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# Thermal decomposition of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$

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**Abstract**

A series of Co(II)–La(III)–oxalate codepositions have been prepared and their molecular formulae can be expressed as $Co_xLa_y(C_2O_4)_{(x+1.5y)}$. The results of X-ray diffraction showed that these codepositions were solid solutions rather than simple mixtures. Thermal decomposition of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ in Ar and $H_2$ was investigated by GC, and it was found that methanation of the CO and $CO_2$ produced during the decomposition in hydrogen took place, and that the catalytic activity depended on the La/Co ratio.

## INTRODUCTION

Using Ni and Co catalysts, methanation of carbon oxides producing $H_2$ and $NH_3$ has been used in industry to eliminate trace carbon oxides from gases. Efficient methane synthesis from carbon oxides by hydrogenation is particularly important for producing clean energy fuel from abundant coal resources instead of using more limited petroleum naphtha supplies. Therefore, much attention has been paid to the methanation of carbon oxides [1–4]. A great number of catalytic reactions have been investigated on rare earth intermetallics [5]. For instance, the La–Co system is used as a catalyst for the methanation of carbon monoxide [6]. In this paper, we report on the preparation of a series of solid solutions $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ and their decomposition in Ar and $H_2$. Attention is also paid to the methanation of CO and $CO_2$ when the thermal decomposition is carried out in hydrogen; as will be shown, the catalytic activity is dependent on the La/Co atomic ratio.

## EXPERIMENTAL

### *Materials*

The $CoCl_2$, $La_2O_3$, $H_2C_2O_4$, $La_2(C_2O_4)_3$, $CoC_2O_4 \cdot 2H_2O$ and hydrochloric acid used were analytical grade; $LaCl_3$ solution was prepared by

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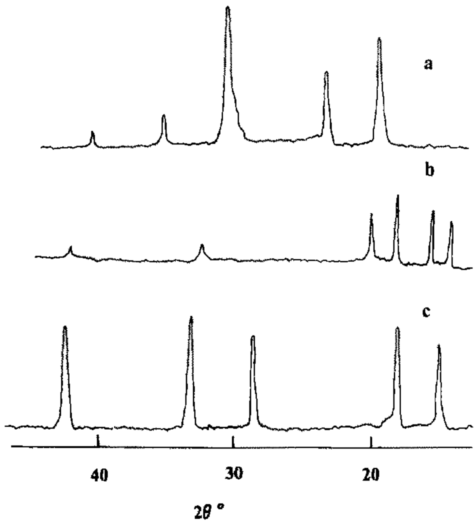



Fig. 1. X-ray diffractograms of: a, $CoC_2O_4$; b, Co(II)–La(III)–oxalate codeposition (La/Co = 2/3); and c, $La_2(C_2O_4)_3$.

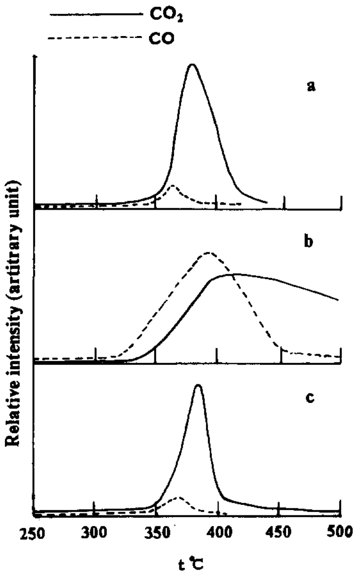
dissolving the $La_2O_3$ in hydrochloric acid. $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ was obtained by the following procedures. $CoCl_2$ aqueous solution and $LaCl_3$ aqueous solution were mixed in different La/Co molar ratios and the pH value was adjusted to within the range 1–2. The solution thus obtained was placed in a water bath set at 100°C and excess oxalic acid was added as the precipitating agent. The resulting solution was cooled to ambient temperature. The precipitate was filtered, washed with dilute $H_2C_2O_4$ and water, and dried in vacuo at 80°C for 24 h.

### *Instrumentation*

The gas chromatographic measurements were made as described elsewhere [7]. X-ray diffraction was recorded using a Shimadsu 1038 diffractometer with Cu K$\alpha$ radiation.

