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MONITORING OF THE GAS PHASE COMPOSITION: A PREREQUISITE FOR UNRAVELLING THE MECHANISM OF DECOMPOSITION OF SOLIDS

Thermal decomposition of cobalt oxalate dihydrate

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Abstract

The complexity of the processes occurring during cobalt oxalate dihydrate (COD) decomposition indicates that an interpretation of the mechanism based only on the TG curve is of little value. Mass change alone does not allow deeper insight into all of the potential primary and secondary reactions that could occur. The observed mass changes (TG) and thermal effects (DTA/DSC) are a superposition of several phenomena and thus do not necessarily reflect COD decomposition alone. Investigation of the mechanism of decomposition requires the application of different simultaneous techniques that allow the qualitative and quantitative determination of the composition of the gaseous products.

Composition of the solid and gaseous products of COD decomposition and heats of dehydration and oxalate decomposition were determined for inert, oxidizing and hydrogen-containing atmospheres. Contrary to previous suggestions about the mechanism of cobalt oxalate decomposition, the solid product formed during decomposition in helium contains not only metallic Co_{met}, but also a substantial amount of CoO (ca 13 mol%). In all atmospheres, the composition of the primary solid and gaseous products changes as a result of secondary gas–solid and gas–gas reactions, catalyzed by freshly formed Co_{met}.

The course of the following reactions has been investigated under steady-state and transient conditions characteristic for COD decomposition: water gas shift, Fischer–Tropsch, CO disproportionation, CoO reduction by CO and H_2, Co_{met} oxidation under rich and lean oxygen conditions.

Keywords: cobalt oxide reduction and oxidation, decomposition of cobalt oxalate, mechanism of thermal decomposition of solids, pulse thermal analysis, thermal analysis combined with mass spectrometry

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Introduction

The interesting influence of the kind of metal on the course of decomposition of metal oxalates and their common application as precursors in the preparation of oxides or metals possessing high surface areas has generated great interest in the investigations of the thermal decomposition of these salts. These investigations have almost reached the status of model application of thermal analysis for explaining the mechanism of the decomposition of solids. The conclusions concerning the mechanisms are based on the observed mass changes, the thermal effects and analysis of the solid products. This commonly applied method can, however, be misleading if possible secondary reactions between components of the surrounding atmosphere and the solid and gaseous products are not taken into account carefully.

According to generally accepted classifications (Boldyrev [1], Dollimore [2] and Brown [3]), the oxalates can be divided into three groups depending on the kind of products formed:

(a) alkali and alkali-earth oxalates which decompose into carbonate and carbon monoxide:

$$MC_2O_4=MCO_3+CO \qquad (1)$$

(b) oxalates, the decomposition of which results in the formation of a metal oxide as the solid and a mixture of carbon monoxide and dioxide as the gaseous products:

$$MC_2O_4=MO+CO+CO_2 \qquad (2)$$

This group includes some of the transition metal oxalates such as zinc, iron or chromium.

(c) oxalates decomposing into metal and carbon dioxide according to the reaction:

$$MC_2O_4=M+2CO_2 \qquad (3)$$

It is generally accepted that oxalates of heavy metals such as cobalt, nickel and cadmium decompose according to the last scheme.

In oxalates of bivalent metals, the extent to which the metal–oxygen bond is covalent is dependent on the electronegativity of the metal. The decomposition starts at temperatures at which the rupture of the Me–O link is possible or at which the rupture of the C–O bond occurs. If the reaction proceeds by breaking the carbon–oxygen bond, it will be followed by the rupture of the second Me–O bond because of the inability of the metal to accommodate two oxygen atoms [4]. The total reaction would lead to the evolution of equimolar amounts of CO and CO_2. The second possibility is the direct rupture of the two Me–O_1 bonds resulting in the formation of a metal and two carbon monoxide molecules. According to Dollimore [4], if two decomposition routes occur, e.g. (b) and (c), it is possible to use the thermodynamic data to decide which oxalate will decompose to a metal in an inert atmosphere and which will decompose to oxide. This prediction is made by comparing the variation of Gibbs energy of formation of the various oxides with temperature, the oxides being the products of decomposition. The comparisons are based on the Ellingham diagrams [5].

Another classification proposed by Vijh [6] used the values of the heat of formation of the corresponding metal oxides as a criterion in determining certain mechanisms of oxalate decomposition.

The simultaneous techniques such as TA-MS or TA-FTIR can increase the ability of thermal analysis to investigate all the various mechanisms of decomposition. These techniques, that enable the analysis of the gaseous phase, combined with pulse thermal analysis (Pulse TA®) [7] allow the quantification of spectroscopic signals**.** The TA-MS- PTA technique also allows the investigation of gas-solid and gas-gas reactions in situ.

A survey of the literature concerning COD decomposition shows many controversial opinions concerning the mechanism of this reaction. Not only the values of the kinetic parameters, which often provoke heated discussion, but also the values of the enthalpy of dehydration and oxalate decomposition are very different. Moreover, the temperature ranges of the particular stages, the composition of the gaseous and even the solid products – all these parameters are very much affected by, mainly, the kind of atmosphere used during the decomposition.

The least controversy occurs over the solid products of COD decomposition in oxidising [9–24] and reducing atmospheres [25, 26] where Co_3O_4 and Co_{met}, respectively, are supposed to be the products. In self-generating atmospheres Co_2O_3 and CoO are reported as products [27, 28]. Under vacuum the products found were: Co_{met} [29–31], a mixture of Co_{met} and CoO [32, 33], and $CoO_{0.83}$ [17]. During decomposition in an inert atmosphere the following solid products were found: Co_{met} [4, 11, 19, 22–24, 34], CoO [13, 17], a mixture of both [10, 16, 20, 21, 35, 36], $CoO_{0.75}$ [37], $CoO_{0.16}$ [17] and a mixture of Co_{met}, CoO and Co_3O_4 [38]. The composition of the gaseous products was reported only in a few papers. Generally, CO_2 has been found as the main gaseous product and, in a few cases, CO has been detected by means of mass spectrometry [24, 27, 39], infrared spectroscopy [35], conductometry [34], and gas chromatography [25]. The evolution of hydrogen during COD decomposition was mentioned only by [27], and in a few other papers, e.g. [24], one finds suggestions concerning possible secondary reactions between gaseous products, without however, any experimental evidence being provided. During the decomposition of COD in hydrogen the presence of water and methane, beside CO and CO_2, was reported [25, 26].

The variety of conclusions concerning the composition of the gaseous products is understandable due to the difficulty of their analysis in situ. The discrepancies in the determination of the composition of the solid products, especially in an inert atmosphere, show that some secondary reactions will have to be taken into account. The following reactions can modify the composition of the products:

$$Co+1/2O_2=CoO \tag{4}$$

$$CoO+CO=Co+CO_2 \tag{5}$$

$$CoO+H_2=Co+H_2O \tag{6}$$

$$2CO=CO_2+C \text{ (Boudouard reaction)} \tag{7}$$

$$CO+H_2O=CO_2+H_2 \text{ (water gas shift reaction)} \quad (8)$$

$$CO_2+4H_2=CH_4+2H_2O \text{ (Fischer–Tropsch reaction)} \quad (9)$$

The main goal of the presented work was to check the possibility of these reactions occurring under the transient conditions that exist during the decomposition of COD. The time for the mutual interaction of gaseous and solid products is limited due to the rather narrow temperature range of the decomposition. The confirmation of the existence of these reactions can explain many of the controversial results and help in the proper interpretation of the thermoanalytical data in elucidation of the decomposition mechanism.

