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## Online-Coupled TG-FTIR Investigations Of Cobalt Acetate Tetrahydrate



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### ABSTRACT

Thermal processes involved in the decomposition course of cobalt acetate tetrahydrate ( $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ ) in atmosphere of  $\text{N}_2$  and  $\text{H}_2$  were monitored by non-isothermal gravimetry. Results showed that the dehydration of the parent salt occurs in two steps. The dehydration step was followed by one-step major decomposition of the acetate group, forming intermediate basic acetate, which then produces  $\text{CoO}$  and  $\text{Co}$ , in treatment atmospheres of  $\text{N}_2$  and  $\text{H}_2$ , respectively. The conclusions were confirmed by monitoring solid residues and evolved gases employing IR spectrometry. A set of reactions linked to the decomposition of cobalt acetate was proposed to account for the solid and gas products detected

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### KEYWORDS

IR spectroscopy;  
Thermogravimetry;  
Decomposition;  
Cobalt acetate tetrahydrate.

### INTRODUCTION

The favored method for preparation of supported catalysts is often referred as impregnation and drying, in which porous supports are impregnated with a solution of the active metal, followed by evaporation of the solvent and calcinations in air to generate the oxidic phases that are precursors of the active (usually reduced) centers. Supported cobalt catalysts comprise one of the most important classes of

heterogeneous catalysts, due to their widespread applications, like NO reduction<sup>[1]</sup>, ammonia synthesis<sup>[2]</sup>, partial oxidation<sup>[3]</sup>, and Fischer-Tropsch synthesis<sup>[4]</sup>. Cobalt acetate is an interesting alternative to conventional cobalt precursor, enabling the preparation of cobalt-supported catalysts essentially through a one-step impregnation and decomposition mild route. Thermal decomposition of acetate is a feasible route to synthesize metal or metal oxide based catalyst<sup>[5,6]</sup>. Thermal decomposition of cobalt

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acetate has been the subject of several previous studies<sup>17-91</sup>. Atmospheres employed include vacuum, flowing N<sub>2</sub>, dry oxygen, air, water, and self-generated atmospheres. The intermediates and the end products were characterized by X-ray diffraction and IR and UV-VIS spectroscopy<sup>100</sup>. However, gases evolved during the thermal decomposition of cobalt acetate have received limited consideration. The present study set out to characterize the decomposition course of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O by thermogravimetry (TG). The gaseous decomposition products were analyzed by IR-spectroscopy. Additionally the intermediates and the end products were characterized by IR-spectroscopy.

### EXPERIMENTAL

#### Starting materials

The starting materials used in this experiment were AR grade Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, abbreviated as Co(Ac)<sub>2</sub>·4H<sub>2</sub>O, Ac = CH<sub>3</sub>COO<sup>-</sup>.

#### TG analysis

TG measurements were carried out using a Setaram Setsys 16 TG-DTA/DSC instrument. 5.0±0.2 mg of sample was spread thinly over the alumina crucible to minimize bed effects during decomposition of the cobalt acetate samples. The heating rate was 10°C/min, and the gas employed was N<sub>2</sub> or H<sub>2</sub> of high purity (>99.999%), at a flow of 40 ml/min.

#### IR analysis

IR spectra of residuals were obtained at a resolution 8 cm<sup>-1</sup>, between 4000 and 400 cm<sup>-1</sup>, using a model FTIR 410 JASCO (Japan). IR spectra of Co(Ac)<sub>2</sub>·4H<sub>2</sub>O and its decomposition products at several selected temperature (in different atmospheres) were obtained from thin, lightly loaded KBr-supported discs.

IR identification of gaseous decomposition products was done with the help of the TG-FTIR system composed of the Setaram Setsys 16 TG-DTA/DSC instrument and a Thermo Nicolet Nexus 670 Fourier transform infrared spectrometer. The transfer line used to connect TG and FTIR was a 1 m long stain-

less steel tube with an internal diameter of 2 mm, of which the temperature was maintained at 200°C. The TGA accessory of the IR spectrometer was used, in which the 45ml gas cell with a 200 mm path length was also heated at a constant temperature of 200°C. The IR spectra were collected at 8 cm<sup>-1</sup> resolution, co-adding 8 scans per spectrum. This resulted in a temporal resolution of 4.32 s. Lag time that the gas products went from furnace to gas cell was about 7 sec.

