

A TGA/EGA study of the thermal decomposition of Cu–Co–Al mixed hydroxycitrates

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Abstract

The decomposition of metal hydroxycitrates under air and nitrogen atmospheres was studied by thermogravimetry and evolved gas analysis. The Cu–Co–Al amorphous precursors were prepared by the citric complexing method. The thermal decomposition of the catalytic precursors was carried out between 25 and 500°C. The overall decomposition mechanisms under the different atmospheres were interpreted in terms of a reaction scheme based on the decomposition of several structural arrangements proposed to account for the chemical composition of metal hydroxycitrates.

INTRODUCTION

Metal hydroxycitrates obtained by the complexation method [1,2] are interesting catalytic precursors because citrate complexes have an amorphous glass-like structure with no evidence of inhomogeneity [3,4]. However, these glassy precursors often decompose in air both rapidly and exothermically. A strong tendency for uncontrolled decomposition has been reported when the solid contains a metal catalytically active in oxidation reactions [5]. In a previous paper [6], we studied the preparation of Cu–Co–Al catalysts by the amorphous citrate process. These catalysts are used in the conversion of synthesis gas to methanol and higher alcohols under low pressure conditions [7–9]. By employing IR spectroscopy and differential thermal analysis (DTA), we studied the influence of the chemical composition on the exothermic transformations occurring during the decomposition of citrate precursors. In this paper we present a TGA/EGA

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TABLE 1

Composition of the starting solutions used for preparation of precursors

Precursor	R^a	r^a	Amount of metal nitrate (mol)			Citric acid (mol)
			$\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (y)	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (z)	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (x)	
A	1	1	0.020	0.020	0.040	0.067
B	3	1	0.030	0.030	0.020	0.060
C	12	1	0.019	0.019	0.003	0.028
D	3	0.5	0.020	0.040	0.020	0.060
E	3	5	0.050	0.010	0.020	0.060

^a Theoretical atomic ratios $R = (\text{Cu} + \text{Co})/\text{Al}$ and $r = \text{Cu}/\text{Co}$. y, z, x represent moles of Cu^{2+} , Co^{2+} and Al^{3+} , respectively.

thermal decomposition study of citrate precursors in air and nitrogen atmospheres in order to obtain insight into the chemical nature of the metal hydroxycitrates.

EXPERIMENTAL

Citrate precursors were prepared by the complexation method as described in ref. 6. The citric acid was added to a concentrated aqueous solution which contained all the required ions as metal nitrates. The compositions of the starting solutions are given in Table 1. In all cases an acid to metal ratio of 1 equiv of acid per 1 equiv (total) of metal was used. The solution was held at boiling temperature for 20–30 min and was then evaporated under vacuum in a revolving flask at 75°C until a viscous liquid was obtained. Finally, dehydration was completed by drying the sample in a vacuum oven at 80°C for 13 h. The chemical compositions of the five precursors used in this work are given in Table 2. A mass balance calculation showed that the metal ions present in the starting solutions were totally incorporated into the solid precursors.

The thermal decomposition of the precursors was studied in the range 25–500°C by thermogravimetry using a Cahn 2000 electrobalance. The amount of sample was 10–15 mg and the temperature program corresponded to a non-uniform temperature rise. The heating rates were progressively varied from 1.2°C min⁻¹ in the range 25–220°C to 5°C min⁻¹ from 220–300°C and a final step of 7°C min⁻¹ above 300°C. Nitrogen was carefully purified to remove water and traces of oxygen.