## RESULTS

As can be clearly seen from Fig. 1, for $CoC_2O_4$, there are three main peaks in the X-ray diffraction pattern at $2\theta = 18.9°$, 23.0° and 30.3° respectively; for $La_2(C_2O_4)_3$, there were five main peaks at $2\theta = 14.9°$, 17.9°, 27.4°, 32.7° and 42.5°; however, for the Co(II)–La(III)–oxalate codeposition (La/Co = 2/3), there are four peaks appearing at $2\theta = 13.8°$, 15.2°, 17.9° and 19.1°. If the Co(II)–La(III)–oxalate codeposition (La/Co = 2/3) had been a simple mixture, the main diffraction peaks of $CoC_2O_4$ and $La_2(C_2O_4)_3$ would have appeared in its X-ray diffractogram. Therefore, the



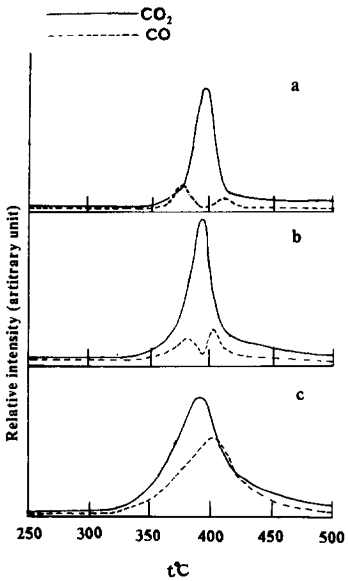




Fig. 2. Thermal decomposition in Ar: a, $CoC_2O_4$; b, $La_2(C_2O_4)_3$; and c, $Co_xLa_y$-$(C_2O_4)_{(x+1.5y)}$ (La/Co = 1/4).

Fig. 3. Thermal decomposition in Ar: a, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 2/3); b, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 3/2); and c, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 4/1).

Co(II)–La(III)–oxalate codeposition (La/Co = 2/3) is solid solution rather than a simple mixture; the molecular formula of the codepositions might be represented as $Co_xLa_y(C_2O_4)_{(x+1.5y)}$.

As shown in Fig. 2a, the decomposition of $CoC_2O_4$ in Ar begins at around 250°C, and is complete above 400°C. During decomposition, CO and $CO_2$ are released. When $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ of different La/Co ratios is decomposed in He (Figs. 2c, 3a, 3b, 3c), CO and $CO_2$ are expelled. They begin to decompose at about 250°C, and main decomposition stage is in the range 360–430°C. It was found that with an increase in La content, the single CO peak was split into two peaks, the second peak gradually predominating, and the two peaks finally combining. It was also found that the peak temperature changed from 380 to 390°C for $CO_2$ and from 370 to 400°C for CO, which suggested that with a higher La content, the thermal stability of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ increased. Decomposition of $La_2(C_2O_4)_3$ begins at 200°C, with evolution of CO and $CO_2$ (Fig. 2b). When decomposition of $CoC_2O_4$ is carried out in $H_2$, the decomposition starts at 200°C, and CO and $CO_2$ are expelled in the range 230–320°C. Above 320°C, a considerable amount of $CH_4$ is produced (Fig. 4a). The initial decomposition of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ in $H_2$ takes place at around 200°C and a great deal of $CH_4$ is formed between 300 and 500°C (Figs. 4c, 5a, 5b, 5c). The decomposition of $La_2(C_2O_4)_3$ in $H_2$ is almost the same as in Ar (Fig.