### RESULTS AND DISCUSSION

#### TG/DTG curves of Co(Ac)<sub>2</sub>·4H<sub>2</sub>O

The results of thermogravimetric measurements in H<sub>2</sub> and N<sub>2</sub> are presented in figures.1 and 2, respectively. The values in percentage of mass retained at selected temperatures during the thermogravimetric analysis are also presented in figures.1 and 2. Under the experimental conditions, Co(Ac)<sub>2</sub>·4H<sub>2</sub>O decomposition undergoes a maximum of four thermal processes, named as I ~ IV in the TG or DTG curves depicted in figures 1 and 2. Stages I,II, and III are common to all treatments, but stage IV obtained under H<sub>2</sub> atmosphere (figure 1) differs from that obtained under N<sub>2</sub> atmosphere (figure 2).

No matter the treatment atmosphere employed during the thermal decomposition of Co(Ac)<sub>2</sub>·4H<sub>2</sub>O, a large mass loss for stage I is registered in all the TG curves; it can be assigned with a high degree of cer-

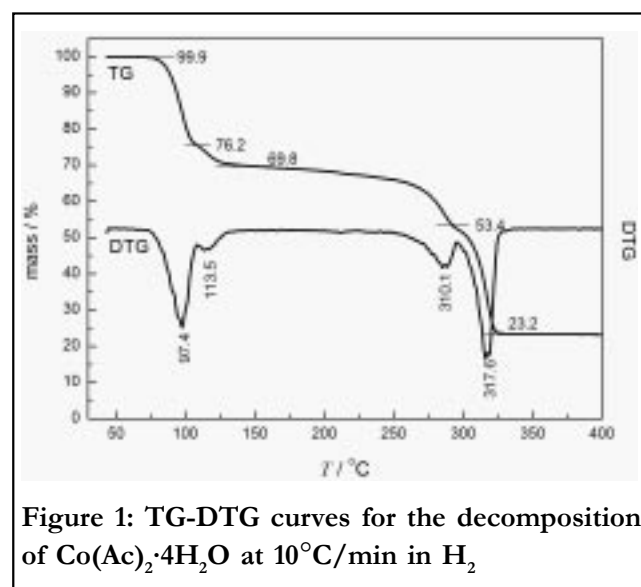


Figure 1: TG-DTG curves for the decomposition of Co(Ac)<sub>2</sub>·4H<sub>2</sub>O at 10°C/min in H<sub>2</sub>

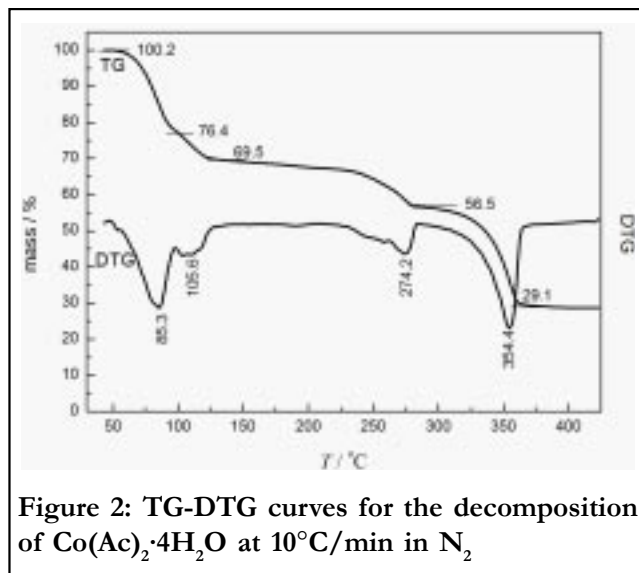


Figure 2: TG-DTG curves for the decomposition of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  at  $10^\circ\text{C}/\text{min}$  in  $\text{N}_2$