Experimental

Experiments were carried on a Netzsch STA 409 simultaneous thermal analyser equipped with a gas pulse device that enables the injection of controlled amounts of two different pure gases or gaseous mixtures into the carrier gas stream. The decompositions were carried out under inert, oxidising and reducing atmospheres. In order to minimise the influence of diffusion in course of the decomposition, all experiments used helium as the carrier gas with an addition of 20 vol% oxygen or hydrogen, respectively. An exact flow of 50 ml min^{-1} was achieved using mass-flow controllers (Brooks model 5850E). The TG curves for each atmosphere were corrected to minimise the buoyancy effect by subtracting the TG base line obtained with the empty crucibles. The sensitivity of the DSC signal was calibrated by measuring the enthalpy changes of the synthetic sapphire cylinder (NBS Standard Reference Material 720) under each of the applied atmospheres.

The injection of 1 ml pulses of CO, CO_2, and CH_4 into the carrier gas stream enabled the quantification of the mass spectrometric curves recorded during the decomposition. Details of this procedure are given in [7, 8].

The composition of the solid products were analysed by means of X-ray diffraction on a Siemens powder X-ray diffractometer using Ni-filtered CuK_α radiation in step mode with a step size of 0.01° and 0.3 s.

Cobalt oxalate was synthesised from p.a. grade solutions of cobalt chloride and oxalic acid. The purity was tested by elemental analysis and gave the following results: Co: 32.6 found, 32.21% calculated; H: 2.35 found, 2.19% calculated; C: 13.1 found, 13.12% calculated. XRD analysis confirmed the presence of two phases only: α-$CoC_2O_4{\cdot}2H_2O$ as the major phase and traces of the β-form as the minor phase.

Results

The TA and MS signals obtained during the decomposition of COD in helium, 20 vol% H_2, balance He and 20 vol% O_2, balance He are presented in Figs 1–3, respectively. Figure 4 depicts the XRD patterns of the solid products of the COD decomposition under different atmospheres.

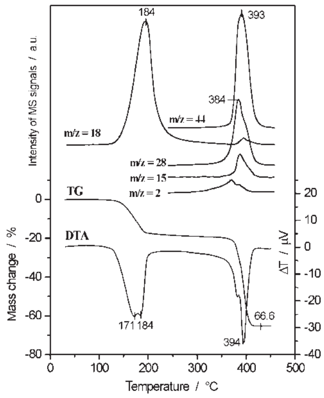

Fig. 1 Decomposition of COD in helium. Heating rate of 10 K min^{-1}

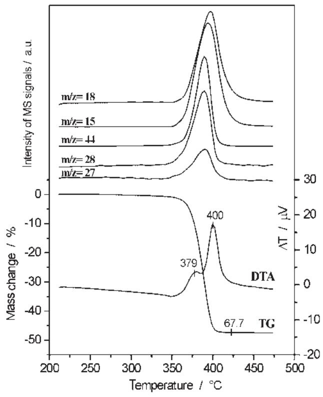

Fig. 2 Decomposition of COD in hydrogen (20 vol%, balance He). Heating rate of 10 K min^{-1}

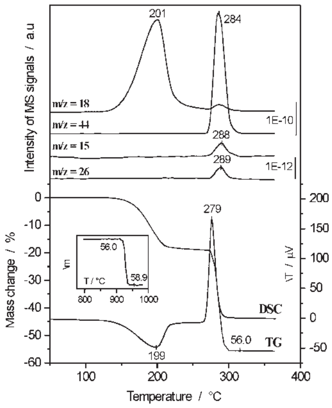

Fig. 3 Decomposition of COD in oxygen (20 vol%, balance He). Heating rate of 10 K min^{-1}

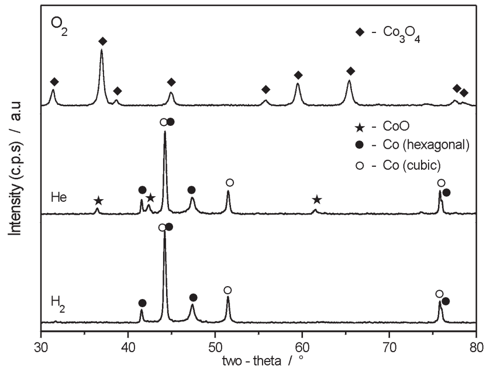

Fig. 4 XRD patterns of the products of COD decomposition in O_2, He and H_2, respectively

To use the analysis of the composition of the solid products for the interpretation of the decomposition mechanism it is necessary to take into account possible redox reactions in the system Co–O. The oxidation of the metallic Co formed during decomposition occurs very rapidly in an oxygen atmosphere – note the strong exothermic effect on the DSC curve as depicted in Fig. 3. The temperature rise during decomposition of even very small masses of sample (ca 10 mg) exceeds 3–4 degrees. The decomposition of samples of ca 30 mg was so exothermic that it led to the partial removal of the decomposed solid from the crucible due to a violent temperature jump of more than 13 degrees during a period of ca 15 s (not shown).

The shape of the m/z=18 signal and the continuous shift of the TG curve indicate that, independently of the atmosphere, the evolution of crystallised water is not completed before the beginning of the oxalate decomposition. In inert and oxidising atmospheres, Figs 1 and 3, small amounts of water are clearly detectable in the gaseous products resulting from decomposition. The interpretation of the presence of water in an inert atmosphere is further complicated by the catalytic reaction leading to the formation of methane (reaction (9)) and other hydrocarbons as indicated by the mass spectrometric signals m/z=15, 26, 27 and 30. In hydrogen, Fig. 2, the formation of methane and CO by the reaction of CO_2 (the main primary gaseous product of COD decomposition) with H_2 results in the formation of secondary water and therefore the presence of primary, residual hydrating water cannot be confirmed. The experimental proofs of the possible secondary reactions are given below.

Reaction of metallic cobalt with oxygen

From the experimental point of view it is very difficult to carry out a thermoanalytical experiment in a totally oxygen-free atmosphere. Even several evacuations and flushes after the insertion of a sample into a vacuum-tight system will not guarantee a completely oxygen-free atmosphere. Tiny amounts of oxygen in the system can noticeably change the composition of the solid products. For a 30 mg sample of COD, 2.03 cm^3 of oxygen will fully oxidise the resulting metallic cobalt to CoO. Heating at a rate of

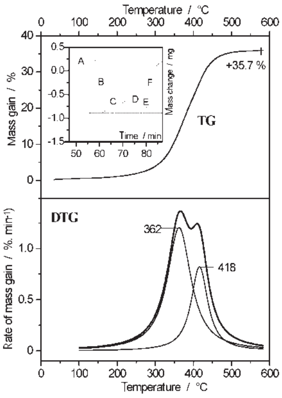

Fig. 5 Oxidation of metallic cobalt in oxygen rich (20 vol%, balance He) and lean (inset) atmospheres. The explanation of the meaning of the letters A–E is given in the text

10 K min^{-1} will cause the decomposition in helium to occur after ca 10 min at a temperature around 350–450°C. Assuming that cooling to room temperature requires an additional 20 min, then an oxygen concentration of only 0.133 vol% will lead to the complete transformation of Co into CoO at a carrier gas flow of 50 cm^3 min^{-1}.