The precursor decomposition was also characterized by temperature-programmed decomposition and evolved gas analysis (EGA). The experiments were carried out at atmospheric pressure in a flow system provided with a fixed-bed reactor. Approximately 0.5 g of precursor was heated in air or nitrogen from room temperature to 500°C. Gases were sampled from

TABLE 2

Decomposition of precursors in air: weight losses in the range 100–500°C

Precursor	Metallic composition by AAS			Weight loss (%)			Structures I and II
	Co (%)	Cu (%)	Al (%)	Experimental	Predicted		
					w/o NO ₃ ^a	w NO ₃ ^b	
A	5.9	6.0	5.6	72.8	67.6	81.8	71.8
B	8.8	10.3	2.7	67.1	62.7	78.4	66.5
C	11.6	12.2	0.8	63.8	59.0	75.7	62.4
D	11.5	7.0	2.8	65.7	62.5	78.3	66.4
E	3.2	16.5	2.9	75.4	62.9	78.5	66.8

^a Weight losses calculated by considering that the precursors do not contain any nitrate ions.

^b Weight losses calculated by considering that all the nitrate ions were retained in the precursors.

a quartz reactor which was positioned in a temperature-programmed furnace. The gaseous effluent was analyzed by gas chromatography using a thermal conductivity detector and a Porapak QS column.

The carbon content of the samples was measured by combustion–volumetry.

RESULTS

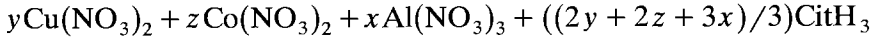
Nature of precursors: gravimetric results

The amorphous solid precursors consist of mixed metal hydroxycitrates. Previous workers [10–12] investigated the chemical structure of these compounds by IR spectroscopy. It was established that the citric acid chains in the precursor structure contain free carboxyl groups, carboxylate groups attached to metal ions, and intramolecular hydrogen bonds. Additionally, a variable amount of nitrate ions was always detected. The polyfunctionality of the citric acid (hydroxy and carboxylic functions) and the formation of chelate bonds favor the formation of citrate complexes with polymeric structures. There have been few suggestions for the structures of these complexes, not only in the case of citrates but also for related glycolate, tartrate or lactate complexes [13–16].

The weight losses detected during the decomposition treatments can guide speculation on the possible precursor structural arrangements. From the compositions of the various starting solutions (Table 1) and by considering that, after decomposition in air, the resulting mixed oxides contain

CuO, Co₃O₄ and Al₂O₃, the precursor formation–decomposition process can be represented as

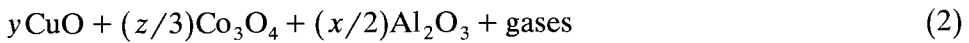
Starting solutions



Formation of precursor



Decomposition step (air up to 500°C)



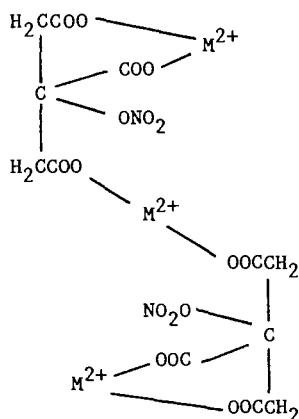
where CitH₃ is citric acid.

The crystallization water was not considered in the reaction scheme because the complete removal of water during the preparation procedure was assumed.

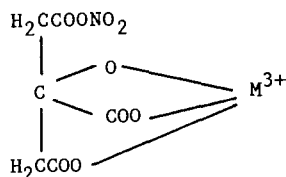
The experimental weight losses determined during the decomposition in air up to 500°C are given in Table 2. Two limiting cases regarding the presence of nitrate ions (in brackets in eqn. (1)) can be considered in the formation of precursors: (i) all the nitrate ions are retained in the precursor after the reaction described by eqn. (1) takes place; (ii) the precursors are formed only by metal citrates and do not contain any nitrate ions, which have been released as gaseous products during reaction (1). Based on these two situations, the weight losses calculated from eqn. (2) are presented in Table 2. By comparing these calculations with the experimental weight losses, it is clear that, although most of the nitrate ions were removed during the preparation steps, the precursors still contain part of the nitrate ions originally present in the starting solution.