tainty to the dehydration of crystallized water in the initial precursor. The possible residue in  $\text{H}_2$  is  $\text{Co}(\text{Ac})_2 \cdot 0.49\text{H}_2\text{O}$  and that in  $\text{N}_2$  is  $\text{Co}(\text{Ac})_2 \cdot 0.74\text{H}_2\text{O}$ . After the dehydration is completed as stage II, the average mass percent recorded under  $\text{H}_2$  and  $\text{N}_2$  atmosphere are  $69.66\% \pm 0.42\%$  and  $69.56\% \pm 0.13\%$ , respectively, which are clearly below the value expected for the release of four water molecules (71.07%), indicating an evolution of additional amounts of materials to the gas phase. It is to assume that hydrolysis of surface acetate groups occurred during the dehydration of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ , resulting in simultaneous evolution of acetic acid to the gas phase, and generating cobalt acetate hydroxides,  $\text{Co}(\text{OH})_{0.08}(\text{Ac})_{1.92}$  in  $\text{H}_2$  and  $\text{Co}(\text{OH})_{0.09}(\text{Ac})_{1.91}$  in  $\text{N}_2$ .

The stage III in figures 1 and 2 correspond to the decomposition of the dehydrated intermediate. In  $\text{H}_2$ , the mass retained is  $53.54\% \pm 0.65\%$ , which is consistent with the theoretical value for the formation of  $\text{Co}(\text{OH})_{1.04}(\text{Ac})_{0.96}$ . Meanwhile in  $\text{N}_2$ , the mass retained is  $56.26\% \pm 0.43\%$ , which is compatible with the value expected for the formation of  $\text{Co}(\text{OH})_{0.88}(\text{Ac})_{1.12}$ .

The residual compositions for above stages are similar regardless of atmosphere used. However, the mass retained in  $\text{H}_2$  in step VI is  $23.16\% \pm 0.39\%$ , which is conform to the theoretical value for the formation of pure metal Co, while that in  $\text{N}_2$  is  $29.60\% \pm 0.50\%$ , which is conform to the theoretical

value for the formation of pure oxide CoO. After stage VI, no additional changes in the mass of the residue are observed in treatments of either  $\text{H}_2$  or  $\text{N}_2$ .

The quantitative TGA results indicates that the decomposition of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  is critically controlled by the reaction atmosphere. By comparing the results obtained for the thermal decomposition of the parent salt in  $\text{H}_2$  with those obtained in  $\text{N}_2$ , it is possible to propose the formation of either metallic cobalt or CoO, respectively. The average mass value retained after step II under two different types of atmospheres (about 70%) is well below that expected for stoichiometric loss of four water molecules (71.07%). The extra weight loss obtained during the dehydration step suggested the possible formation of a basic acetate as intermediated compound  $[\text{Co}(\text{OH})_x(\text{Ac})_{2-x}]$ , and in considering the value of weight loss obtained systemically for the residue of step I and II, we can assume the stoichiometry of the hydrolysis reaction to allow roughly an estimation of the x value for the formation of basic cobalt acetate.

### IR analyses of solid residues

Information regarding the pattern of the species generated during the decomposition of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  was obtained from FTIR measurements of solid residues obtained at different temperatures. As shown in figure 3, two important observations could summarize the IR spectra taken at different temperatures for both atmospheres:

1. The bands at 738, 810 and 881  $\text{cm}^{-1}$  in the IR spectrum of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  have been assigned to water librations and a two-phonon water mode, respectively. And the first two are identified as wag and twist vibrations of the molecules of water of crystallization<sup>[11]</sup>. These bands appear rather weak or disappear completely for the dehydrated or decomposed products.
2. The spectra for the dehydrated or decomposed products at different temperatures in both atmospheres are very similar. The region between 3000 and 3600  $\text{cm}^{-1}$ , which is attributed to hydroxide group vibrations, demonstrates that water molecules are absent in the dehydrated or decomposed products