The determination of the phase composition of the solid products of COD decomposition has been carried out ex situ in all reported papers. XRD measurements have been made at room temperature after allowing the solid products to cool. This generally used procedure can be the reason for the misleading conclusions concerning the mechanism of the reaction. The metallic cobalt formed during decomposition is very active and reacts violently with oxygen (oxygen-containing atmosphere) or its traces ('inert' atmosphere). The values of $\Delta_r G$ and $\Delta_r H$ of the reaction of the oxidation of cobalt into Co_3O_4 amount to –226.1 and –303 kJ mol^{-1} at 600 K, respectively. The process of the oxidation of passivated Co_{met}, containing ca 3 wt% of CoO, is depicted in Fig. 5. The deconvolution of the DTG curve makes it possible to roughly estimate the rates of the two consecutive processes i.e. the formation of CoO and Co_3O_4. Under the applied experimental conditions (heating rate 10 K min^{-1}, oxygen concentration 20 vol%) oxidation begins slowly at temperatures as low as 100°C and accelerates distinctly at ca 300°C. The maximum rate, in the first stage of the process i.e. oxidation of Co to CoO, is observed at a temperature of 362°C, this is similar to the temperature at the onset of COD decomposition under He. At this temperature there is a distinct difference in the rates of formation of CoO and Co_3O_4 and only one oxide phase, CoO, is formed in the range 350–450°C under oxygen-lean conditions.

The above remarks are well illustrated by the results of the oxidation of the products of COD decomposition under helium (the inset in Fig. 5) by traces of oxygen (0.03 vol%) at 475°C. The continuous mass gain due to Co oxidation is clearly visible (parts A, C and E of the TG curve) occurring at a rate of ca 10 μg min^{-1} for the mass of solid products amounting to 25.1 mg. The first pulse of hydrogen (B) reduced both, primary CoO, being with Co_{met} the product of the decomposition, and secondary CoO

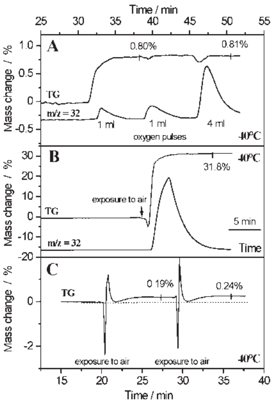

Fig. 6 A) Passivation of metallic cobalt formed during COD decomposition in 20 vol% H_2 by oxygen pulses at 40°C, B) Violent oxidation of Co_{met} obtained by decomposition of COD in 20 vol% H_2 due to exposure to air at 40°C, C) Passivation of the solid product of COD decomposition in He due to exposure to air at 40°C

formed during period A. The second 1 ml pulse of H_2 (D) reduced only freshly formed CoO in period C, indicating that all primary CoO resulting from COD decomposition was reduced during the first pulse. The 1 ml pulse of oxygen (F) resulted in rapid formation of CoO, as confirmed by XRD.

The partial oxidation of very active Co_{met} by traces of oxygen also occurred during the cooling of the sample after decomposition and, to a lesser extent, during exposure of the sample to air at room temperature. This low-temperature oxidation of pyrophoric cobalt is especially noticeable during exposure to air of the pure Co_{met} formed during COD decomposition in hydrogen. In order to prevent the uncontrolled, rapid oxidation of the sample in air, it was allowed to cool in the experimental atmosphere (20 vol% H_2). At 50°C the hydrogen was replaced by helium and the system purged for ca 1h in order to remove all traces of hydrogen. This was confirmed by monitoring the intensity of the mass spectrometric signal m/z=2. At 40°C, three pulses of oxygen were injected into the carrier gas stream (Fig. 6A). The first pulse resulted in the partial oxidation and passivation of the cobalt surface. The following two oxygen pulses did not change the mass of the product further. The amount of cobalt oxide formed (2.9 wt%) was determined by its reduction with hydrogen (see next paragraph). The presence of CoO was not detectable by XRD (Fig. 7) and X-ray diffraction could only confirm the presence of two metallic cobalt phases, hexagonal and cubic. In order to check the lower limit of detectability of CoO in the mixture CoO and Co_{met}, samples containing different amounts of the cobalt(II) oxide phase were synthesised by the controlled oxidation of Co_{met}. The resulting XRD measurements of these mixtures are presented in Fig. 7 and indicate that only Co_{met} phases were detected when the amount of CoO was lower than ca 4–5 wt%.

If the Co_{met} obtained during COD decomposition in hydrogen was not passivated then its exposure to air at room temperature resulted in a violent, exothermic oxida-

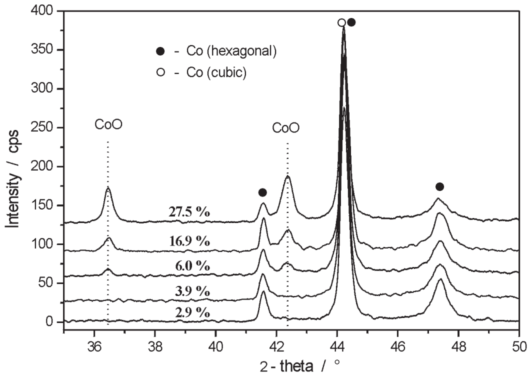

Fig. 7 XRD patterns of solid products of COD decomposition containing different amounts of CoO phase marked in wt% on the curves

tion. The Co_3O_4 formed contained only a minor amount of Co_{met} and CoO, as was confirmed by XRD and the observed mass gain (Fig. 6B). The product of COD decomposition in helium was only partly passivated by the traces of oxygen in the system during cooling to room temperature as opposed to the sample that had been passivated with the 1 ml oxygen pulse. Exposure to air, carried out while continuously monitoring mass changes, confirmed the mass uptake for this sample (Fig. 6C).

Reduction of CoO by the gaseous products of COD decomposition

The phase ratio in the solid products CoO–Co_{met}, formed in the primary reaction of COD decomposition, can be altered not only by secondary reactions with the carrier gas as happens with oxygen (oxidation of both solid products to Co_3O_4) and hydrogen (reduction of CoO to Co_{met}). It can be changed by the gas–solid reaction with the decomposition gases as well. The CoO reacts with gases such as hydrogen, CO and hydrocarbons formed during decomposition. In order to check if these processes can take place in the range of the decomposition temperatures, a sample, containing 18.9 wt% of CoO, was reduced in atmospheres containing 20 vol% of H_2 and 20 vol% of CO respectively. The sample was prepared by controlled oxidation using 1 ml pulses of oxygen on the products of COD decomposition in hydrogen. The results, depicted in Fig. 8A, show that the reduction of CoO by hydrogen occurs at much lower temperatures. It begins at ca 180 and is complete at ca 330°C. The exothermic peak of the reduction is hardly visible on the DSC curve due to the very small thermal effect of this reaction $\Delta_r H = -10.2$ kJ mol^{-1} at 600 K).

