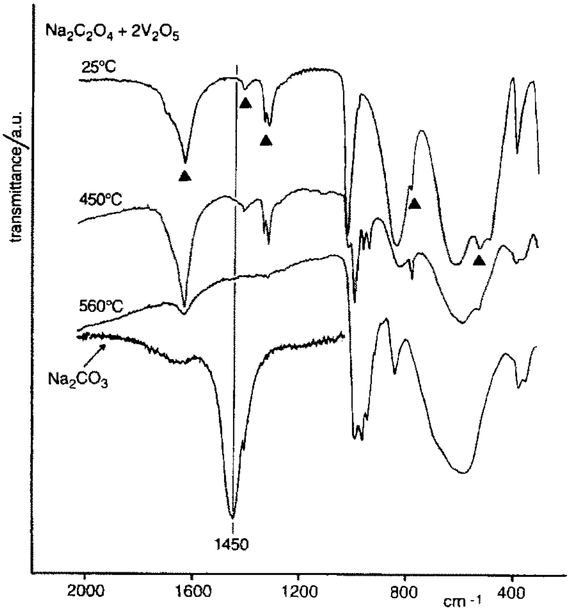

Fig. 3. IR spectra of (i) the initial mixture $Na_2C_2O_4 + 2V_2O_5$ (▲, $Na_2C_2O_4$), at 25°C, (ii) after heating under dynamic vacuum at 450 and 560°C, and (iii) Na_2CO_3.

$$CO + V_2O_5 \rightarrow V_2O_4 + CO_2 \tag{7}$$

$$V_2O_4 + 2NaVO_3 \rightarrow 2NaV_2O_5 \tag{8}$$

According to this sequence, the decomposition of sodium oxalate leads to Na_2CO_3 and CO (eqn. (5)), both of which react independently with V_2O_5 to form respectively $NaVO_3$ (eqn. (6)) and V_2O_4 (eqn. (7)). $NaVO_3$ and V_2O_4 then react together (eqn. (8)). The later reaction corresponds to the former procedure used for the synthesis of α'-NaV_2O_5 [18, 19].

A set of experiments was undertaken with the aim of detecting the reaction intermediates, Na_2CO_3 and CO. This could be expected since the reaction occurs over a wide temperature range (200–525°C). Gas phase analysis experiments revealed the formation of CO_2 from the beginning of the mass loss. IR spectra of the residue taken at different stages of the reaction showed the absence of Na_2CO_3 during the whole process (Fig. 3). Sodium oxalate bands were still present at 450°C, and disappeared above 560°C under the experimental conditions used. At 560°C, the bands in the region 1000–300 cm^{-1} correspond to those of α'-NaV_2O_5.

As no evidence was found for Na_2CO_3 and CO formation, we examined the validity of the sequence (5)–(8) by studing the temperature at which steps (6)–(8) are occurring. The TG profile resulting from heating, under nitrogen, a well-ground mixture of Na_2CO_3 and V_2O_5 in a 1:2 ratio showed that mass loss occurs stepwise from 275 up to 545°C. Only the last two sharp steps produced exo- and endothermic peaks respectively (Fig. 4). The mass

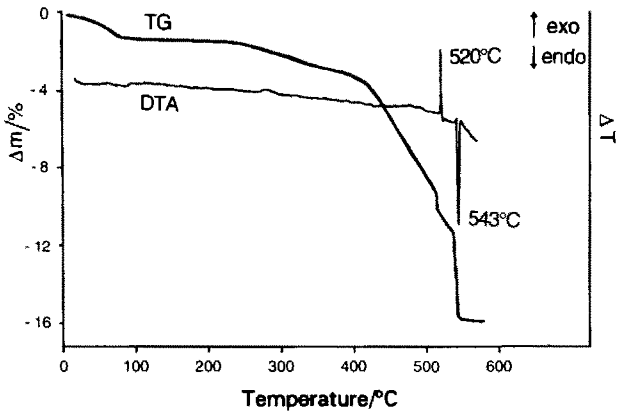

Fig. 4. TG and DTA traces of $Na_2CO_3 + 2V_2O_5$ (31.68 mg): heating rate, 3°C min^{-1}; nitrogen flow rate, 17 cm^3 min^{-1}.