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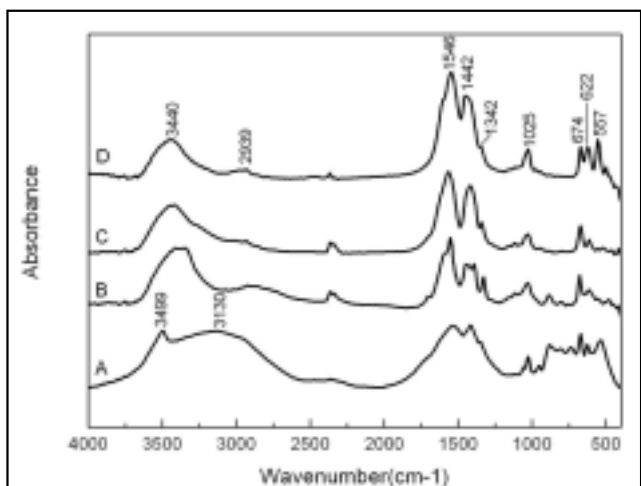


Figure 3: Absorbance vs. wave number curves at various temperature of solid residues from  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ , (heating rate:  $10^\circ\text{C}/\text{min}$ ; initial mass: 5.0mg;  $\text{N}_2$ ), in which A: parent salt; B:  $93^\circ\text{C}$ ; C:  $123^\circ\text{C}$ ; D:  $281^\circ\text{C}$

and that hydroxyl groups are still present in the species. Absorption band at  $2948\text{ cm}^{-1}$  is due to the characteristic C-H vibrations in acetate groups. The most interesting characteristic of the IR spectra is the maintenance of absorption bands of carboxyl groups. Peaks observed at  $1422\text{ cm}^{-1}$  attributed to symmet-

ric C=O vibrations and  $1548\text{ cm}^{-1}$  attributed to asymmetric C=O in the dehydrated or decomposed products. The IR spectra in the region of  $500\text{--}700\text{ cm}^{-1}$  are characterized with the acetate groups. The absorption band at  $535\text{ cm}^{-1}$ , attributed to water vibrations, is observed as a strong band in the IR spectra of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  only. The vibrations at  $616$  and  $676\text{ cm}^{-1}$  are easily assigned to the  $\text{CO}_2$  rocking vibration and symmetrical bending, respectively.

We conclude that  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  decomposes through the formation and subsequent decomposition of cobalt acetate hydroxides as a reaction intermediate.

### Online evolved gas analysis by TG-FTIR

The volatile decomposition products of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$  were identified using the TG-FTIR system. The volatile products in  $\text{H}_2$  were quite similar to that produced in  $\text{N}_2$ . The TG-FTIR evolution curve of the identified evolved gaseous species as absorbance vs. temperature in  $\text{N}_2$  can be seen in figures 4 and 5, respectively.

The bands at  $3735$  and  $1517\text{ cm}^{-1}$  observed between  $50$  and  $130^\circ\text{C}$  in stages I and II are attributed to the absorbance of gas water and can be related to