The reduction of the mixture Co_{met}–CoO by carbon monoxide is overlapped by the disproportionation of CO (see next paragraph) catalysed by the metallic cobalt. The observed mass loss is influenced by the formation of carbon, the solid product of CO disproportionation (reaction 7). After the total reduction of CoO, the rate of disproportionation increases – note the change of intensity of the m/z=44 signal (CO_2) and faster mass gain. In order to determine the mass of deposited carbon, CO was re-

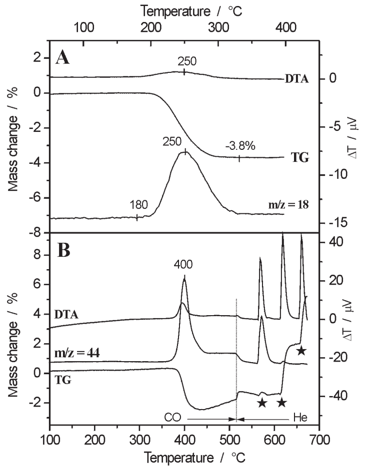

Fig. 8 Reduction of mixture Co_{met} – CoO in 20 vol% H_2 (A) and 20 vol% CO (B). The pulses of oxygen injected into He after exchange of atmosphere at 515°C (B) are marked by asterisks

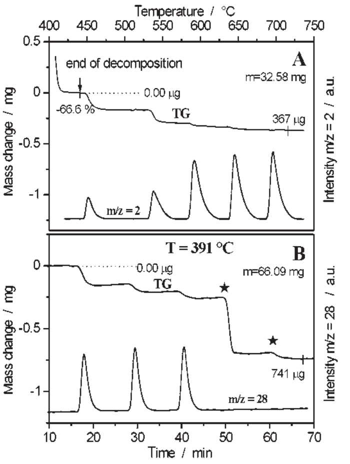

Fig. 9 In situ determination of the composition of the solid products by CoO reduction due to pulses of hydrogen (A) and CO (B) immediately after the end of COD decomposition

moved from the carrier gas and three pulses of oxygen were injected into the helium (Fig. 8B). The first pulse resulted in the combustion of carbon (note the CO_2 formation). The mass loss due to this reaction was overlapped by the mass gain due to the partial oxidation of Co_{met}. The next two oxygen pulses resulted in the formation of CoO. The amount of deposited carbon, as calculated by the quantification of the mass spectrometric signal of *m/z*=44, amounted to 232 µg.

The ease of the oxidation of the Co_{met} and the formation, in this reaction, of secondary CoO leads to the conclusion that to correctly determine the contents of the

COD decomposition products the measurement has to be carried out in situ, immediately after the reaction has ended. This procedure is illustrated by the results shown in Fig. 9. The reduction of CoO was done by the injection of 1 ml pulses of hydrogen into the carrier gas stream (He) after completion of the COD decomposition. The results, presented in Fig. 9A, indicate that four hydrogen pulses were required for the total reduction of the CoO. The recorded mass loss of 367 μg for the 32.58 mg COD sample makes it possible to determine the composition of the solid product. Beside the main phase, Co_{met}, it contains 15.8 wt% of CoO, which is equivalent to 12.9 mol%.

In the second experiment, depicted in Fig. 9B, CoO formed during the decomposition of COD under helium was reduced by carbon monoxide at constant temperature of 391°C, i.e. just after the total decomposition. The yield of the reduction, due to 1 ml CO pulses, was less than the yield due to hydrogen. This agrees well with the results shown in Fig. 8. After the first three pulses of CO only about one third of the CoO had been reduced. The next two pulses, this time of hydrogen, marked by asterisks on the TG curve, reduced the CoO much faster. For the 66.09 mg sample of COD the total mass loss due to CoO reduction amounted to 741 μg. The results shown in Fig. 9 reveal the importance of using hydrogen as a reducing agent. The reduction of CoO by CO proceeds much more slowly and the observed mass change can be influenced by CO disproportionation.

Disproportionation of CO

The equilibrium constant of the disproportionation of CO (Boudouard reaction) $2CO=C+CO_2$ amounts to $5.74\cdot10^5$ and $4.02\cdot10^3$ at 600 and 700 K, respectively, confirming the possibility of solid carbon formation within the temperature range of COD decomposition. CO disproportionation is catalysed by the metallic cobalt. In order to check the course of this reaction, the Co_{met}, obtained during decomposition of COD under hydrogen, was heated at a rate of 10 K min^{-1} in an atmosphere of 10 vol%

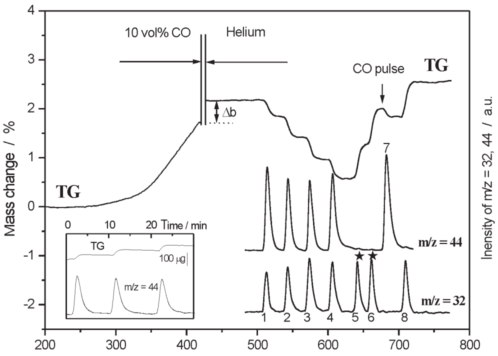

Fig. 10 Disproportionation of CO (10 vol%, balance He) over metallic cobalt followed by the combustion of the deposited carbon due to the pulses of oxygen. The further explanations are given in text. The inset presents the disproportionation occurring during pulses of CO over Co_{met} at 315°C, note the formation of CO_2 and mass gain due to carbon deposition

CO, balance He. The results, shown in Fig. 10, indicate that CO disproportionation starts at ca 250°C, note the beginning of the mass gain due to carbon deposition. The atmosphere was changed to pure helium after 1.21 mg of carbon had been deposited. This resulted in an apparent change of mass due to the buoyancy effect (marked as Δb in Fig. 10). The carbon deposited on the surface is very active and prevents the cobalt oxidation during contact with oxygen. The four 1 ml oxygen pulses (labelled 1–4) injected into the carrier gas stream reacted with the carbon: note the formation of CO_2 combined with a mass loss. The next two oxygen pulses (5 and 6, labelled by asterisks) led to the oxidation of the cobalt. This resulted in a mass gain with no CO_2 evolution. A CO pulse (7) followed by a pulse of oxygen (8) confirm the occurrence of the redox reactions in the system CoO–Co_{met} at higher temperatures.

The inset in Fig. 10 presents the change of mass of Co_{met} and the formation of CO_2 due to pulses of CO over metallic cobalt at a temperature of 351°C (within the range of COD decomposition). The results clearly indicate CO disproportionation at this temperature under transient conditions. This simulates well the time-limited interactions between gaseous and solid products during the decomposition period.

