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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 LaOHCO_3 , H_2O is analyzed by electrical impedance spectroscopy, from 25°C to 950°C, under air. The catalytic properties of LaOHCO_3 , $\text{La}_2\text{O}_2\text{CO}_3$ and La_2O_3 polycrystalline phases are studied by FTIR spectroscopy, in presence of gas mixtures CO-air and CH_4 -air, at temperatures ranging between 100°C to 525°C. The three materials behave differently in presence of CO or 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 CO_2 , and interacting with toxic gases (CO , 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 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 La_2O_3 phase stable above this temperature, under air atmosphere. Each phase can be sensitive to partial pressure of H_2O or CO_2 . Consequently, these phases can be used as sensing materials reacting with wet air and 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 LaOHCO_3 , $\text{La}_2\text{O}_2\text{CO}_3$, and La_2O_3 , to convert CH_4 and CO present in air- 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 LaOHCO_3 , H_2O 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

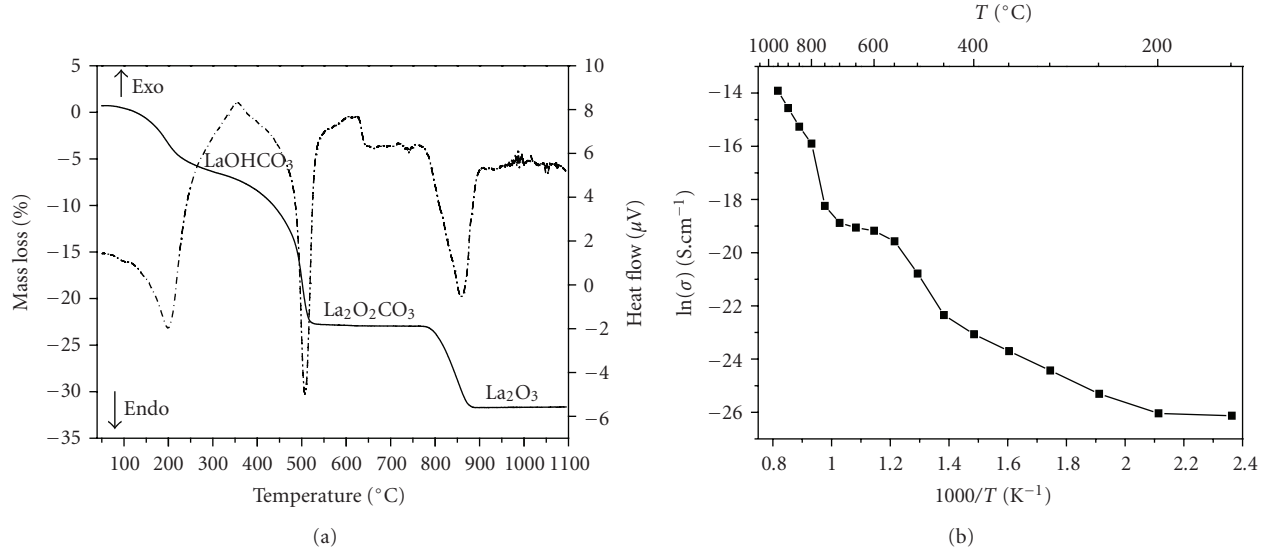
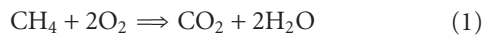


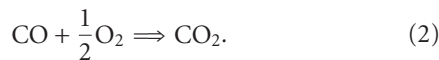
FIGURE 1: (a) Thermal decomposition analysis (DTA-TG) of hydrated hydroxycarbonate: successive phases LaOHCO₃ (LHC), La₂O₂CO₃ (LOC), and La₂O₃ (L), (b) Electrical impedance analysis of hydrated hydroxycarbonate: variation of $\ln\sigma$ versus $1000/T$. Existence of electrical changes corresponding to 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 LaOHCO₃, La₂O₂CO₃, and La₂O₃ were subjected successively to air-CH₄ 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 CO₂ vibrational band at 2340–2360 cm⁻¹ 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 La₂O₃, La₂O₂CO₃, or LaOHCO₃). 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 CO₂ bands by the surfaces S_i of

samples. The values S_i are successively in m²: $S(i = \text{La}_2\text{O}_3) = 0.61$, $S(i = \text{La}_2\text{O}_2\text{CO}_3) = 2.31$, $S(i = \text{LaOHCO}_3) = 5.62$.

