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Decomposition of mixed Mn and Co nitrates supported on carbon

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Abstract

The effect of varying amounts of carbon support on the decomposition of mixed Mn and Co nitrates and the formation of spinel $MnCo_2O_4$ is studied in this work. The molar ratios of the studied samples were n(Mn):n(Co):$n(NO_3^-)$:n(C) = 1:2:6:Y and Y was varied from 0 to 25. IR and XRD measurements of the samples heated at various temperatures revealed spinel formation from the pure nitrates at 240 °C but from the supported nitrates (Y = 15) already at 160 °C. The spinel prepared from pure nitrates at temperatures ≤400 °C was clearly non-stoichiometric. The supported nitrates produced a less non-stoichiometric spinel with smaller crystallite size. TG measurements revealed that compared with the pure nitrates, the decomposition of the supported nitrates initiated and was completed at lower temperatures. When carbon content was increased from Y = 0 to 20, the onset of the nitrate decomposition was shifted to lower temperatures. The increase of carbon amount beyond Y = 20 did not result in any considerable change. The decomposition of the supported nitrates was completed at temperatures 50–70 °C lower than the pure nitrates. Both the decomposition of nitrates and the presence of spinel oxide enhanced the oxidation of carbon.

Keywords: $MnCo_2O_4$; Carbon; Supported nitrates; Thermogravimetry; Decomposition gases

1. Introduction

An interesting and feasible way to prepare small metal oxide particles is to use carbon as a support for nitrate precursors [1–4]. Our interest has been focused on the preparation of spinel $MnCo_2O_4$, which has several applications, for instance as catalysts for decomposition of NO and CO [5], reduction of nitrogen oxides into N_2 [6], and oxygen reduction reaction [3,4,7,8]. For optimal preparation conditions it is essential to know what factors affect the decomposition of the nitrate precursors. No detailed information on the decomposition of the mixed Mn–Co nitrates was found in the literature, but several reports for both the Mn and Co nitrates exist. Different decomposition temperatures, mechanisms, and intermediates are reported for the Mn and Co nitrates, depending on factors such as heating rate, moisture content of the atmosphere [9], hydration degree of the nitrates [10], crystal size and support [11], and the sample mass and the diameter of the crucibles used in the measurements [10].

In air or oxygen manganese nitrate decomposes up to 200–220 °C [10–14], and cobalt nitrate up to 240–280 °C [11,12,15–17]. The decomposition of the nitrates can occur simultaneously or after the water evaporation and its mechanism can be rather complicated. Transition metal nitrates usually dehydrate below 180 °C followed by the decomposition of the anhydrous nitrate below 280 °C [12]. Mn [10] and Co [11] nitrates have been reported to first lose water followed by the decomposition of the anhydrous nitrate, but also simultaneous water evaporation and nitrate decomposition for Co-nitrate has been reported [17]. Formation of different unstable intermediates has been reported, such as $MnO_{1.2}(NO_3)_{0.8}$ [13], $MnONO_3$ [9], $Co_2(NO_3)_2(OH)_2$, $CoO{\cdot}CoONO_3$, Co_2ONO_3 [14], and CoO and Co_2O_3 [17].

In moist atmosphere the decomposition of the nitrates can occur at lower temperatures than in dry atmosphere [9]. More-

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over, hydrated Mn nitrate has been reported to decompose at lower temperatures than nearly dehydrated one [10]. The decomposition of supported nitrates can be strongly affected by the nature of the support. The results by Tiernan et al. [15] show that, depending on the properties of the support, the decomposition of the supported cobalt nitrate can either be delayed or enhanced. Further, the crystal size of the nitrates can affect the decomposition; Cseri et al. [11] have reported that compared with the pure metal nitrates the decomposition of metal nitrates supported on a clay started and was completed at 0–40 and 5–105 °C lower temperatures, respectively. Since the decomposition shifted to lower temperatures pronouncedly for the most amorphous nitrates, it was expected that this shift was due to the small crystal size of the nitrates. They also note that some decomposition steps that were observed during the decomposition of pure nitrates were not observed for the supported samples. The effect of varying amounts of carbon support on the decomposition of the mixed Mn and Co nitrates to form spinel $MnCo_2O_4$ is studied in this report.

