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Gases evolved in the thermal decomposition of potassium cobalt hexacyanoferrate(II)

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Abstract

CO_2, N_2O, NO, NH_3 and NO_2 were found to be evolved from potassium cobalt hexacyanoferrate, $K_2CoFe(CN)_6 \cdot 1.4H_2O$, when heated at temperatures between 240 and 360°C in synthetic air. Determinations of the gases were carried out with an FTIR spectrometer. The amount of carbon dioxide released corresponded closely with the amount of carbon initially present in the sample. However, the total amount of nitrogen obtained in the nitrogen-containing gases was only 39% of the initial nitrogen. It is assumed that N_2, which is undetectable by IR spectroscopy, was also released and made up the remaining 61% of the total nitrogen emission. Since the compound does not contain any hydrogen other than that in water, we assume that the hydrogen in the ammonia released originated from the water evaporated at lower temperatures and condensed on the tube walls between the pyrolysis oven and the detector gas cell.

Keywords: Decomposition; FTIR; Gas; Potassium cobalt hexacyanoferrate

1. Introduction

A previous study, based on X-ray diffractometric and thermoanalytical methods, on the thermal decomposition of potassium cobalt hexacyanoferrate(II) [1] revealed that $K_2CoFe(CN)_6 \cdot 1.4H_2O$ loses its water in the temperature range of 20–170°C. Between 230 and 350°C, $K_2CoFe(CN)_6$ decomposes and forms the solid products K_2CO_3, Co_3O_4, Fe_2O_3 and $CoFe_2O_4$. According to the evolved gas analyses, gases were given

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off in this temperature range. In this study, these gases were identified. For the identification and concentration measurements of the gases we used FTIR gas detection, which is a rather novel technique.

2. Experimental

Samples of potassium cobalt hexacyanoferrate (0.2 g) were placed in Pyrex glass tubes and heated in a muffle furnace. "Synthetic air", containing 20% O_2 and 80% N_2, was passed into the furnace at a flow rate of 1 dm^3 min^{-1} (Fig. 1). From the furnace, the gas flow was directed through a 1-m long stainless steel tube to the white cell (2.4 m optical path length, volume 1.5 l) of the FTIR spectrometer (GASMET, Temet Instruments). The IR spectrum of the gas mixture was measured in the range 4000–950 cm^{-1}. Analysis of the multicomponent spectra was based on reconstruction of the measured spectra as a linear combination of the 'library' spectra of the pure compounds [2]. This method enables quantitative analysis at ppm levels for mixtures of approximately twenty gases within a few seconds.

Prior to raising the oven temperature, the system was flushed with the carrier gas until there was no sign of carbon dioxide or water vapour in the spectrum. This procedure was carried out at room temperature and took upto 2.5 h. Thereafter, the temperature was increased manually at an average rate of 1.7°C min^{-1}. The temperature of the gas cell was held at 41°C during the measurements. The IR spectrum of the gas mixture was recorded for 20 s at 10°C intervals in the ranges of 30–230°C and 310–360°C, and at about 5°C intervals in the range 230–310°C. The temperature was measured with an FeCuNi thermoelement placed between the sample-containing glass tube and the furnace wall. The temperature of the oven was stopped at 360°C, but the spectrum of the gas was followed until the concentrations of the gases had dropped to zero.

The effect of oxygen on the nature of the decomposition gases was considered by carrying out measurements in pure N_2 and Ar atmospheres as well.

3. Results and discussion

Up to about 200°C, only water vapour was seen in the IR spectrum of the decomposition gases of potassium cobalt hexacyanoferrate. At 230–240°C, ignition of

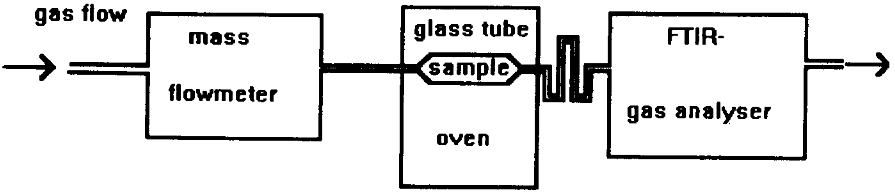

Fig. 1. Experimental apparatus used in the detection of gases in the thermal decomposition of potassium cobalt hexacyanoferrate(II).

the compound took place and the gases detected were, in order of decreasing concentration, CO_2, N_2O, NO, NH_3, NO_2 and water vapour (Fig. 2). The excellent fit of the measured spectra with a linear combination of the library spectra of the gas mixture given above indicates that it is highly improbable that there were any other gases present (Fig. 3). The flat areas in Fig. 3 represent wavenumber ranges where the absorbance was too strong to be included in the analysis.