Many structural arrangements may be postulated to represent citrate precursors. In the present case it appears preferable to avoid structural arrangements based on equimolar amounts of citric acid and metal nitrates [13], as the metal ions are in excess taking into account the composition of the starting solutions (Table 1). Structures **I** and **II** are the proposed formulations of the citrate precursors for divalent and trivalent metal ions, respectively. Similar structures have been postulated by Baythoun and Sale [16].

The formation of such structures would allow all metal ions to be bound to the citric acid molecules. The nitrate ions are incorporated by replacing either the hydrogen or the hydroxyl from the COOH groups (NO₂ and NO₃ radicals, respectively). Table 2 summarizes the weight losses predicted from the decomposition of structures **I** and **II**. Except for sample E, a reasonable agreement with the experimental weight losses was obtained.



Structure I. Divalent metal ions.



Structure II. Trivalent metal ions.

Decomposition: EGA results

The EGA curves corresponding to decomposition in air of precursor A are presented in Fig. 1B. The DTG curve is given as reference in Fig. 1A. The decomposition of precursor A in air occurred mainly through two exothermic transformations: (i) a low-temperature peak at 150–160°C ($\Delta W = 31\%$) and (ii) a high-temperature peak at 280–300°C ($\Delta W = 28\%$).

The evolved gas analysis results presented in Fig. 1B showed that in the range of the low-temperature transformation the gases eliminated were H_2O , CO_2 and NO_2 ; for the final decomposition step only CO_2 and H_2O were detected. Water and CO_2 traces overlapped considerably, although the CO_2/H_2O ratio increased during the high-temperature transformation. Water was also detected at temperatures below 100°C as a result of dehydration. The EGA data suggest that nitrate ions are completely removed in the first decomposition step, which is in good agreement with previous IR results [4].

The evolution of the carbon content in precursor A during the decomposition in air is shown in Fig. 2a. The elimination of carbon took place mainly during the high-temperature transformation, thereby indicating that the second decomposition step corresponded to the oxidation of the citrate

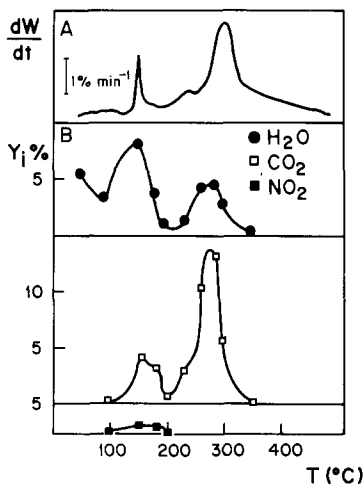


Fig. 1. Decomposition of precursor A in air. (A) DTG profile, in which the ordinates W represents the percentage weight loss; (B) EGA results, $Y_i\%$ are the molar fractions of the gaseous products, including air.

chains. The amount of carbon remaining in the decomposed sample was lower than 0.5%.

The DTG and EGA results obtained during the decomposition in N_2 of precursor A are presented in Fig. 3. Two main decomposition steps can be distinguished from the DTG curve. In the first step (20–280°C) an exothermic peak was detected with a maximum at 150°C ($\Delta W = 31.4\%$), which was very similar to that obtained for the decomposition in air. Moreover, the evolved gases were the same (H_2O , CO_2 and NO_2). In the second step (280–500°C) the general pattern of the DTG curve was clearly different from that recorded in air. The gases eliminated were CO_2 , CO and, in a

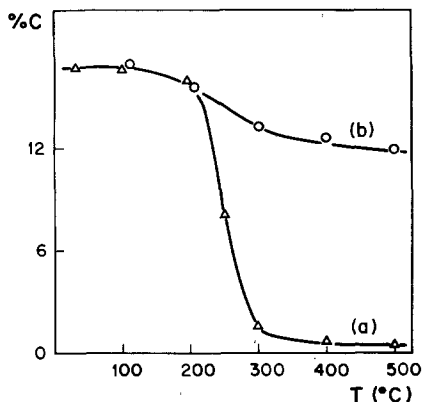


Fig. 2. Evolution of the carbon level in precursor A during the decomposition step. (a) Decomposition in air; (b) decomposition in nitrogen.