Formation of hydrocarbons

The course of TA and MS signals in an inert atmosphere at temperatures laying between oxalate dehydration and decomposition indicate that the separation of these two events is impossible. The results presented in Fig. 11, showing a magnified image of the course of the TG and *m/z*=2, 28 and 44 signals, indicate that the removal of two molecules of water is not complete before the beginning of the oxalate decomposition which results in the formation of CO and CO_2. The course of the *m/z*=28 mass spectrometric curve (characteristic for both CO and the strongest fragment of CO_2) compared to the course of *m/z*=44 (characteristic for CO_2 only) reveals that the evolution of CO begins earlier than the evolution of CO_2. The temperature onsets of the MS signals of carbon monoxide and carbon dioxide can be estimated as 223 and 254°C, respectively. Water evolves continuously in this range, note the shape of the *m/z*=18

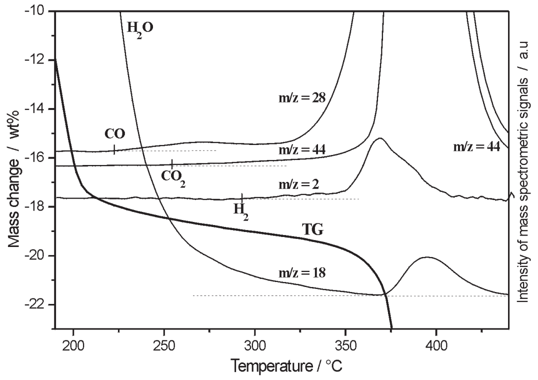

Fig. 11 End of dehydration and beginning of decomposition of COD in helium during heating with a rate of 10 K min^{-1}

signal before oxalate decomposition and the additional peak that occurs between 370–430°C. The quantification of the *m/z*=18 signal indicates that ca 2% of the total amount of hydrated water is evolved during COD decomposition.

The evolution of water during the beginning of oxalate decomposition explains the presence of the hydrogen (*m/z*=2 signal) which is formed in the reaction: $CO+H_2O=CO_2+H_2$. The equilibrium of this reaction is shifted to the right at temperatures of COD decomposition. The value of the equilibrium constant which amounts to 27.67 and 9.22 at 600 and 700 K, respectively, confirms the possibility of the formation of detectable amounts of hydrogen. Its concentration decreases distinctly during the main course of CO and CO_2 evolution indicating a Fischer–Tropsch reaction catalysed by the newly formed metallic cobalt. Methane is formed as a main product in this reaction which is confirmed by the intensity of the *m/z*=15 mass spectrometric signal. The less intensive *m/z*=27 signal indicates the formation of higher hydrocarbons as well. The formation of methane is clearly visible during the decomposition of COD in hydrogen (Fig. 2).

In order to investigate more exactly the reaction between CO, CO_2 and hydrogen in the presence of active metallic cobalt under conditions of COD decomposition, two experiments were carried out:

(i) the Co_{met} sample obtained by the decomposition of COD in hydrogen was heated at a rate of 10 K min^{-1} in an atmosphere of CO_2 and H_2 mixed in the ratio 1:2 (Fig. 12A).

(ii) pulses of CO_2 were injected into a system in which Co_{met} was heated in an atmosphere of 20 vol% H_2, balance helium (Fig. 12B)

The goal of the first experiment was to check the range of methane formation under steady-state concentration of the gaseous reactants. The second experiment was used to calculate the yield of methane formed under the transient conditions

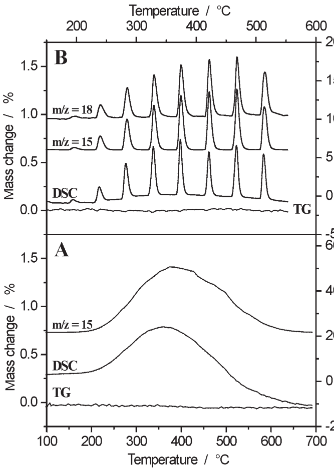

Fig. 12 Formation of methane and water due water gas shift and Fischer–Tropsch reactions: A) heating of Co_{met} in CO_2:H_2 atmosphere, B) pulses of CO_2 over Co_{met} heated in 20 vol% H_2

characteristic for COD decomposition. Experiment (i) confirmed that the exothermic process of methane formation according to the reaction $CO_2+4H_2=CH_4+2H_2O$ begins under the applied experimental conditions at ca 190°C (heating rate 10 K min^{-1}, total gas flow 50 ml min^{-1}, mass of Co_{met} 11.0 mg). The maximal yield of methane formation occurs at ca 400°C. At higher temperatures the formation of methane decreases distinctly due to the change of the equilibrium constant (412.3, 7.86 and 0.344 at 700, 800 and 900 K respectively). The yield of the methane formed, as calculated from the results of the transient experiment (ii), amounts to ca 21% according to the stoichiometric Eq. (9).

Discussion

The present results and a critical consideration of the published data clearly indicate that an evaluation of the TG and DTA/DSC signals alone is not sufficient for the determination of the mechanism of COD decomposition. The several secondary reactions change the composition of the solid and gaseous products and influence the course of the thermoanalytical curves. Observed mass changes and/or thermal effects are not intrinsic values of the oxalate decomposition but are the sum of many additional reactions occurring simultaneously alongside the main reaction. The explanation of the complicated course of COD decomposition is possible only by the use of additional techniques. These must investigate the composition of the gaseous phase and provide the opportunity to investigate the gas–solid reaction in situ, i.e. under conditions that exist during the decomposition. The application and usefulness of the particular TA techniques used in the determination of the COD decomposition mechanism are discussed below.

Application of thermogravimetry

Observed mass changes during COD decomposition are not only due to the primary reaction but also to additional gas–solid processes occurring in the system during, and/or after decomposition. The interpretation of the stoichiometry of the decomposition based on a TG signal is rendered more difficult by the relatively small differences in mass change as related to the various compositions of the solid products. Under a reducing atmosphere, the only product reported in the literature is metallic cobalt, the reported mass loss of 67.5 wt% [26] agrees well with the stoichiometric value of 67.78% required during Co_{me} formation. The mass loss observed by us during the heating of cobalt oxalate in a hydrogen atmosphere amounted to 67.7 wt% confirming the formation of Co_{met} as the final product of the reaction. This mass change results from the primary reaction and additional gas–solid processes occurring in the system during, and/or after decomposition, and therefore cannot be considered as an intrinsic value for COD decomposition.

The occurrence of the secondary reactions has also to be taken into account when heating COD in an oxygen-containing atmosphere. The oxalate decomposition is overlapped by strong oxidation processes. Both solid products, CoO and very active metallic cobalt, are oxidised immediately after formation to Co_3O_4, which decomposes further, at higher temperatures, back to CoO (inset in Fig. 3). The stoichiometric mass loss during formation of Co_3O_4 amounts to 56.12 wt% (56.0% found in the presented paper), the values reported in the literature vary between 53.8 [24], through 54.7 [40], 55.0 [22], 55.9 [13] to 56.0% [11, 20].

In both cases, i.e. under oxidising and reducing atmospheres, the composition of the solid products Co_{met} or Co_3O_4 can be unambiguously confirmed by the TA results due to the reasonable agreement of the experimental mass losses with the stoichiometric calculations. It is also easy to confirm the existence of Co_3O_4 by XRD analysis, but the conformation of the phase composition after heating in hydrogen can be difficult due to the pyrophoric character of Co_{met} which reacts violently with oxygen even at room temperature. Before exposure to air, it is necessary to passivate the Co_{met} by exposing it to an atmosphere containing only a small amount of oxygen. This leads to the formation of a thin oxide layer and prevents any further oxidation (Fig. 6). The partial oxidation of Co_{met} at room temperature as determined by us (formation of 2.9 wt% of CoO) coincides well with the results of [41]. The authors have found the traces of oxygen, equivalent to the presence of 3.0 wt% of CoO, in the final products from the reduction of cobalt oxides under severe conditions (650°C). The commercial Co_{met} samples (e.g. Johnson–Matthey, Stock No 10456) contain similar amounts of CoO. The determination of its content by the reduction in hydrogen (data not submitted) indicated the presence of 2–3 wt% of CoO.

