



HAL
open science

Temperature Dependent Electrical Properties and Catalytic Activities of La₂O₃–CO₂–H₂O Phase System

Madjid Arab, Bahcine Bakiz, Frédéric Guinneton, Sylvie Villain, Abdeljalil Benlhachemi, Jean-Raymond Gavarri

► **To cite this version:**

Madjid Arab, Bahcine Bakiz, Frédéric Guinneton, Sylvie Villain, Abdeljalil Benlhachemi, et al.. Temperature Dependent Electrical Properties and Catalytic Activities of La₂O₃–CO₂–H₂O Phase System. *Advances in Materials Science and Engineering*, 2009, 2009, pp.612130. 10.1155/2009/612130 . hal-01872934

HAL Id: hal-01872934

<https://hal.science/hal-01872934v1>

Submitted on 3 Dec 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License

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

Bahcine Bakiz,¹ Frédéric Guinneton,¹ Madjid Arab,¹ Sylvie Villain,¹
Abdeljalil Benlhachemi,² and Jean Raymond Gavarri¹

¹Institut Matériaux Microélectronique & Nanosciences de Provence, IM2NP, UMR CNRS 6242, Université du Sud Toulon-Var, BP 20132, 83957 La Garde Cedex, France

²Laboratoire Matériaux et Environnement Faculté des Sciences, Université Ibn Zohr, P.O. Box 8106, 80000 Agadir, Morocco

Correspondence should be addressed to Jean Raymond Gavarri, gavarri.jr@univ-tln.fr

Received 10 July 2009; Accepted 20 September 2009

Recommended by Steven Suib

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.

Copyright © 2009 Bahcine Bakiz et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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

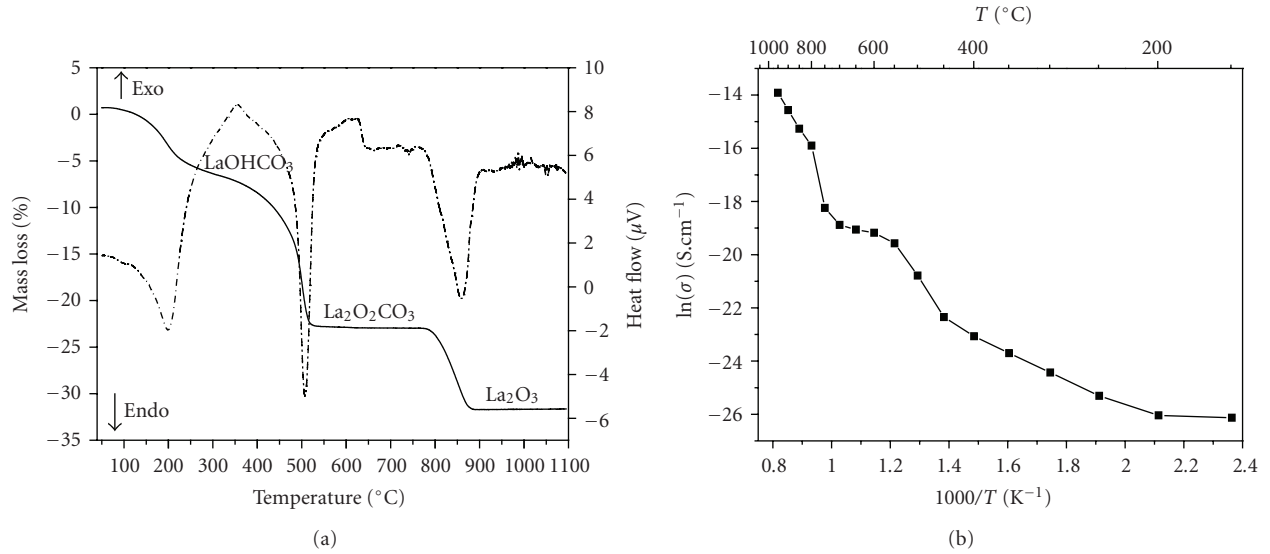
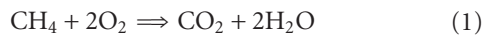


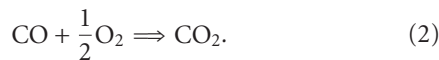
FIGURE 1: (a) Thermal decomposition analysis (DTA-TG) of hydrated hydroxycarbonate: successive phases LaOHCO_3 (LHC), $\text{La}_2\text{O}_2\text{CO}_3$ (LOC), and La_2O_3 (L), (b) Electrical impedance analysis of hydrated hydroxycarbonate: variation of $\ln\sigma$ versus $1000/T$. Existence of electrical 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_3 , $\text{La}_2\text{O}_2\text{CO}_3$, and La_2O_3 were subjected successively to air- CH_4 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_2 vibrational band at $2340\text{--}2360\text{ cm}^{-1}$ 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 La_2O_3 , $\text{La}_2\text{O}_2\text{CO}_3$, or LaOHCO_3). 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_2 bands by the surfaces S_i of

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

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 $^{\circ}\text{C}$ are clearly visible with a first lattice water departure, then the change of hydroxycarbonate into $\text{La}_2\text{O}_2\text{CO}_3$ and, finally, the final formation of La_2O_3 .

