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## Research Article

# Temperature Dependent Electrical Properties and Catalytic Activities of $\text{La}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ Phase System

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We present a study of electrical properties and catalytic activities of materials belonging to the hydrated carbonated system  $\text{La}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$ . The polycrystalline hydroxycarbonate, dioxycarbonate, and oxide are prepared via a coprecipitation route followed by heat treatment. The electrical conduction of the phases obtained by thermal decomposition from  $\text{LaOHCO}_3$ ,  $\text{H}_2\text{O}$  is analyzed by electrical impedance spectroscopy, from 25°C to 950°C, under air. The catalytic properties of  $\text{LaOHCO}_3$ ,  $\text{La}_2\text{O}_2\text{CO}_3$  and  $\text{La}_2\text{O}_3$  polycrystalline phases are studied by FTIR spectroscopy, in presence of gas mixtures CO-air and  $\text{CH}_4$ -air, at temperatures ranging between 100°C to 525°C. The three materials behave differently in presence of CO or  $\text{CH}_4$  gases.

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## 1. Introduction

The general aim of this study is to test the reactivity of materials sensitive to environmental water and  $\text{CO}_2$ , and interacting with toxic gases ( $\text{CO}$ ,  $\text{CH}_4$ ). Presently we deal with the system  $\text{La}_2\text{O}_3\text{-CO}_2\text{-H}_2\text{O}$  that presents hydrated and carbonated phases, stable at various temperatures [1–6]; the hydroxycarbonate phase  $\text{LaOHCO}_3$  stable up to 380°C [7]; the dioxycarbonate phase  $\text{La}_2\text{O}_2\text{CO}_2$  stable up to 700°C, and finally the  $\text{La}_2\text{O}_3$  phase stable above this temperature, under air atmosphere. Each phase can be sensitive to partial pressure of  $\text{H}_2\text{O}$  or  $\text{CO}_2$ . Consequently, these phases can be used as sensing materials reacting with wet air and  $\text{CO}_2$ . In a first step, we try to determine the evolution of electrical conduction of these phases with increasing temperature; in a second step, we compare the temperature and time dependent catalytic efficiencies of  $\text{LaOHCO}_3$ ,  $\text{La}_2\text{O}_2\text{CO}_3$ , and  $\text{La}_2\text{O}_3$ , to convert  $\text{CH}_4$  and CO present in air- $\text{CH}_4$  and air-CO flows.

## 2. Experimental

The samples were prepared by a coprecipitation route described in a recent work [8]. A first step consisted in

mixing three aqueous solutions: (1)  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , (2) urea  $\text{CO}(\text{NH}_2)_2$ , and (3) polyvinyl-pyrrolidone (PVP) polymer. The initial pH was 3.2. A similar approach was proposed by Li et al. [9]. A second step consisted in heating the solution in a reactor equipped with a vapor condenser, at 80°C. In all experiments, solutions were permanently agitated through a magnet rotating with a fixed rate of 300 rpm. During heating, temperature was fixed, and vapors were condensed through a water-cooled circuit to avoid vanishing of the aqueous solution. A white solid was obtained by precipitation.

The thermal decomposition of this solid (the polycrystalline initial hydroxycarbonate phase  $\text{LaOHCO}_3 \cdot \text{H}_2\text{O}$ ) was initially studied by thermogravimetry, from room temperature to 1100°C. Then, the same  $\text{LaOHCO}_3$ ,  $\text{H}_2\text{O}$  phase was compacted in form of cylindrical pellet, and placed in a heating cell, in a Solartron electrical impedance equipment. Platinum circular electrodes were fixed on the two faces of pellet. The electrical analyses that were performed in the temperature range of 25 to 950°C and in the frequency range of 1 to  $10^7$  Hz, with a maximal tension of 1 V. The conductivities were determined from extrapolation of the Nyquist representations delivered by the software of the