Surprisingly, the literature data shows that during the decomposition of COD in an inert gas the interpretation of the TG data is the most controversial. The following mass losses have been reported during the decomposition of COD in an inert atmosphere: 61.2 [37], 61.8 [38], 63.2 [40], 63.9 [24], 65.0 [23], 65.2 [24], 65.5 [10], 65.8 [38], 65.9 [35], 66.0 [11], 66.4[20] and 67.7% [22]. The value found in the presented study is 66.6%.

The stoichiometric values of the mass losses of COD during the formation of the respective solid products are as follows:

Co_{met}	67.78%
CoO	59.04%
Co_3O_4	56.12%

The dependence between mass loss and CoO content is presented in Fig. 13. The presented relationship relates to the system Co–CoO only due to the fact that only one oxide, namely CoO, was detected by XRD analysis among the decomposition products under a helium atmosphere. The crucial question as to whether the CoO is formed during COD decomposition or later in a secondary reaction with oxygen traces will influence the conclusion concerning the course of the reaction. The formation of CoO in the primary reaction would indicate the rupture of C–O bonds (reaction 2). This is generally not assumed in the case of cobalt oxalate, the metallic cobalt is thought to be formed as one phase only, according to generally accepted classifications of oxalate decomposition. The comparison of, as reported in the literature, mass losses with the relationships depicted in Fig. 13 show unequivocally that the solid

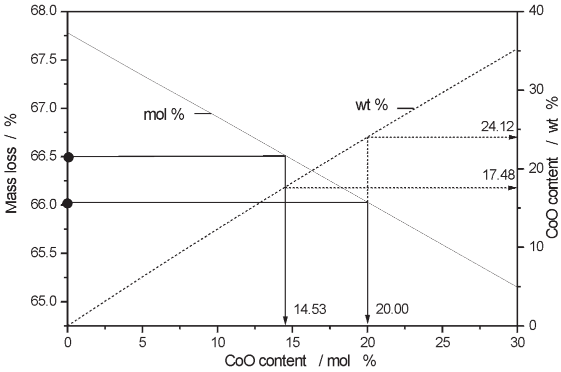

Fig. 13 Determination of CoO content in the solid products from the observed mass loss during COD decomposition. For the observed mass loss 66.05% the CoO content amounts to 20.00 mol% and 24.12 wt%

product contains a large amount of CoO beside the main phase Co_{met}. Its content varies from 0.7 [22] to ca 75 mol% [38], indicating: (i) a very distinct influence of the experimental conditions on the secondary reaction of Co_{met} oxidation, or (ii) a very different contribution of both possible mechanisms of the decomposition to the overall process.

Our results reveal that there are two main reasons for the discrepancies in the experimental results reported in the literature. The main reason is the high reactivity of the newly formed Co_{met} which reacts with any traces of oxygen present in the system. Even if all the oxygen traces that are accidentally introduced into any thermoanalytical system during sample handling are very carefully removed, a flow of 50 ml min^{-1} over a 30 min period of carrier gas with a purity of 99.996 vol% (balance oxygen) is sufficient to supply enough oxygen to oxidise 10% of the Co_{met} formed during the decomposition of 10 mg of COD.

The second factor that changes the course of the recorded TG curves and leads to an observable difference of mass loss is the occurrence of the secondary redox-reactions between the solid and gaseous products formed during the decomposition of COD in an inert atmosphere. The rate of the particular reactions can vary, depending on the experimental conditions, which change the progress of the gas–solid reactions during the relatively short transient period of COD decomposition. This problem will be discussed in the next paragraph.

It emerges from the presented results (Fig. 11) that the correct determination of mass loss characteristic for one, particular stage of COD decomposition i.e. dehydration or oxalate decomposition, is impossible. The almost horizontal dependence between mass loss and temperature between the first and second stages (Figs 1–3) apparently allows the determination of the Δm characteristic for the dehydration. This arbitrary value cannot be correct because the MS curves indicate an overlapping of both processes. The decomposition of the oxalate begins before the total evolution of water from the sample is complete; moreover, about 2% of the total water content is released during the second stage. This contribution of residual water to the mass change during the second stage (2 from 19.67%) introduces an error of ca 0.4% (Fig. 13) which gives an error of ca 4% in CoO content determination. The only possible way to interpret the TG curve correctly is by determining the total mass changes that occur during both processes. This procedure requires a careful determination of the TG-baseline in order to avoid errors caused by the buoyancy effect. It could, by changing the Δm by only 0.1%, lead to an inaccuracy in CoO determination in the order of 1%.

All the above remarks illustrate the difficulties in the correct application of TG signals when determining the composition of the solid products (amount of CoO). This is decisive for the interpretation of the mechanism of COD decomposition. The application of XRD can cause severe problems or even rule out an exact compositional analysis. This is due to the fact that, on one hand, XRD will detect both, primary and secondary CoO, on the other, that small amounts of CoO (below ca 4 wt%) will not be detected (Fig. 7). The one and only efficient method seems to be to determine the CoO in situ, immediately after the completion of the oxalate decomposition. Such a method, based on Pulse TA®, as used in the present study has shown that the amount of CoO in the solid products of the decomposition amounts to 12.9 mol% (15.8 wt%). It confirms that the decomposition of COD proceeds simultaneously via both paths, according to reactions (2) and (3).

This result is of importance for the preparation of dispersed cobalt by the oxalate route. In contrary to common opinion, it is impossible to obtain a pure cobalt phase during the decomposition of COD under an inert atmosphere. The formation of CoO during decomposition has to be accompanied by the formation of carbon monoxide as was confirmed by our results.

Application of differential thermal analysis

The application of DTA/DSC signals for the confirmation of certain types of COD decomposition mechanisms is much more difficult and uncertain than with thermogravimetric data. Accurate and reliable thermodynamic values of the Gibbs free energy and the enthalpy of the formation of the reactant are missing, data reported in the literature are not certain and therefore the comparison of experimental values with those from thermodynamic tables is of little value. The main problem, however, is the impossibility of determining the intrinsic value of the reaction heat of COD decomposition. Observed thermal effects in reducing and oxidising atmospheres are the sum of the enthalpy changes of the decomposition and the secondary reactions of gaseous and solid products with the surrounding atmosphere. Lack of knowledge of the kind of reactions that occur and their yields and thermal effects, makes the interpretation of experimental $\Delta_r H$ values incorrect.

The simplest case is the determination of $\Delta_r H$ of COD dehydration. The type of atmosphere changes only the sensitivity of the DTA signals but has no influence on the intrinsic value of the heat of the reaction whereby two water molecules are removed. The heats of dehydration under helium, 20 vol% of hydrogen and 20 vol%

oxygen, amounted to 98.0, 99.1 and 97.1 kJ mol^{-1}, respectively. The reported data presents the mean value from four measurements made in each atmosphere.

The differences of the heats of dehydration reported in the literature are not significant. Their values vary from 88 [43], through 96 [43], 97 [21], 100 [27], 101 [21] 102 [24], 107 [9], 112 [21], 113 [9], 114.5 [34] up to 141 kJ mol^{-1} [24] for an inert, oxidising and self-generated atmosphere. Much less consistent are the values of the heat of the decomposition of the oxalate. This is, however, fully understandable because the observed thermal effects are the sum of the primary and several secondary reactions occurring in the system during the second stage of the COD heating.