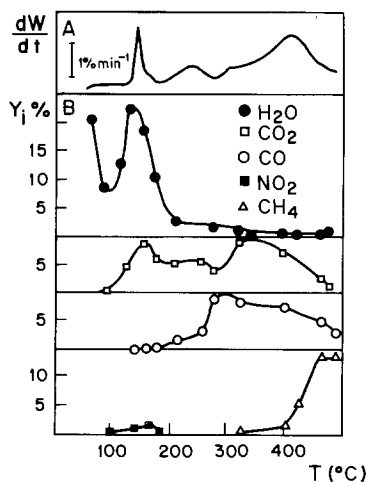


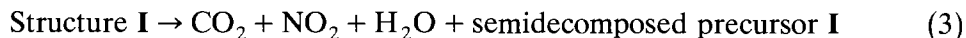
Fig. 3. Decomposition of precursor A in nitrogen. (A) DTG profile; (B) EGA results; $Y_i\%$ are the molar fractions of the gaseous products, including nitrogen.

minor proportion, H_2O . Methane was detected above ca. 400°C . The CH_4 concentration in the gaseous products increased with the temperature and exhibited an opposite trend compared with CO_2 and CO traces. On the other hand, the amount of carbon remaining in the decomposed sample was significant, as shown in Fig. 2b. Thus, although break-up of the citric acid structure took place, only a partial elimination of the carbon from the solid precursor was detected.

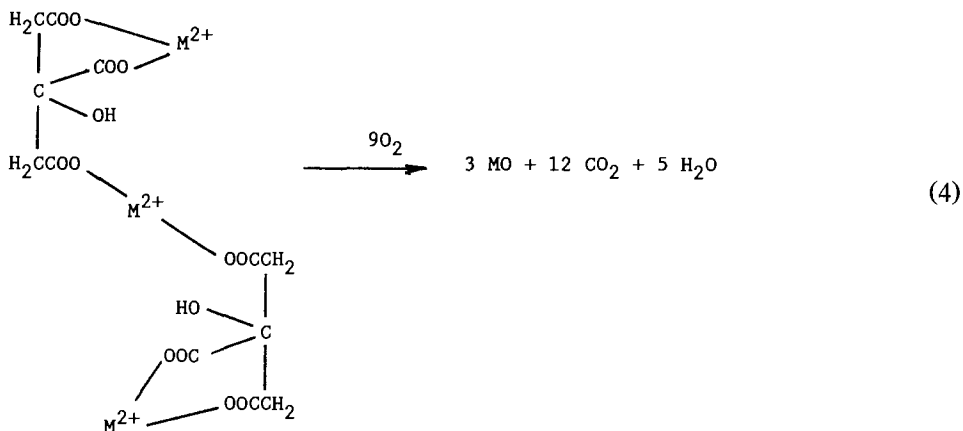
DISCUSSION

The decomposition mechanism of citrate precursors under air can be inferred from the results summarized in Figs. 1 and 2 and from previous results reported elsewhere [6]. EGA results (Fig. 1B) showed that during the low-temperature decomposition between 135 and 150°C the nitrate ions are removed from the precursors. This result agrees with those from previous studies [6] which demonstrated that calcination at 200°C eliminates most of the nitrate ions and free carboxyl groups, thereby suggesting that an internal exothermic reaction between nitrates and carboxylic groups takes place.