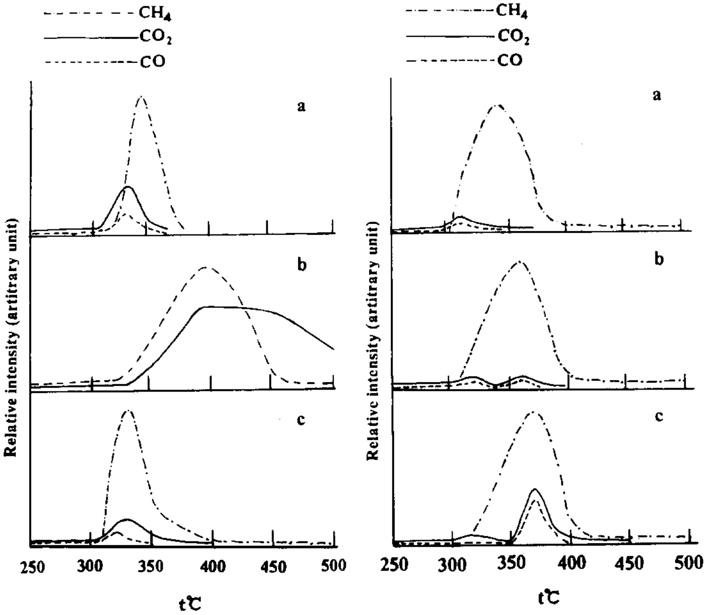



Fig. 4. Thermal decomposition in $H_2$: a, $CoC_2O_4$; b, $La_2(C_2O_4)_3$; and c, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 1/4).

Fig. 5. Thermal decomposition in $H_2$: a, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 2/3); b, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 3/2); and c, $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ (La/Co = 4/1).

4b), indicating that pure $La_2(C_2O_4)_3$ has no catalytic activity for the methanation of CO and $CO_2$.

Comparing the decomposition of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ in He and in $H_2$, we found that the decomposition temperature of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ is higher in He than that in $H_2$. This suggested that the thermal stability of $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ is lower in hydrogen because of the methanation of $CO_2$ and CO in $H_2$. The $CH_4$ yields from $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ with different La/Co ratios at different temperatures are plotted in Fig. 6.

## DISCUSSION

In argon, the decomposition reactions of $CoC_2O_4$ may be considered to proceed according to the following schemes

$$CoC_2O_4 \longrightarrow Co + 2CO_2 \quad (1)$$

$$CoC_2O_4 \longrightarrow CoO + CO + CO_2 \quad (2)$$

with reaction (1) predominant [8].

The thermal decomposition of $La_2(C_2O_4)_3$ in argon can be expressed [9]

$$La_2(C_2O_4)_3 \longrightarrow La_2(C_2O_4)(CO_3)_2 + 2CO \quad (3)$$

$$La_2(C_2O_4)(CO_3)_2 \longrightarrow La_2(CO_3)_3 + CO_2 \quad (4)$$

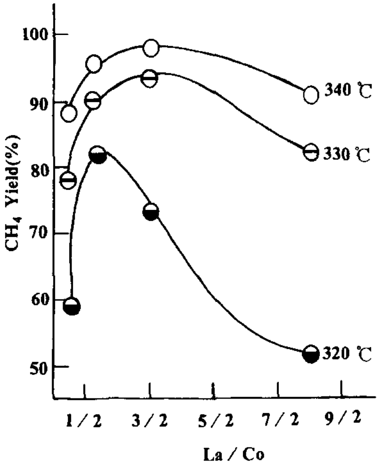



Fig. 6. Plot of $CH_4$ yield vs. La/Co ratio.

$$La_2(CO_3)_3 \longrightarrow La_2O(CO_3)_2 + CO_2 \quad (5)$$

$$La_2O(CO_3)_2 \longrightarrow La_2O_3 + 2CO_2 \quad (6)$$

The thermal stability of $La_2(C_2O_4)_3$ is higher than that of $CoC_2O_4$ and this leads us to propose that for $Co_xLa_y(C_2O_4)_{(x+1.5y)}$, the $C_2O_4^{2-}$ ions bound with Co(II) decompose at a lower temperature, resulting in the reduction of Co(II), followed by the decomposition of the $C_2O_4^{2-}$ ions chelated to La(III). As a result, when the La content of $Co_xLa_y$-$(C_2O_4)_{(x+1.5y)}$ is low, the decomposition will be similar to that of $CoC_2O_4$, and it will be analogous to that of $La_2(C_2O_4)_3$ if the La content is very high.

When decomposition of $CoC_2O_4$ or $Co_xLa_y(C_2O_4)_{(x+1.5y)}$ is carried out in hydrogen, methanation of CO and $CO_2$ takes place

$$CO + 3H_2 \longrightarrow CH_4 + H_2O \quad (7)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad (8)$$

As shown in Fig. 6, at a fixed temperature, there is a certain La/Co ratio which is the most efficient for methanation of CO and $CO_2$.

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