The values of the changes of the enthalpy and Gibbs free energy listed in Table 1 clearly confirm that the observed thermal effect on the DTA/DSC curves cannot be related to the decomposition of COD itself. This is clearly illustrated by the comparison of DTA curves for COD decomposition under three different atmospheres as presented in Fig. 14 (note the change of scale of the DTA signal in oxygen to allow a better comparison of the curves). In an oxidising atmosphere the large exothermic effect of the oxidation, of both Co_{met} and CoO, overlap the relatively small effect of COD decomposition which results in the global exothermal event. With hydrogen, the situation is even more complicated due to the occurrence of highly exothermal secondary gas–gas reactions. The reduction of CoO, present in solid products, proceeds with a relatively small exo-effect. The enthalpy change during the reduction of CoO by H_2 amounts to only –10.2 kJ mol^{-1}, which is much too little to explain the change of the endothermic process of COD decomposition into its observed exothermic effect. The exothermic character of the overall process results from the secondary reactions of hydrogen with the gaseous products of COD decomposition, i.e. CO and CO_2. Without knowledge of the course and yield of these processes, any quantitative interpretation of the thermal events is impossible.

The application of thermodynamic data can also not help in the interpretation of DTA/DSC signals in the case of decomposition under an inert atmosphere. Firstly, the course of the secondary reactions is unknown; secondly, the reported values of the heat of COD formation are divergent and uncertain. Any trials of the quantitative in-

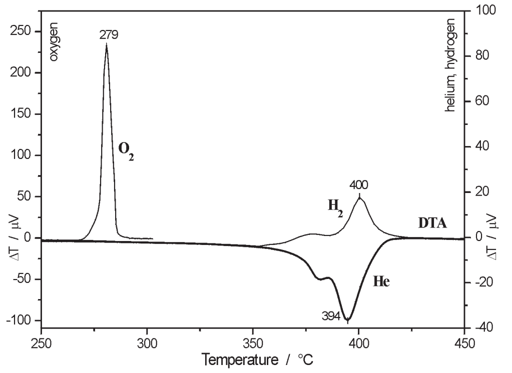

Fig. 14 DTA signals recorded during decomposition of COD in O_2, H_2 and He, respectively. Note change of the sensitivity of ΔT axis for decomposition in oxygen

terpretation of DTA signals in order to help interpret the mechanism are unsuccessful. Conformation of this remark can be found in a very interesting paper of Coetzee *et al.* [24] concerning the COD decomposition. The authors were not successful in the quantitative interpretation of the observed thermal effects due to the lack of a definite thermodynamic value for the heat of COD formation.

Without knowledge of the real course of the reaction and without good thermodynamic data one cannot successfully interpret the mechanism of the reaction based on DTA results. This remark is well illustrated by the observed discrepancies in the reported heats of the COD decomposition under inert atmospheres. Reported values vary from 30 [27] through 65.6 [9], 79.4 [21], 97.5 [24], 124.1 [21] up to 142.1 kJ mol^{-1} [17]. Our determination of the heat of the reaction for the decomposition of COD in helium gave a value of 49.4 kJ mol^{-1}. Reported heats of reaction under an oxidising atmosphere vary between –43.6 [11] and –261 kJ mol^{-1} [9], our value was found to be –159.5 kJ mol^{-1}. To

Table 1 The values of the enthalpy of the formation Δ_fH, the heat of the reaction Δ_rH and Gibbs energy of reaction Δ_rG at 600 K for reactions occurring during COD decomposition (in kJ mol^{-1})

Reaction	Δ_fH	Δ_rH	Δ_rG	References
$CoC_2O_4{\cdot}2H_2O$ formation	–1640			[24]
CoC_2O_4	–882			[46]
	–820			[24]
	–851			[47]
	–869			[48]
	–886			[24]
$CoC_2O_4=Co+2CO_2$[a]		94.2	–67.4	[46]
		32.4		[24]
		62.4		[47]
		81.4		
		98.4		[24]
$CoC_2O_4=CoO+CO+CO_2$[a]		143.2	–28.4	[46]
		81.4		[24]
		111.4		[47]
		130.4		[48]
		147.4		[24]
$CoC_2O_4+2/3O_2=1/3Co_3O_4+2CO_2$[b]		204.5–270.6	–293.5	[24, 46–48]
$Co+1/2O_2=CoO$		–234.6	–191.6	[49]
$Co+2/3O_2=1/3Co_3O_4$		–303.0	–226.1	[49]
$CoO+CO=Co+CO_2$		–49.0	–39.0	[49]
$CoO+H_2=Co+H_2O$		–10.2	–22.5	[49]
$2CO=CO_2+C$		–173.4	–66.1	[49]
$CO+H_2O=CO_2+H_2$		–38.9	–16.6	[49]
$CO_2+4H_2=CH_4+2H_2O$		–179.0	–55.9	[49]

[a,b] the values of the heat of the reaction were calculated using the heats of formation taken from the cited references

our knowledge, no reports exist in the literature concerning the heat of reaction of the COD decomposition in hydrogen. The value found by us was –21.6 kJ mol^{-1}.

Evolved gas analysis

The thermodynamic data, submitted in Table 1, of possible primary and secondary reactions indicates that these reactions, under equilibrium conditions, can take place within the temperature range of COD decomposition. However, some of these reactions can be hindered for kinetic reasons. Theoretical prediction of their occurrence, therefore, is of little value and has to be confirmed experimentally. This confirmation is difficult due to:

(i) The transient character of the processes. The concentration of gaseous reactants varies considerably over relatively short periods of time. The confirmation of possible processes should be made under conditions which simulate the real decomposition process. This has been done, in our work, by injection of the particular reactants into the carrier gas stream at temperatures that lay within the range of COD decomposition.

(ii) The possible overlapping of several gas–solid and gas–gas reactions. To obtain more information concerning the process under investigation the applied technique has to provide the opportunity to quantify the evolved gases.

Both of the above mentioned difficulties were avoided, to a large extent, due to the application of the Pulse TA® technique which enables quantitative investigation of gas–solid and gas–gas reactions under transient conditions. The proposed course of COD decomposition, taking the results of EGA into account, is as follows.

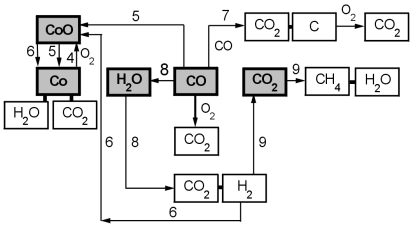

Fig. 15 Secondary reactions occurring during decomposition of COD in helium. Primary products of decomposition are shown as grey rectangles. The numbers by arrows refer to the numbers of the particular reactions described in the text (e.g. (7) indicates the disproportionation of CO)

The decomposition occurs mainly due to the rupture of cobalt–oxygen bonds, which results in the formation of Co_{met} and CO_2. In contradiction to common opinion, however, there is not only one mechanism of reaction, the second process occurs simultaneously with the first. It results in the breaking of carbon–oxygen bonds and the formation of CoO and CO. The shape of the *m/z*=28 and 44 signals (Fig. 11) reveals that this second mechanism dominates at the beginning of the decomposition. The amount of CO in the gaseous products, determined by quantifying the MS signals, was 6.0 vol%. This agrees well with the detected 12.9 mol% content of CoO in the solid products. The amount of CO should be half that of CoO, taking into account a simultaneous contribution of the stoichiometric Eqs (2) and (3) presented in the introduction.