Figure 2 shows that the quantity of carbon eliminated in the low-temperature decomposition is not significant, thereby indicating that the chain structure of the citrates is preserved during low-temperature decomposition. Thus, this decomposition step may be represented as



where the citrate precursor represented by structure I (divalent metals) is taken as an example. The semidecomposed precursor is essentially an



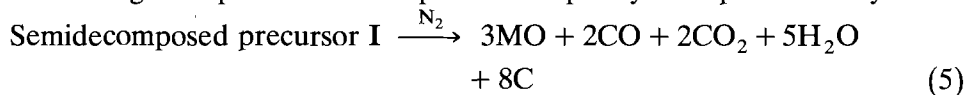
Semidecomposed precursor I.

anhydrous mixed citrate in which the nitrate ions have been substituted by OH groups. A possible structural arrangement is given in eqn. (4).

The high-temperature decomposition corresponded to the energetic oxidation of the citrate chains remaining in the semidecomposed precursors (pyrolysis step). The gaseous products detected during combustion of the citric acid structure were CO_2 and H_2O only (Fig. 1B). Therefore the formation of mixed oxides through the pyrolysis step may be represented by eqn. (4).

According to reaction (4), formation of MO occurs with simultaneous production of CO_2 and H_2O in a molar ratio of $\text{CO}_2/\text{H}_2\text{O} = 2.4$. This value is consistent with the experimental ratio of 2.8 determined from Fig. 1B by considering the amount of evolved gases above ca. 250°C . Similar reactions account for thermal decomposition in air of structure II (trivalent ions). Of course, additional oxygen consumption is included in eqn. (4) when divalent metal M^{2+} is oxidized to M^{3+} , as in the case of cobalt ions. The pyrolysis step eliminates carbon from the organic groups at relatively low temperature (Fig. 2), and rapid evolution of gaseous products leads to solids of open structure and high surface area.

Regarding the decomposition of citrate precursors in nitrogen, the DTG and EGA results showed that the decomposition mechanism in the low-temperature region up to ca. 250°C was the same as represented in eqn. (3) for decomposition in air. Above 250°C , decomposition in nitrogen involved breakup of citrate chains in several consecutive transformations without measurable thermal effect. Taking into account our EGA results shown in Fig. 3, the formation of mixed oxides from the semidecomposed precursor via the high-temperature decomposition step may be represented by

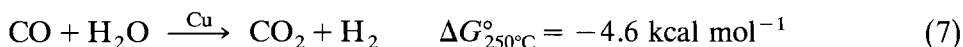


where again the chemical structure of semidecomposed precursor **I** given in eqn. (4) is taken as an illustration. Equation (5) accounts for such experimental observations as formation of residual carbon and generation of CO and CO₂. The metal oxides, MO, which are probably formed from the beginning of the high-temperature decomposition step, are susceptible to reduction in the presence of CO in the gaseous products according to



where the free energy change for the reaction (6) at 350°C is $\Delta G^\circ = -29.7$ kcal mol⁻¹ for Cu²⁺ and $\Delta G^\circ = -10.0$ kcal mol⁻¹ for Co²⁺. Indeed, metallic copper and cobalt have been detected by XPS after reduction [12].

The generation of CO began at approximately 220°C and increased rapidly with a maximum at 300°C. The maximum of the CO₂ curve was found at ca. 360°C. On the other hand, the quantity of water in the products was lower than the value expected on the basis of eqn. (5). These experimental observations suggest that the water gas shift (WGS) reaction occurs



It is well known that copper based catalysts like Cu/ZnO/Al₂O₃ have a high WGS activity between 200 and 250°C [17].

Finally, CH₄ was detected at 400°C; its concentration increased with increasing temperature as the CO and CO₂ concentrations simultaneously decreased. This behavior suggests that methane was generated by hydrogenation of CO and CO₂. It is well known that cobalt is one of the most active Group VIII metals for the methanation reaction [18].



Therefore the reaction scheme represented by eqns. (5)–(8) accounts for the main experimental observations: the metallic state of Cu and Co upon decomposition, the high amount of residual carbon, and the formation of CH₄ in the high-temperature region.

In conclusion, the decomposition mechanism of citrate precursors under air and nitrogen atmospheres was interpreted in terms of a reaction scheme based on the decomposition of several intermediate citrate complexes.

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