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 La₂O₂CO₃ and, finally, the final formation of La₂O₃.

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⁻) 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⁻ and CO₂ species departure, involving defect formation in hydroxycarbonate and formation of dioxy carbonate La₂O₂CO₃;

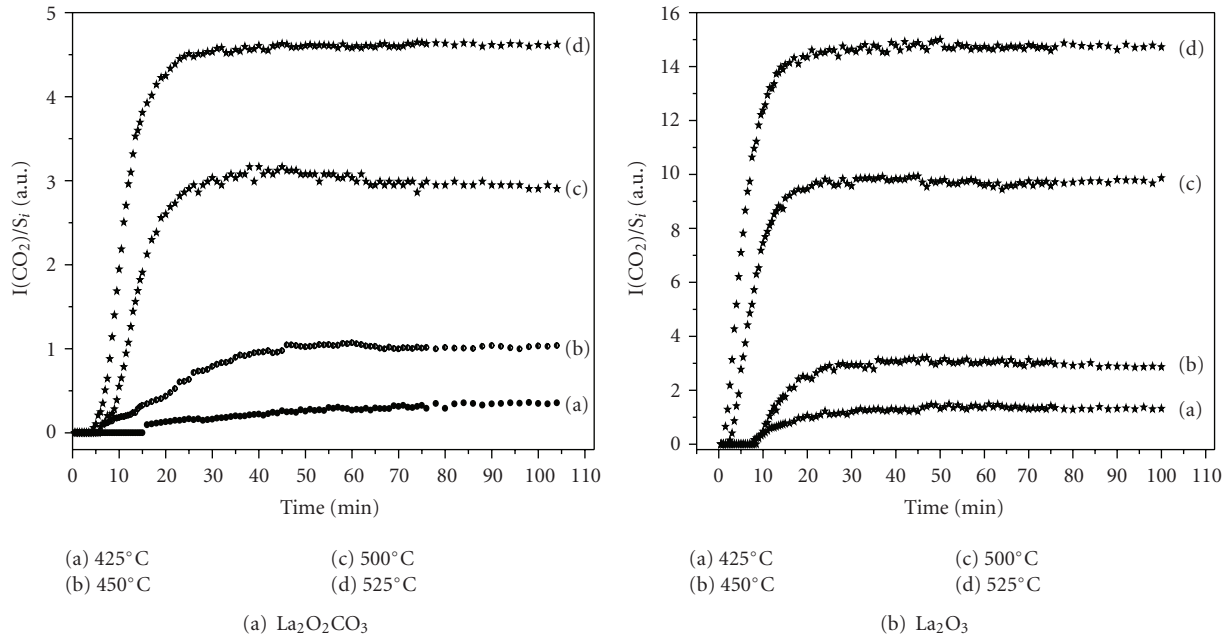


FIGURE 2: (a) catalytic conversion of CH_4 interacting with $\text{La}_2\text{O}_2\text{CO}_3$ as a function of time and temperature, (b) catalytic conversion of CH_4 interacting with La_2O_3 as a function of time and temperature. The normalized efficiencies are expressed in arbitrary units (a.u.).

