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Application of CO_2-TPD in the Synthesis of Composite Oxides from Metal-Organic Precursors

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Abstract: CO_2-TPD was demonstrated an effective way to investigate the phase formation during pyrolysis for the preparation of composite oxides using metal-organic molecules as precursors. Based on the CO_2-TPD results, it was found that calcination condition had deep effect on the carbonate formation and the minimum firing temperature to acquire pure phase composite oxide. An optimized calcination schedule was then developed.

Keywords: CO_2-TPD, composite oxide, synthesis, metal-organic precursors.

Pyrolysis using metal-organic molecules as precursors was one of the extensively used methods for the preparation of high-quality composite oxides in recent years [1]. However, it was found that the properties of final product are greatly influenced by the firing condition. Due to the difficulty in characterization, information about the process from the precursor to the calcined product, however, is lack. In this letter, we report the successful application of CO_2-TPD technique in the investigation of phase formation during pyrolysis. Combined with IR, TG, DTA and XRD techniques, it can provide us a clear picture about the pyrolysis process. Optimization of calcination process then can be made.

There are abundant carbon resources in metal-organic precursors, and carbonate is easily formed during pyrolysis. With the programmed rise of temperature, the produced carbonate can re-decompose into oxides and CO_2, the discharged CO_2 can be detected by TCD quantitatively, that we named as CO_2-TPD technique.

Investigation was made on the pyrolysis process of synthesis of $La_{0.8}Sr_{0.2}CoO_3$ (a catalyst with high catalytic activity for hydrocarbon combustion and also an oxygen permeable membrane material), by the cellulose adsorption method.

The preparation of perovskite-type $La_{0.8}Sr_{0.2}CoO_3$ by cellulose adsorption method was presented in details elsewhere[2]. In investigation 1 and 2 (reported later), small amount of precursor was used for pyrolysis study, and the crucible for holding the precursor was open to air to ensure sufficient oxygen supply and free elution of produced carbon dioxide during pyrolysis. In investigation 3, relatively large amount of precursor was used with cover on the crucible to create a condition of insufficient oxygen supply and more contacting time between CO_2 with the produced oxides. CO_2-TPD study was conducted in a homemade multipurpose TP apparatus, helium was used as the carrier gas, TCD was used to detect the discharged carbon dioxide and computer was used for data acquisition and processing. Before CO_2-TPD experiment, the samples were predried at 100°C, the amount of sample was about 100mg. An inorganic absorbent was used for the elimination of possible water production. Assistant XRD, TG characterization was also conducted.

Investigation of calcination temperatures on the phase formation by CO_2-TPD (1)

The precursors were calcined at different temperatures for 2hrs, the acquired samples were then submitted to XRD characterization. It was found that no other diffraction peak except perovskite was detected at a calcination temperature higher than 500°C. The corresponding CO_2-TPD profiles are shown in **Figure 1**. A sharp desorption peak appeared around 600°C for the samples calcined at 400°C, the easy re-decomposition of carbonate indicated its high dispersity in the bulk oxides. Weak but certainly existing desorption peak was observed for the samples calcined at 500°C and 600°C. Due to the high dispersity and small amount, the carbonate residue was undetectable by the XRD technique, but was easily detected by the CO_2-TPD technique for the high sensitivity of TCD. The amount of carbon residue was calibrated according to the discharged CO_2, the results were listed in **Table 1**. It shows that the sensitive temperature for carbonate formation is around 400°C.

Figure 1. CO_2-TPD profiles of samples calcined at different temperatures for 2hrs, a: 400°C, b: 500°C, c: 600°C, d: 800°C

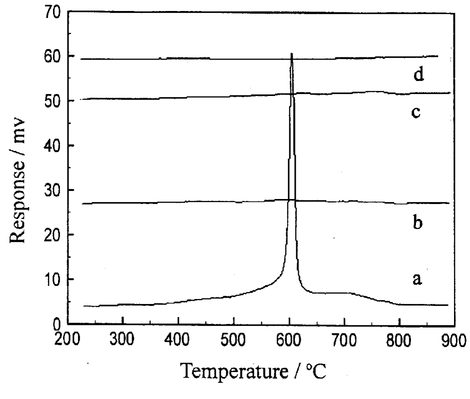

Table 1. Carbon residue calculated from CO_2-TPD

Temperature (°C)	400	500	600	800
Carbon content (%)	2.17	0.196	0.145	0.019

Investigation of firing time on the phase formation by CO_2-TPD (2)

The influence of firing time on carbonate formation was investigated at 400°C. CO_2 desorption peaks were all observed for the samples calcined at 400°C for different hours.