On ignition, the temperature of the sample increased suddenly by approximately 50°C; thereafter it dropped rapidly. Therefore, temperatures between 240 and 290°C could not be measured accurately. The shoulders in the concentration curves (Fig. 2) were caused by this rapid decrease in the temperature after ignition.

In a previous study of the thermal decomposition of potassium cobalt hexacyanoferrate [1], it was observed that all the water was released up to 170°C. Fig. 2, however, shows that in this study water was also detected even at much higher temperatures. We assume that this water had condensed at lower temperatures on the walls of the tubes and the cell and was released when the temperature was increased. The hydrogen in ammonia is also assumed to originate from water since this is the only hydrogen-containing compound in the system. It is, however, possible that the compound was somewhat hydrolysed due to rinsing with water after its synthesis:

$$K_2CoFe(CN)_6 + H_2O \rightarrow H_2CoFe(CN)_6 + 2K^+ + 2OH^-$$

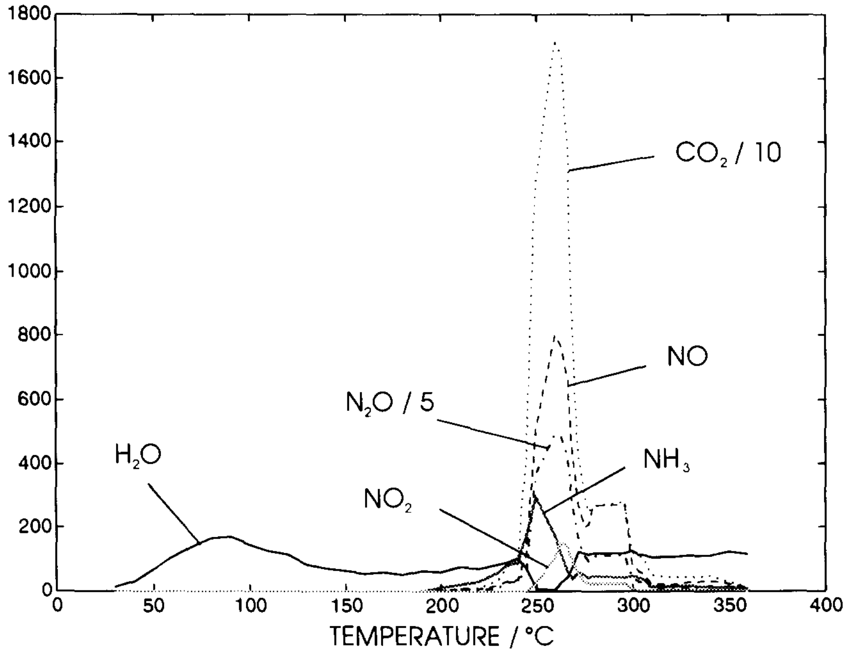

Fig. 2. Concentrations of decomposition gases of $K_2CoFe(CN)_6 \cdot 1.4H_2O$ in synthetic air as a function of temperature.

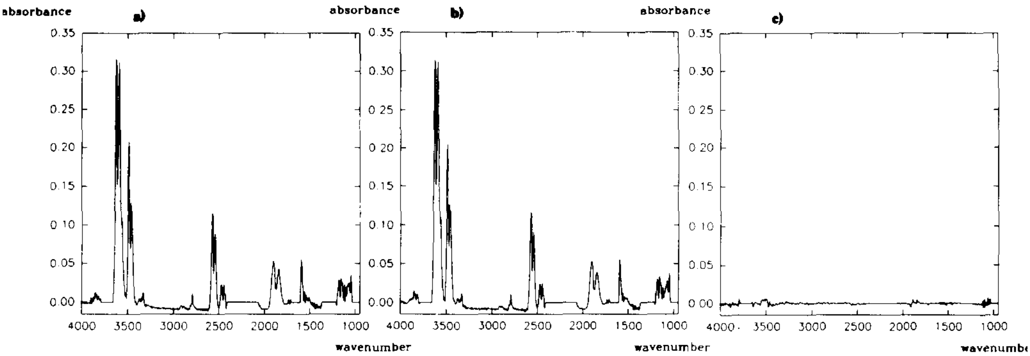

Fig. 3. (a) IR spectrum of the gas mixture at an oven temperature of 250°C. (b) Linear combination of the library spectra of CO_2, N_2O, NH_3, NO, NO_2 and water vapour. (c) Their difference.

The amount of ammonia observed corresponded to 0.559 moles of hydrogen atoms per mole of $K_2CoFe(CN)_6 \cdot 1.4H_2O$. If all the hydrogen in ammonia originated from the hydrogen-converted form, this would mean that as much as 28% of the $K_2CoFe(CN)_6$ was in the hydrolysed form, which is very improbable [3].