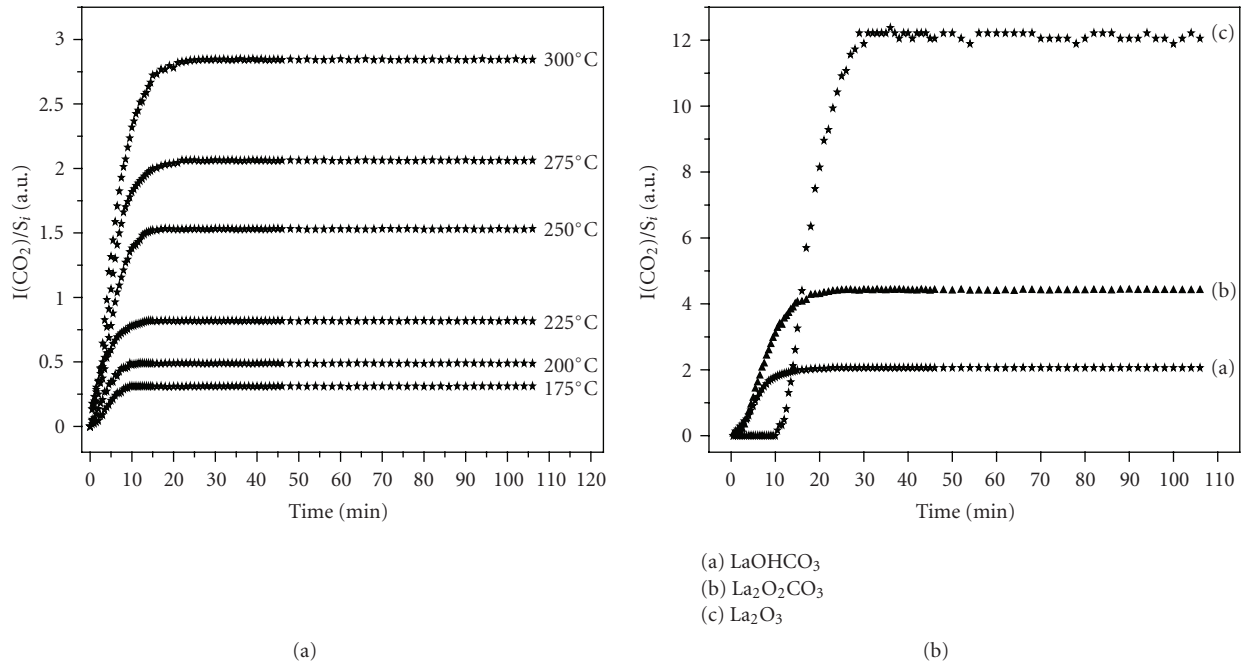


FIGURE 3: (a) catalytic efficiencies of LaOHCO_3 in presence of air-CO flows at various temperatures, (b) compared catalytic efficiencies of La_2O_3 , $\text{La}_2\text{O}_2\text{CO}_3$ and LaOHCO_3 in presence of air-CO flows, at a fixed temperature of 275°C ; the normalized efficiencies are expressed in a.u.

(c) Between 700°C and 800°C , a very weak abnormal evolution is observed (undulation), probably due to the last CO_2 departure from the oxycarbonate, with transformation into oxide La_2O_3 (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^- and one of the CO_3^{2-} species are unstable in the lattice, should be highly sensitive to water and CO_2 exchanges. This

might be used to detect water and CO₂ molecules in a gas sensor.

3.2. Catalytic Studies. Figures 2(a), 2(b) give the normalized catalytic efficiencies (intensities of CO₂ vibrational frequency band) of La₂O₂CO₃ and La₂O₃ subjected to CH₄-air flow (2500 ppm CH₄) at different temperatures. Because of thermal decomposition occurring at a temperature greater than 350°C, no experiment was possible for LaOHCO₃. Figure 3(a) reports the results for the LaOHCO₃ 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 CH₄ 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 La₂O₃ (per surface unit) is greater than that of the two other compounds.

4. Conclusion

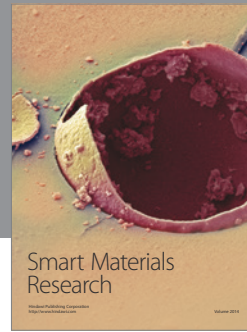
In this study, we have developed an electrical approach allowing determining the electrical responses of a phase change involving H₂O and CO₂ molecules elimination, from electrical impedance analyses. The departure of the couple H₂O + CO₂ can be linked to an increase of conductivity (the slope of the ln(σ) 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⁻ 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 CO₂. Specific experiments involving action of CO₂ on La₂O₃ 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 CO₂ departure and formation of final stable oxide. From the analyses of catalytic interactions, it should be noted that LaOHCO₃ and La₂O₂CO₃ 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 + CO₂ + H₂O); they might be stable in presence of CO₂ and could interact with CO. At low temperature, they might only interact with environmental CO₂ or H₂O. At higher temperature, they might only interact with CO, not with these environmental gases.

Acknowledgments

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