2. Experimental

The molar ratios of the studied samples were n(Mn):n(Co):n(NO_3^-):n(C) = 1:2:6:Y. Samples with $Y = 0$ (no carbon), 5, 10, 15, 20, and 25, were prepared by dissolving analytical grade nitrates $Co(NO_3)_2{\cdot}6H_2O$ (Merck, 98.5%) and $Mn(NO_3)_2{\cdot}4H_2O$ (Merck, 99%) in water. Aqueous solutions of the nitrates were mixed with varying amounts of carbon powder (Ketjenblack® EC-300J, Akzo Nobel) having a specific surface area of 950 $m^2\,g^{-1}$. The samples were dried at 40 °C in air.

The formation of the gaseous species during heating of the nitrates was studied by thermogravimetry combined with Fourier transformed infrared (TG–FTIR). Mass loss was recorded by Perkin-Elmer Thermogravimetric Analyser TG7. The measurements were carried out in air. The sample masses were 22 ($Y = 0$) and 17 mg ($Y = 20$), and the heating rate was 10 K min^{-1}. The TG analyser was coupled by a heated transfer line to a 10 cm^3 gas cell and Perkin-Elmer System 2000 FTIR. The temperatures of the transfer line and the gas cell were 186 and 190 °C, respectively. FTIR measurements were made with resolution of 2 cm^{-1} and 16 scans per slice.

The effect of varying carbon content on the decomposition of the mixed Mn–Co nitrates was studied by thermogravimetry combined with differential scanning calorimetry (TG–DSC). The measurements were carried out in a Netzsch STA449C Jupiter analyser in air. The sample masses were 20–21 mg. While the heating rate of 10 K min^{-1} was found feasible for TG–FTIR measurements in order to receive well readable FTIR spectra, the heating rate of 5 K min^{-1} was used in TG–DSC measurements in order to get more detailed information on the decomposition steps.

The samples for infrared (IR) and powder X-ray diffraction (XRD) studies were prepared with carbon contents of $Y = 0$ and 15. The dried samples, 3 g for $Y = 0$ and 3.5 g for $Y = 15$, were heated in air from room temperature up to 400 °C, at temperatures just below or above the temperatures at which mass losses were observed in TG measurements, or at 50 °C intervals. Each temperature was held for 30 min. The crucibles containing the samples were covered with lids, which were loose enough to allow gas exhaust but which prevented loss of sample during the burning of carbon, which initiated below 300 °C. IR measurements were recorded with a Perkin-Elmer Spectrum GX with DTGS detector with resolution of 4 cm^{-1} and 64 scans, and the KBr pellets contained 0.2 wt.% of the sample. XRD patterns were taken with a Philips diffractometer with Cu Kα as a radiation source, using step size 0.02° and step time of 1 s.

3. Results

To be able to compare the results with varying amounts of carbon, all TG results are normalised. In the mass scale (Figs. 2,3 and 5), 100% corresponds to the mass of the weighed hydrated nitrates with molar ratios of n(Mn):n(Co):n(NO_3^-):n(H_2O) = 1:2:6:16. The composition of $MnCo_2O_4$ corresponds to 28.4%.

3.1. Formation of gaseous species during decomposition

Fig. 1 shows the FTIR spectra of the gaseous species developed during the heating of the sample with $Y = 20$. The strongest absorptions bands of NO_2 and CO_2 together with TG curves for samples $Y = 0$ and 20 are plotted in Fig. 2. During drying at 40 °C part of the original water has evaporated. That is why the mass of Mn–Co nitrate in the beginning of the measurement is <100%. For the supported nitrates the presence of carbon raises the starting point beyond 100%.

When Mn–Co nitrate ($Y = 0$) was heated in air, evaporation of water had maximum rate around 200 °C and ceased before 260 °C, which is before the maximum of NO_2 formation. The formation of NO_2 gas started soon above 200 °C, had maximum at 270 °C, and ceased around 300 °C. In the case of supported nitrates ($Y = 20$) the evaporation of water had maximum rate at 140 °C and continued up to 220 °C simultaneously with NO_2 formation, although started to slow down when NO_2 formation had reached the maximum. The formation of NO_2 started above 100 °C, had maximum at 190 °C and ceased around 230 °C. The comparison of samples $Y = 0$ and 20 reveals that for the supported nitrates the decomposition initiated, had maximum, and ceased 100, 80, and 70 °C earlier, respectively. While sample $Y = 0$ showed NO_2 formation with several steps, only one step was clearly observable for $Y = 20$. This kind of fusing of the steps for supported nitrates has been reported previously [11].

When carbon was studied alone with TG its burning did not start before 550 °C in air. However, it is known that the