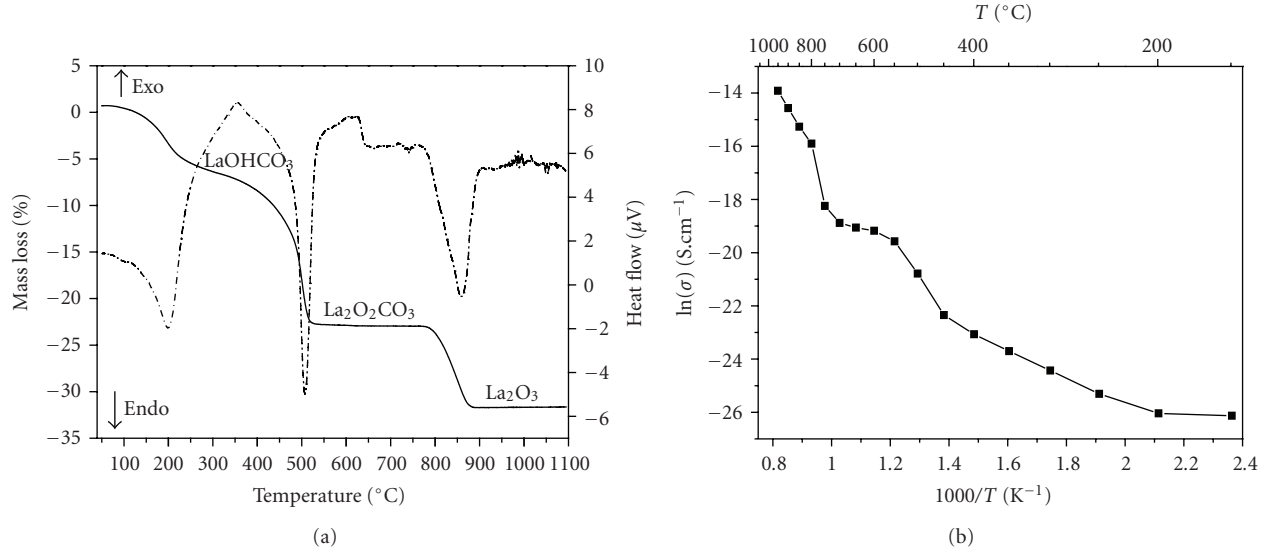
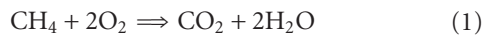


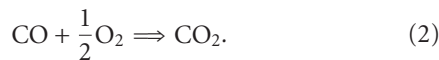
FIGURE 1: (a) Thermal decomposition analysis (DTA-TG) of hydrated hydroxycarbonate: successive phases LaOHCO<sub>3</sub> (LHC), La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (LOC), and La<sub>2</sub>O<sub>3</sub> (L), (b) Electrical impedance analysis of hydrated hydroxycarbonate: variation of  $\ln\sigma$  versus  $1000/T$ . Existence of electrical changes corresponding to chemical decomposition.

equipment, and taking into account the dimensions of samples.

The catalytic activities were determined using an infrared (FTIR) spectrometer, adapted for analyses of emitted gases. This homemade equipment was described in previous works [10]. Samples are placed in a catalytic cell and a gas flow cross through the powder at various temperatures and various flow rates. The polycrystalline phases LaOHCO<sub>3</sub>, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, and La<sub>2</sub>O<sub>3</sub> were subjected successively to air-CH<sub>4</sub> and air-CO flows, at various temperatures and as a function of time. In all experiments, we used flow rates of 10 sccm and gas concentrations in air of 2500 ppm. The catalytic efficiency is defined as being the intensity of the CO<sub>2</sub> vibrational band at 2340–2360 cm<sup>-1</sup> resulting from the following transformations:



or



Additional studies by transmission electron microscopy allowed to determine the distributions of sizes and shapes of crystal grains in each sample (not presented here). From these microstructural analyses, we could define calculated grain surfaces  $S_i$  and grain volumes  $V_i$  for each phase noted  $i$  (the index  $i$  represents La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, or LaOHCO<sub>3</sub>). This allowed calculation of specific surfaces  $S_i/V_i$ . Then, from the mass of each sample used for catalytic analyses, it has been possible to determine an approximate total surface  $S_i$  for each powdered sample. This surface  $S_i$  has been used to normalize our FTIR data and allow comparison of catalytic efficiencies. The normalized intensities ( $I/S_i$ ) are calculated by dividing the intensities of CO<sub>2</sub> bands by the surfaces  $S_i$  of

samples. The values  $S_i$  are successively in m<sup>2</sup>:  $S(i = \text{La}_2\text{O}_3) = 0.61$ ,  $S(i = \text{La}_2\text{O}_2\text{CO}_3) = 2.31$ ,  $S(i = \text{LaOHCO}_3) = 5.62$ .

### 3. Results and Discussion

**3.1. Thermal Analyses and Electrical Responses.** Using first classical TG-TDA analysis of the hydrated hydroxycarbonate sample, we have determined the various temperature ranges of phase stabilities. These preliminary results were useful to better interpret our electrical measurements. Figure 1(a) gives the conventional thermal analysis using thermogravimetry data coupled with differential thermal analysis (TG-DTA). The various mass losses versus temperature in °C are clearly visible with a first lattice water departure, then the change of hydroxycarbonate into La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and, finally, the final formation of La<sub>2</sub>O<sub>3</sub>.

Figure 1(b) gives the corresponding thermal evolution of the logarithm of conductivity  $\ln\sigma$  as a function of  $1000/T$  ( $T$  being in K) of the initial hydrated hydroxycarbonate phase; as temperature increases, the electrical modifications due to thermal decomposition are observed through undulations on the curve  $\ln\sigma$  versus  $1000/T$ . In Figure 1(b), as  $1000/T$  decreases, several domains are observed as follows

- At low temperature (25–300°C), an increasing low conductivity is observed, with weak activation energy; this is typically relative to extrinsic conduction linked to surface water and proton (OH<sup>-</sup>) mobility;
- Between 350 and 700°C, if we extrapolate the previous lower temperature results, we can observe an abnormal variation of conductivity; it is due to the OH<sup>-</sup> and CO<sub>2</sub> species departure, involving defect formation in hydroxycarbonate and formation of dioxy carbonate La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>;