loss between 105 and 575°C corresponds to 14.51%, close to the calculated value of 15.28%. The difference is due to the presence of carbon residue in trace amounts. Monitoring the pressure change due to self-generated atmosphere showed the same profile with temperature. A total amount of 0.98 mol of CO_2 per mole of Na_2CO_3 was released at 570°C. The reduction of V_2O_5 under CO has been recently described to pass through the intermediate phases V_6O_{13} and V_2O_4, V_2O_3 being the final product [20]. In our experimental conditions, the formation of CO_2 due to the reduction of V_2O_5 under a flow of pure CO at a 3°C min^{-1} heating rate started at 550°C, and a temperature range of 670–705°C was necessary for the reduction to proceed quantitatively in agreement with previous work [21]. When the experiment was performed in a closed CO atmosphere with the appropriate 1:1 stoichiometry, the transformation of CO into CO_2 became significant at temperatures above 500°C. At 530°C, the CO:CO_2 ratio reached an equilibrium within 6 h, and the total disappearance of CO was only observed after 2 h heating at 700°C, V_2O_4 being the final product. Heating a mixture of V_2O_4 and $NaVO_3$ in a ratio 1:2 ratio did not produce any mass loss up to 700°C. The XRD patterns of the solid after heat treatment at increasing temperatures showed that α'-NaV_2O_5 appears in significant amounts at 550°C, its formation being quantitative at 650°C. The one-pot synthesis of pure α'-NaV_2O_5 was also possible by combining eqns. (7) and (8) after heating at 600°C for 10 h. For the success of the synthesis, the V_2O_5:CO ratio has to be equal to 2. A two-fold excess of CO led to the formation of unidentified XRD lines. The presence of CO has also been found to inhibit the synthesis of α'-NaV_2O_5 starting from $Na_2C_2O_4$ and V_2O_5. This set of experiments stresses that, among the reactions studied in the sequence (5)–(8), it is the reduction of V_2O_5 by CO which proceeds quantitatively at the higher temperature (700°C). Therefore it is the rate-determining step, and CO should accumulate and be detected in the reaction vessel, while this was not observed. It is also worth mentioning that the nature of the gas formed during the reaction has no influence on the course of the reaction. Whether the reaction was conducted under nitrogen or under dynamic or static vacuum, pure α'-NaV_2O_5 was always obtained. Hence CO does not appear to be the reducing species starting from $Na_2C_2O_4$ and V_2O_5 to obtain α'-NaV_2O_5.

The first step of the decomposition of sodium oxalate is the C–C bond cleavage which provides $2CO_2^{-\cdot}$ (eqn. (2)). However in the presence of V_2O_5, a promoting effect was observed. This suggests that electron transfer is occurring before C–C bond cleavage between $C_2O_4^{2-}$ and V_2O_5. The following reaction scheme could be operative for NaV_2O_5 synthesis:

$$C_2O_4^{2-} + 2V_2O_5 \rightarrow 2V_2O_5^{-\cdot} + 2CO_2 \tag{9}$$

$$Na^+ + V_2O_5^{-\cdot} \rightarrow NaV_2O_5 \tag{10}$$

The XRD study of the solids obtained at different reaction temperatures points out the formation of intermediate $Na_xV_2O_5$ phases with x increasing with the reaction temperature [10]. At 455°C, unreacted V_2O_5 and $Na_2C_2O_4$ are present together with β-$Na_{0.33}V_2O_5$ and α'-NaV_2O_5 bronzes. At 555°C, α'-NaV_2O_5 is the predominant species, and at 655°C only α'-NaV_2O_5 is detected. The presence of $Na_xV_2O_5$ with $x < 1$ indicates that the migration of sodium ions in the vanadium oxide matrix is a progressive process.

The promoting effect of vanadium pentoxide on the decomposition under nitrogen atmosphere of sodium oxalate, here described, also occurs with potassium oxalate, but not with cupric oxalate [10]. Therefore this behaviour is strongly related to the respectively redox potential of the metal ion of the oxalate and of vanadium pentoxide.

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