It is necessary to emphasize that the amount of CoO determined after decomposition cannot be used as decisive proof of the quantitative contribution of the particular mechanisms. The amount of CoO can be changed:

(i) Slightly, by secondary reactions with reducing agents such as CO, CH_4 and H_2 formed during the decomposition.

(ii) Distinctly, by secondary oxidation with oxygen traces.

The determination of the CoO content in situ, just after completion of the decomposition, eliminates problems caused by process (ii) but small changes due to contributions from process (i) are unavoidable.

COD decomposition begins before all hydrated water is removed. Freshly formed Co_{met} acts as a very active catalyst in two secondary reactions. Firstly, hydrogen is formed in the water gas shift reaction i.e. the reaction between evolved CO and water. Secondly, hydrocarbons, mainly methane, are formed in the reaction of CO and CO_2 with hydrogen. In addition to these homogeneous catalytic processes occurs the heterogeneous disproportionation of CO, catalysed by Co_{met}. As a result of all these reactions, and under the experimental conditions applied by us, the composition of the gaseous phase during COD decomposition in helium is as follows (in vol%): CO_2: 92.2, CO: 6.0, H_2O: 1.6, CH_4: 0.2. The main reactions occurring during COD decomposition in an inert atmosphere are presented in Fig. 15.

The change of the composition of the gaseous products due to secondary reactions is more severe in hydrogen. The evolved gases contain (in vol%): H_2O: 39, CO_2: 32, CO: 11 and CH_4: 18. In an oxidising atmosphere, CO_2 was found to be the main gaseous product with detectable amounts of CO (ca 2 vol%) and traces of methane, as well.

All the above secondary reactions, water gas shift, Fischer–Tropsch, CoO reduction and, to a lesser extent, CO disproportionation, depend very much on the experimental conditions, especially those that change the rate of removal of gases from the system. The changing of any of these conditions influences the contribution of that particular reaction to the overall process. This, in turn, leads to changes in the observed mass losses and thermal events, which explains the discrepancies existing in the literature.

Conclusions

Cobalt oxalate decomposition is strongly dependent on the experimental conditions. These, in turn, have a great effect on the redox reactions of the solid products with the surrounding atmosphere. The primary reaction of the decomposition is also influenced by the secondary reactions of the gaseous products catalysed by very active, freshly formed, metallic cobalt. All these reactions have different dependencies on various experimental conditions such as reactant mass, packing of reactant in the crucible, shape, geometry and material of crucible, heating rate, flow rate and kind of carrier gas. The observed mass changes (TG) and thermal effects (DTA/DSC) are not only characteristic for the COD decomposition, they result from the contributions of all reactions to the overall process. Conclusions concerning the mechanism of decomposition are limited in their usefulness if they are not made with full knowledge of the courses of the particular processes involved and their resultant yields.

The main characteristic features of the reactions that occur during the heating of COD under inert, oxidising and hydrogen containing atmospheres can be summarised as follows:

- It is impossible to separate the processes of dehydration and decomposition. The largest amount of water is evolved during the low-temperature dehydration stage; the evolution of the remaining water overlaps the beginning of the decomposition. The reaction of water with CO, evolved during COD decomposition, results in the formation of hydrogen by the water gas shift reaction. This hydrogen, in turn, takes part in further secondary reactions, such as the Fischer–Tropsch, resulting in the formation of methane or the reduction of the solid product CoO. The residual water, amounting to ca 2 wt% of the total content, evolves during the decomposition of the oxalate. The quantification of the various stages of COD decomposition based only on the course of the TG curve is inaccurate and cannot be used to confirm the stoichiometry of these stages. The heat of dehydration amounts to 97 ± 1 kJ mol^{-1} in all of the investigated atmospheres.
- The metallic cobalt formed in the primary reaction is very active and in an oxidising atmosphere is immediately oxidised to Co_3O_4. In inert and hydrogen containing atmospheres, Co_{met} acts as a catalyst for some secondary reactions such as the formation of hydrocarbons, water gas shift reaction or CO disproportionation.
- Secondary gas–solid and gas–gas reactions distinctly influence the course of the TG curves but have an even greater influence on the DTA/DSC curves. The value of the heat of the primary, endothermic COD decomposition is changed by the exothermic effects of the formation of Co_3O_4 (in an oxidising atmosphere), methane and CO (in a hydrogen containing and/or inert atmosphere), or of CoO reduction. The values of heat of reaction in oxidising, reducing and inert atmospheres amount to –159.5, –21.6 and 49.4 kJ mol^{-1}, respectively.
- The solid products of the decomposition of COD in an inert atmosphere contain a substantial amount of CoO (ca 16 wt%). This contradicts the commonly held opinion that only metallic cobalt is formed under these conditions. The CoO content varies according to the secondary redox reactions caused by the oxidation of Co_{met} (by the unavoidable traces of oxygen present in any thermoanalytical system) or the reduction of CoO (by hydrogen, carbon monoxide or methane). Freshly formed Co_{met} is very active and oxidises very quickly. The determination of the amount of primary CoO has to be done in situ, immediately after the completion of COD decomposition. Cooling down, even in an inert atmosphere with only the slightest traces of oxygen, and the subsequent exposition of the decomposition products to air will change the

amount of CoO. This, in turn, makes the correct interpretation of the decomposition mechanism very difficult. The composition of the gaseous products of the decomposition in an inert atmosphere is as follows (in vol%): CO_2: 92.2, CO: 6.0, H_2O: 1.6, CH_4: 0.2.

- The only solid product of the heating of COD in a hydrogen-containing atmosphere is metallic cobalt. Due to its pyrophoric properties, the direct exposure to air results in violent exothermal oxidation. In order to obtain the product with as little of the oxygen phase(s) as possible it is necessary to passivate the Co_{met}. This can be done by the exposure of the sample to an atmosphere with low oxygen content. The formation of a surface layer of CoO prevents the further oxidation of Co_{met}. The lowest CoO content, from the Co_{met} samples passivated by pulses of oxygen at room temperature, was ca 2–3 wt%. This value is in good agreement with the oxygen content found in commercial metallic cobalt samples. The composition of the gaseous products in a hydrogen atmosphere was (in vol%): H_2O: 39, CO_2: 32, CO: 11 and CH_4: 18.
- The complex character of the processes of COD decomposition show that the interpretation of the mechanism based only on the TG curve is of little value. Mass change alone do not allow a deeper insight into all of the potential primary and secondary reactions that could occur. This explains the variation in kinetic parameters that were calculated on the basis of thermogravimetric data alone. The interpretation of values such as activation energy, varying from 167 [44], through 224 [31] to 455 kJ mol^{-1} [15] hardly seems to help in the explanation of the reaction mechanism. Coetzee *et al.* [45], in the paper concerning the kinetics of the decomposition of some mixed metal oxalates have concluded: '...Kinetic analyses usually do not allow any confident conclusions to be made.' Looking at Fig. 15, presenting the complexity of COD decomposition, it would be very difficult not to fully agree with this statement.

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