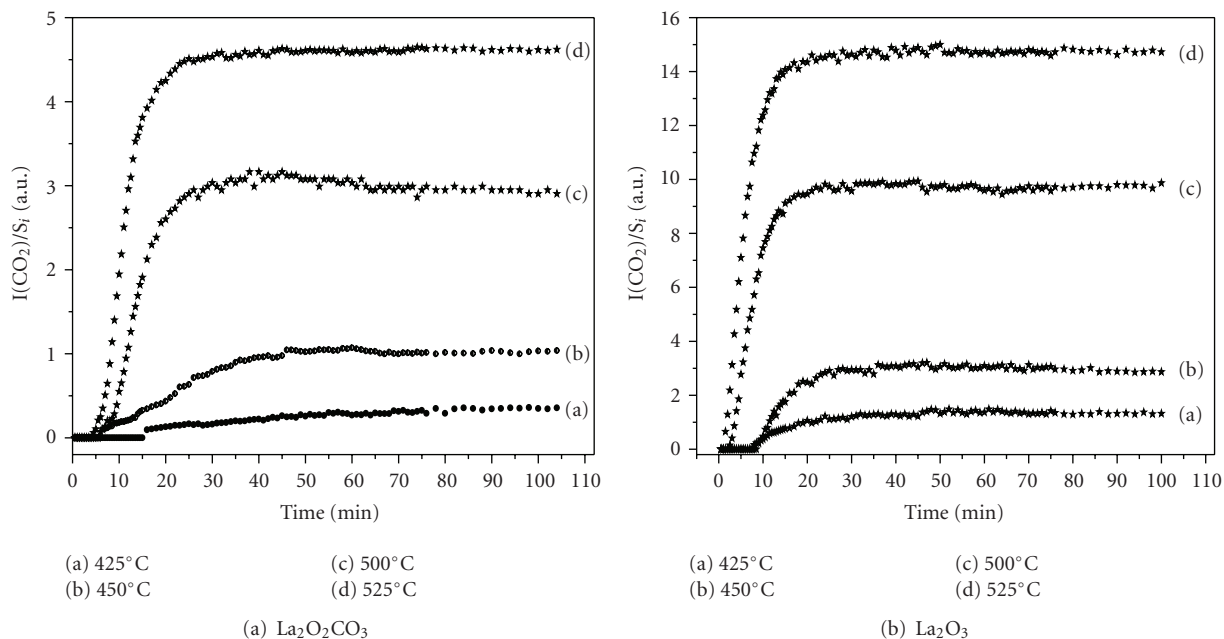


FIGURE 2: (a) catalytic conversion of CH<sub>4</sub> interacting with La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> as a function of time and temperature, (b) catalytic conversion of CH<sub>4</sub> interacting with La<sub>2</sub>O<sub>3</sub> as a function of time and temperature. The normalized efficiencies are expressed in arbitrary units (a.u.).