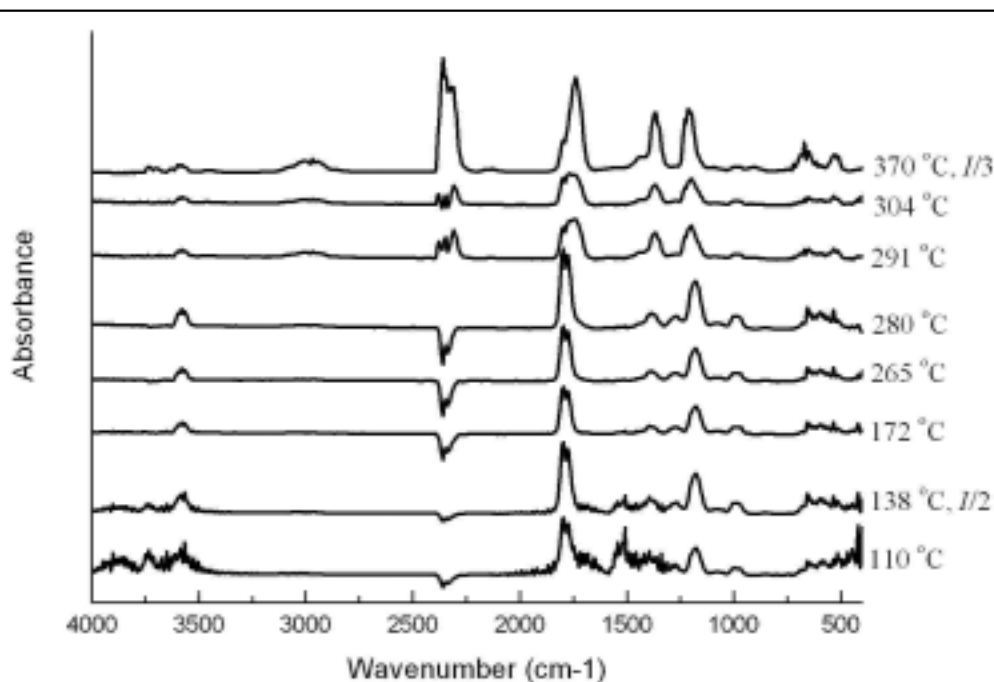
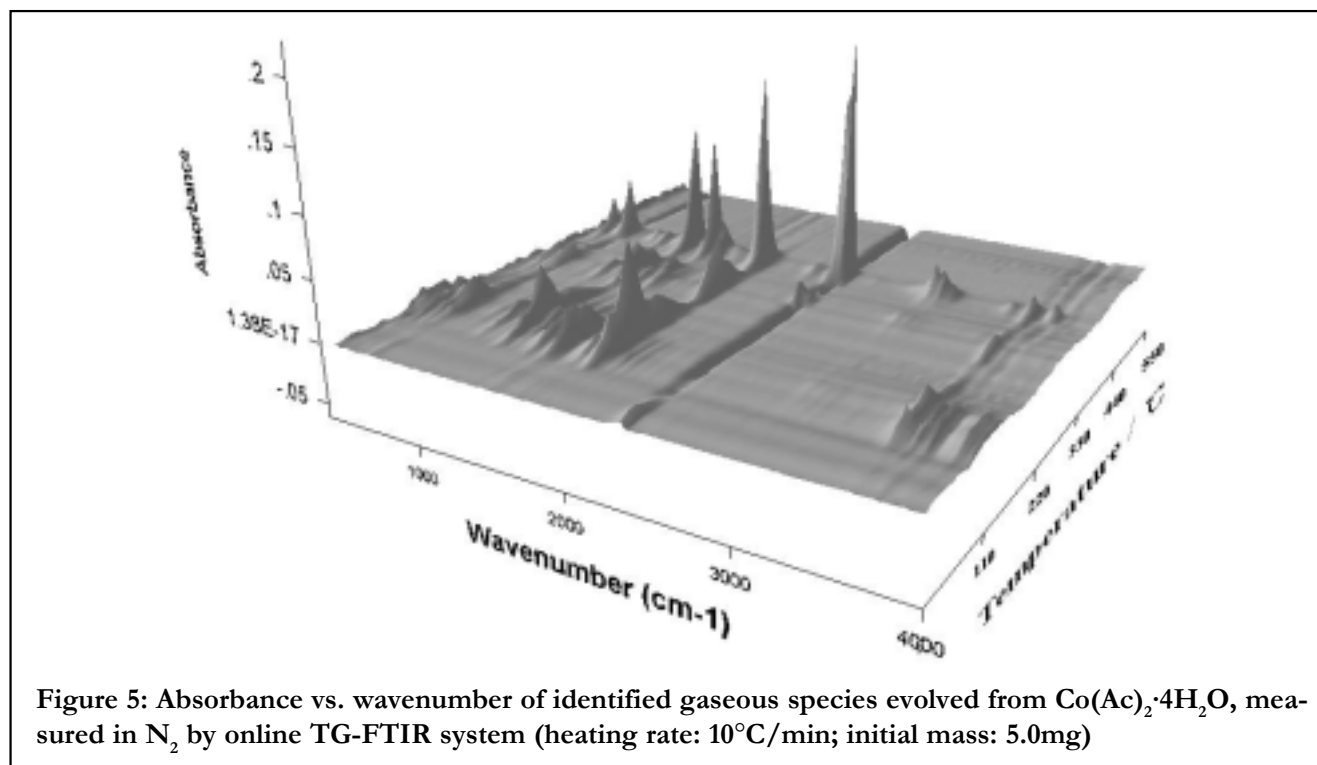
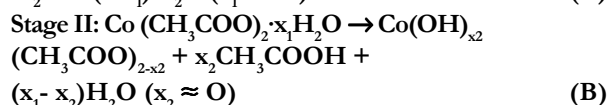
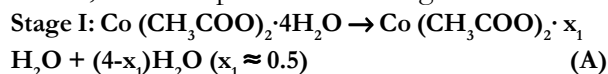