In order to obtain a quantitative picture of the decomposition process, the total amounts of the gases released were calculated by integrating the areas below the curves representing the concentration of each gas as a function of gas flow volume (Fig. 4 gives

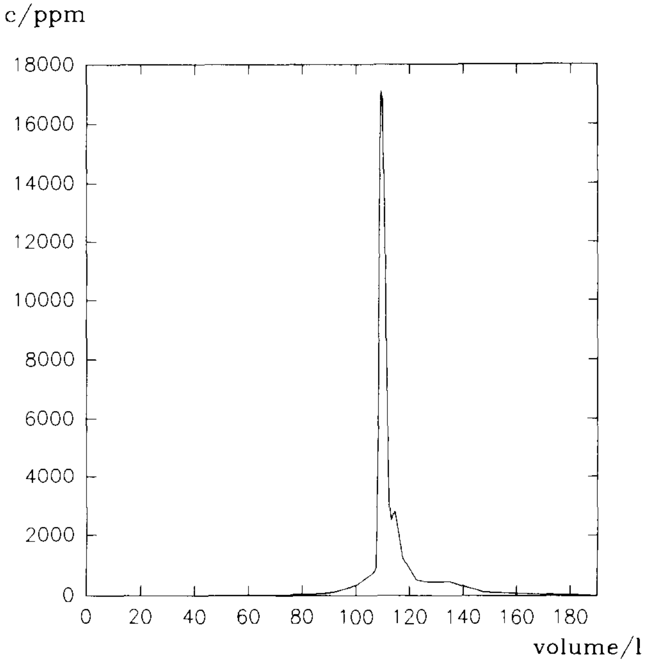

Fig. 4. Concentration of CO_2 in the decomposition gases as a function of gas flow volume.

an example for CO_2). The volume of carbon dioxide thus obtained was 0.0863 litres, which corresponds to 3.38 mmol of CO_2 (Table 1), calculated using the ideal gas law and for a cell temperature of 314 K and a pressure of 767 Torr. In the 0.21 g sample of $K_2CoFe(CN)_6 \cdot 1.4H_2O$, there was initially 3.37 mmol of carbon atoms. This indicates that all the carbon was converted to carbon dioxide.

The total amount of nitrogen in the nitrogen-containing compounds, N_2O, NO, NH_3 and NO_2, was only 1.34 mmol, which is considerably smaller than what was initially present in the sample, 3.37 mmol. We assume that the rest was present as nitrogen gas N_2, which does not form an IR spectrum due to its homonuclear diatomic nature and could therefore not be detected. Calculation by difference gives $(3.37 - 1.34)/2$ mmol $= 1.02$ mmol of N_2 gas released. Thermal decomposition in a nitrogen gas atmosphere gave very different gaseous products (Fig. 5). Ammonia and carbon dioxide also evolved in this atmosphere, but the latter was present at a much

Table 1
Amounts of decomposition gases released in the thermal decomposition of a 0.21 g sample of $K_2CoFe(CN)_6 \cdot 1.4H_2O$

Gas	Amount
CO_2	3.38 mmol
N_2O	0.517 mmol
NO	0.182 mmol
NH_3	0.105 mmol
NO_2	0.019 mmol

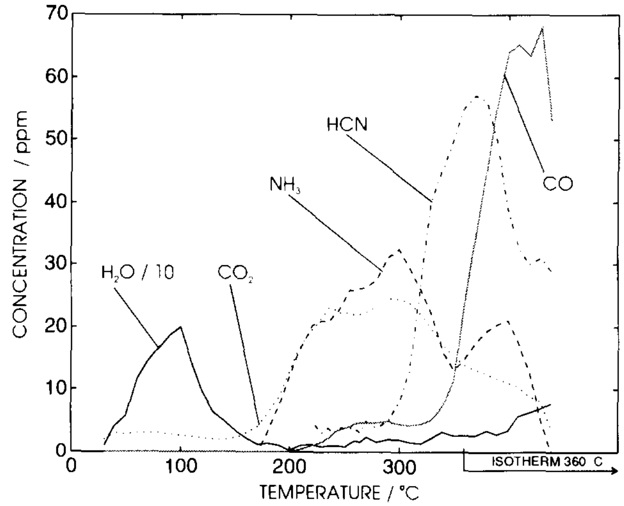

Fig. 5. Concentrations of decomposition gases of $K_2CoFe(CN)_6 \cdot 1.4H_2O$ in nitrogen atmosphere as a function of temperature.

lower concentration than in the synthetic air. This and the presence of carbon monoxide is rather understandable since there was no oxygen in the flow gas. The water condensed on the walls was the most probable source of oxygen and hydrogen in the decomposition gases. The reactions of the primary decomposition gases with condensed water consume water efficiently since there was no water vapour seen in the gas mixture above 170°C. The decomposition in the non-oxygen atmosphere was much slower and the highly toxic gas HCN was also evolved.

References

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