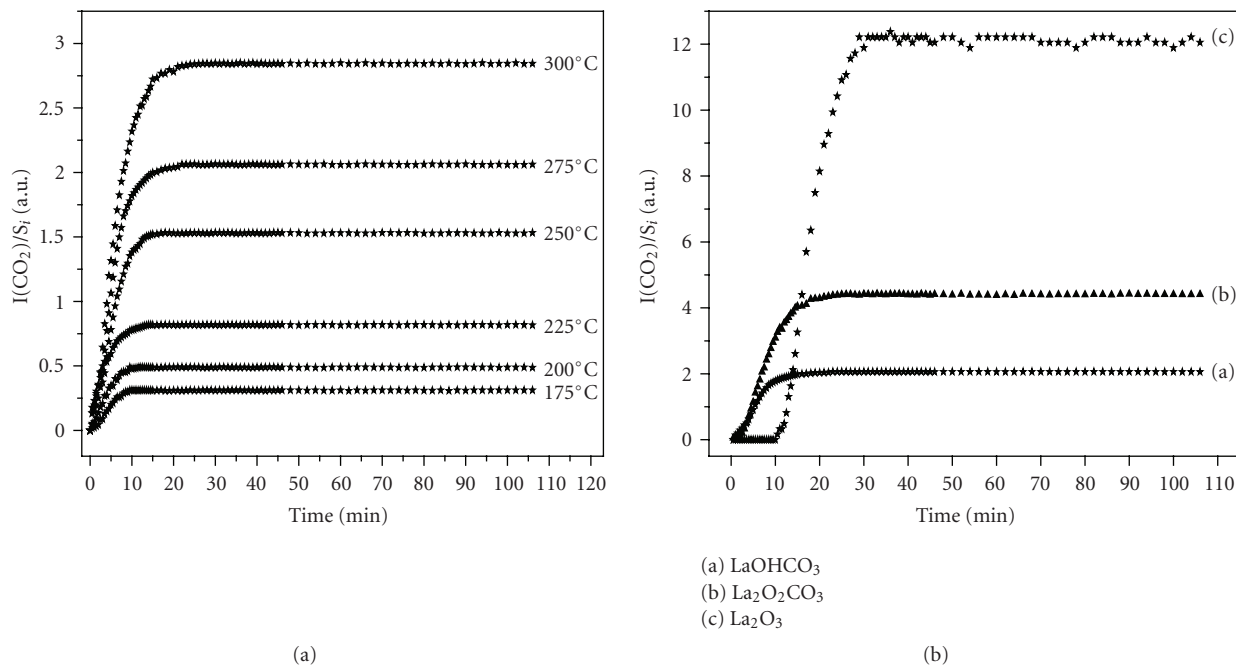


FIGURE 3: (a) catalytic efficiencies of LaOHCO<sub>3</sub> in presence of air-CO flows at various temperatures, (b) compared catalytic efficiencies of La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and LaOHCO<sub>3</sub> in presence of air-CO flows, at a fixed temperature of 275°C; the normalized efficiencies are expressed in a.u.

(c) Between 700°C and 800°C, a very weak abnormal evolution is observed (undulation), probably due to the last CO<sub>2</sub> departure from the oxycarbonate, with transformation into oxide La<sub>2</sub>O<sub>3</sub> (phase with higher activation energy).

Taking into account the logarithmic scale of the graph, we observe a relatively strong variation of the electrical signal between 300 and 600°C; this domain, in which the OH<sup>-</sup> and one of the CO<sub>3</sub><sup>2-</sup> species are unstable in the lattice, should be highly sensitive to water and CO<sub>2</sub> exchanges. This

might be used to detect water and CO<sub>2</sub> molecules in a gas sensor.

**3.2. Catalytic Studies.** Figures 2(a), 2(b) give the normalized catalytic efficiencies (intensities of CO<sub>2</sub> vibrational frequency band) of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> subjected to CH<sub>4</sub>-air flow (2500 ppm CH<sub>4</sub>) at different temperatures. Because of thermal decomposition occurring at a temperature greater than 350°C, no experiment was possible for LaOHCO<sub>3</sub>. Figure 3(a) reports the results for the LaOHCO<sub>3</sub> phase at various temperatures. The maximum catalytic efficiency of each material interacting with CO is obtained at a relatively low temperature (275°C). The catalysis of CH<sub>4</sub> is obtained at higher temperatures (above 450°C). Figure 3(b) gives the normalized catalytic efficiencies of the three phases in presence of air-CO flows at a given temperature of 275°C. It is clearly evidenced that the catalytic efficiency of La<sub>2</sub>O<sub>3</sub> (per surface unit) is greater than that of the two other compounds.

#### 4. Conclusion

In this study, we have developed an electrical approach allowing determining the electrical responses of a phase change involving H<sub>2</sub>O and CO<sub>2</sub> molecules elimination, from electrical impedance analyses. The departure of the couple H<sub>2</sub>O + CO<sub>2</sub> can be linked to an increase of conductivity (the slope of the ln( $\sigma$ ) curve increases in the range of 400–600°C) followed by a stabilization of the conductivity (in the range of 600 to 700°C) associated with last carbonate phase formation. The increase of conductivity might be ascribed to the high mobility of unstable chemical specie, mainly protons that can jump easily from oxygen to oxygen or OH<sup>-</sup> species that can migrate from vacancies to vacancies as soon as they are formed. In this temperature range, the variation of conductivity should be sufficiently significant to be used to detect presence of CO<sub>2</sub>. Specific experiments involving action of CO<sub>2</sub> on La<sub>2</sub>O<sub>3</sub> are in progress and will be published elsewhere. In the range of 700 to 800°C, the observed smooth undulation might be due to a last CO<sub>2</sub> departure and formation of final stable oxide. From the analyses of catalytic interactions, it should be noted that LaOHCO<sub>3</sub> and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> can be good catalysts for CO in air-CO mixtures. These phases might have some interest in selectivity of gas sensors interacting with environmental gas mixtures (CO + CO<sub>2</sub> + H<sub>2</sub>O); they might be stable in presence of CO<sub>2</sub> and could interact with CO. At low temperature, they might only interact with environmental CO<sub>2</sub> or H<sub>2</sub>O. At higher temperature, they might only interact with CO, not with these environmental gases.

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