Figure 4: Absorbance vs. wavenumber curves of evolved gaseous species at various temperatures, (heating rate:  $10^\circ\text{C}/\text{min}$ ; initial mass: 5.0mg;  $\text{N}_2$ )

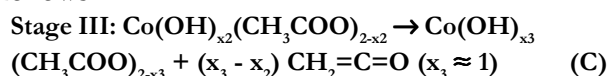


**Figure 5: Absorbance vs. wavenumber of identified gaseous species evolved from  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ , measured in  $\text{N}_2$  by online TG-FTIR system (heating rate:  $10^\circ\text{C}/\text{min}$ ; initial mass: 5.0mg)**

the dehydration of  $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ . In this temperature range, strong double bands at 1780 and 1800 ( $\text{CO}$ )  $\text{cm}^{-1}$  and single band at 3570 ( $\text{OH}$ )  $\text{cm}^{-1}$  observed can be related to acetic acid in gas, which expected to form due to the surface hydrolysis of the acetate groups. The absorbance due to gas acetic acid increases along with the increment of temperature. Thus, the main processes for stages I and II are:



In stage III, at  $170^\circ\text{C}$  the absorbance due to gas water disappeared. All the absorbance can be related to gas acetic acid till to  $265^\circ\text{C}$ . In support, the IR gas phase spectra in this stage exhibits weakening of the absorptions due to water and reinforcement of the absorption bands characteristic of acetic vapor. Thus, the formation of acetic acid at this stage may have occurred via the intervention of ketene ( $\text{CH}_2=\text{C}=\text{O}$ )<sup>[12]</sup> as follows:

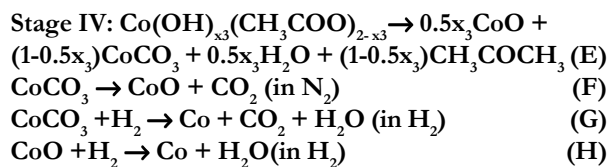


However, the IR absorption of ketene is unde-

tectable in the experimental conditions.

In stage IV, at  $290^\circ\text{C}$ , acetone ( $\text{CH}_3\text{COCH}_3$ ) is unambiguously identified during the thermal decomposition. The bands around 2984 ( $\text{CH}_3$  or  $\text{CH}_2$ ) and 1737 ( $\text{CO}$ )  $\text{cm}^{-1}$  are attributed to acetone. However, acetone production is not obviously detected below  $290^\circ\text{C}$ . At  $370^\circ\text{C}$ , the absorbance at 1780  $\text{cm}^{-1}$  ( $\text{CO}$ ) almost fully shifts to 1746  $\text{cm}^{-1}$  ( $\text{CO}$ ). Meanwhile, 3570 ( $\text{OH}$ )  $\text{cm}^{-1}$  band diminish significantly. Therefore, acetic acid is not the main species any more in the stage IV. Carbon oxides are also detected in this stage. Relatively high amounts of carbon oxides are produced during the major decomposition step of the acetate group. The intensity of bands between 2300 and 2370  $\text{cm}^{-1}$  related to carbon dioxide becomes stronger with increasing the temperature. The IR gas phase spectra in this stage exhibits weakening of the absorptions due to acetic acid vapor and reinforcement of the absorption bands characteristic of acetone and  $\text{CO}_2$ . Furthermore, the bands at 3735  $\text{cm}^{-1}$  related to the absorbance of gas water are detectable again in the stage. Acetone and carbon dioxide produced in stage IV may be due to the decomposition of acetate groups in basic cobalt acetate. Therefore,

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The evolution of acetone during stage IV suggests the involvement of  $\text{CoCO}_3$  as a short-lived intermediate.

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