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 ($25\text{--}300^{\circ}\text{C}$), 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 CO_2 species departure, involving defect formation in hydroxycarbonate and formation of dioxy carbonate $\text{La}_2\text{O}_2\text{CO}_3$;

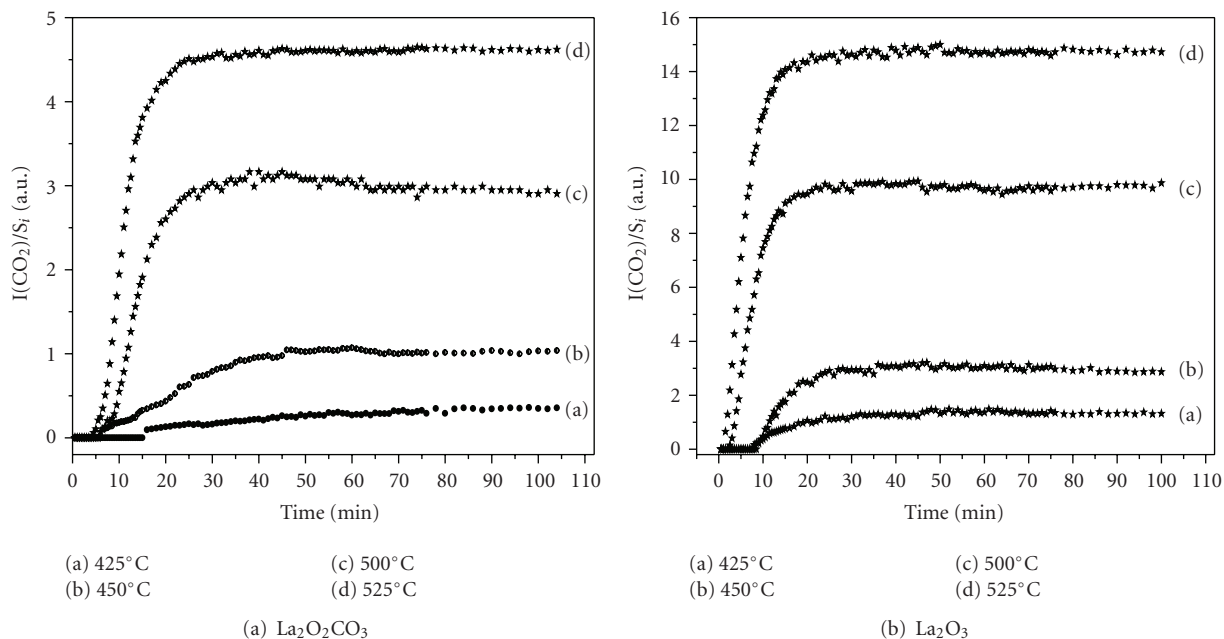


FIGURE 2: (a) catalytic conversion of CH₄ interacting with La₂O₂CO₃ as a function of time and temperature, (b) catalytic conversion of CH₄ interacting with La₂O₃ as a function of time and temperature. The normalized efficiencies are expressed in arbitrary units (a.u.).