The amounts of carbon residue and peak temperatures of desorption were listed in **Table 2**. It demonstrated that it was in vain to eliminate the carbonate residue by elongating the firing time. On the contrary, desorption peaks shifted to the higher temperature with the increase of calcination time slightly, indicated the growth of crystallite size of the carbonate, so higher calcination temperatures were necessary to get rid of it.

Table 2. Peak temperatures and calculated carbon residue for the samples calcined at 400°C for different hours

Time (hrs)	2	4	6	8	10
Peak temperature (°C)	598	603	610	615	614
Carbon content (%)	2.17	2.05	1.86	2.15	2.13

Investigation of calcination atmosphere on the phase formation by CO_2-TPD (3)

Due to the abundant carbon resources presented in metal-organic precursors, the calcination atmosphere may have a great effect on the phase formation during pyrolysis. **Figure 2** shows the CO_2-TPD profiles of samples calcined under above-mentioned condition (investigation 3) at different temperatures for 2hrs. CO_2-TPD peaks appeared for all the calcined samples. A sharp desorption peak around 600°C was detected for the sample calcined at 400°C, which is similar to that calcined at the same temperature under sufficient oxygen supply (investigation 1), only intensity of the peak was strengthened a little bit. So the produced carbonate was also highly dispersed in the bulk, and it could be easily removed by further calcined at a modest high temperature (~600°C). For the samples calcined at a temperature higher than 400°C, the CO_2 desorption peak shifted obviously to the higher temperature zone, which demonstrated the growth of crystallite size of carbonate obviously. A re-firing temperature higher than 800°C was needed to totally get rid of it. Several desoprtion peaks were detected for the samples calcined between 450°C~600°C, which indicated that more than one carbonate species were produced. The calculated carbon residue was listed in **Table 3**, the results from TG were also presented, which agreed with CO_2-TPD results very well as a whole.

Figure 2. CO_2-TPD profiles of samples calcined at different temperatures for 2hrs, a: 400°C (investigation 1), b: 400°C c: 450°C, d: 550°C, e: 600°C, f: 700°C, g: 800°C

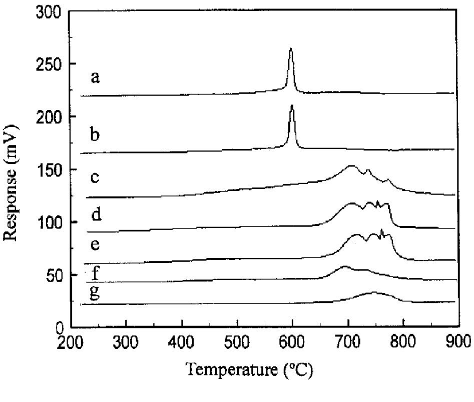

Table 3. Carbon residue calculated from CO_2-TPD and TG experiment for the samples calcined at different temperatures under investigation 3

Temperatures (°C)	400	450	550	600	700	800
C(%)CO_2-TPD	2.59	7.81	5.80	5.43	2.49	1.34
C(%) TG	2.4~2.9	10.5~13.2	5.2~6.3	5.3~6.2	2.3~3.4	1.4~1.9

Based on the CO_2-TPD results, conclusion can be drawn that if the environmental condition is difficult to control, it was preferable to prefire the precursor at properly low temperature (400°C in this study) then calcine further at higher temperature than to calcine the precursor at high temperature directly. The crystallite size of formed carbonate residue grew up obviously when the precursor was first calcined at a temperatures higher than 450°C (in this study), so much higher temperature was needed to get rid of it further. High calcination temperature would impair the advantage of pyrolysis using metal-organic molecules as precursor, such as high surface area which is key to its high catalytic activity.

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