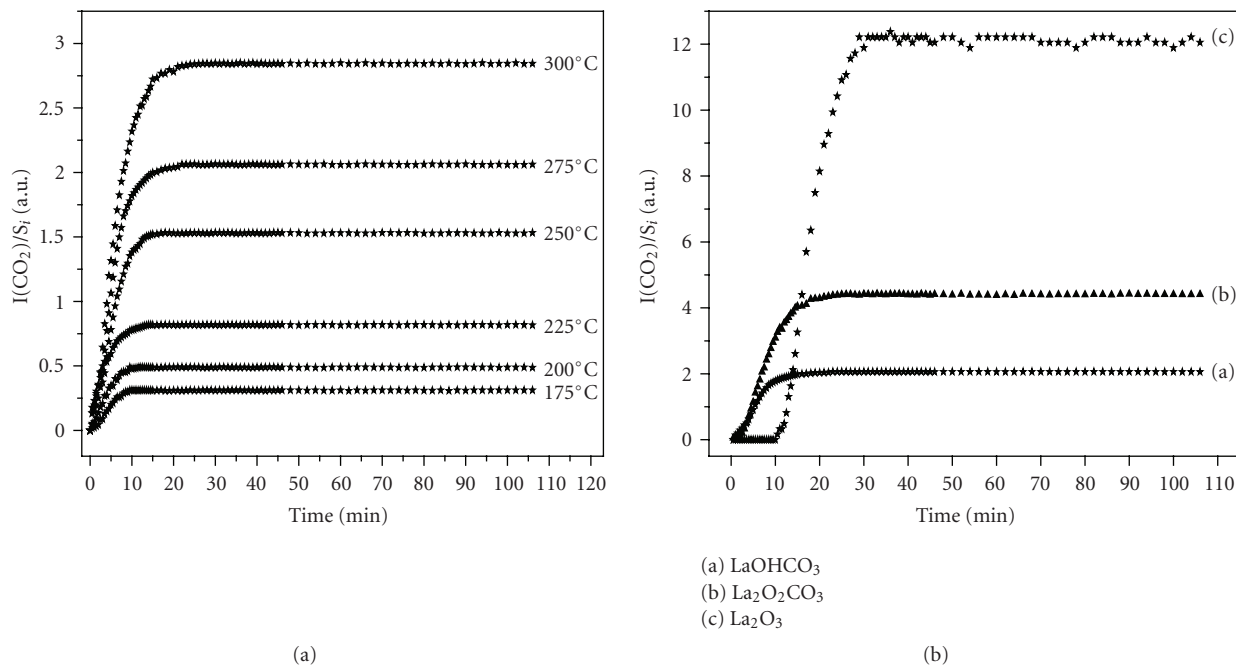


FIGURE 3: (a) catalytic efficiencies of LaOHCO₃ in presence of air-CO flows at various temperatures, (b) compared catalytic efficiencies of La₂O₃, La₂O₂CO₃ and LaOHCO₃ in presence of air-CO flows, at a fixed temperature of 275°C; the normalized efficiencies are expressed in a.u.

(c) Between 700°C and 800°C, a very weak abnormal evolution is observed (undulation), probably due to the last CO₂ departure from the oxycarbonate, with transformation into oxide La₂O₃ (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 CO₃²⁻ species are unstable in the lattice, should be highly sensitive to water and CO₂ 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

The authors acknowledge Council of Region PACA for financial support. This study has been developed in the framework of ARCUS CERES project (2009).

References

- [1] O. K. Nikol'skaya and L. N. Dem'yanets, "Hydrothermal crystallization in the systems La₂(CO₃)₃·6H₂O-CaCO₃(BaCO₃)-R-H₂O (R = Na₂CO₃, K₂CO₃, NaHCO₃, KHCO₃, NaCl, NH₄Cl, CO(NH₂)₂)," *Inorganic Materials*, vol. 41, no. 11, pp. 1206–1212, 2005.
- [2] H. Wakita and S. Kinoshita, "A synthetic study of the solid solutions in the systems and La₂(CH₃)₃ · 8H₂O-Ce₂(CO₃)₃ · 8H₂O and La(OH)CO₃-Ce(OH)CO₃," *Bulletin of the Chemical Society of Japan*, vol. 52, no. 2, pp. 428–432, 1979.
- [3] M. L. Panchula and M. Akinc, "Morphology of lanthanum carbonate particles prepared by homogeneous precipitation," *Journal of the European Ceramic Society*, vol. 16, no. 8, pp. 833–841, 1996.
- [4] S. Valange, A. Beauchaud, J. Barrault, Z. Gabelica, M. Daturi, and F. Can, "Lanthanum oxides for the selective synthesis of phytosterol esters: correlation between catalytic and acid-base properties," *Journal of Catalysis*, vol. 251, no. 1, pp. 113–122, 2007.
- [5] B. Klingenberg and M. A. Vannice, "Influence of pretreatment on lanthanum nitrate, carbonate, and oxide powders," *Chemistry of Materials*, vol. 8, no. 12, pp. 2755–2768, 1996.
- [6] A. N. Shirsat, M. Ali, K. N. G. Kaimal, S. R. Bharadwaj, and D. Das, "Thermochemistry of La₂O₂CO₃ decomposition," *Thermochimica Acta*, vol. 399, no. 1-2, pp. 167–170, 2003.
- [7] D. Zhao, Q. Yang, Z. Han, F. Sun, K. Tang, and F. Yu, "Rare earth hydroxycarbonate materials with hierarchical structures: preparation and characterization, and catalytic activity of derived oxides," *Solid State Sciences*, vol. 10, no. 8, pp. 1028–1036, 2008.
- [8] B. Bakiz, F. Guinneton, J.-P. Dallas, S. Villain, and J.-R. Gavarri, "From cerium oxycarbonate to nanostructured ceria: relations between synthesis, thermal process and morphologies," *Journal of Crystal Growth*, vol. 310, no. 12, pp. 3055–3061, 2008.
- [9] Q. Li, Z. Han, M. Shao, X. Liu, and Y. Qian, "Preparation of cerium hydroxycarbonate by a surfactant-assisted route," *Journal of Physics and Chemistry of Solids*, vol. 64, no. 2, pp. 295–297, 2003.
- [10] P. Nowakowski, S. Villain, A. Kopia, I. Suliga, and J.-R. Gavarri, "Catalytic conversion of air-methane flow by nanostructured ruthenium dioxide: FTIR spectroscopy and modeling," *Applied Surface Science*, vol. 254, no. 18, pp. 5675–5682, 2008.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

