Spectroscopic study of hydration and carbonation effects of La_2O_3-based materials

A. Orera, G. Larraz, M.L. Sanjuán
Instituto de Ciencia de Materiales de Aragón (Universidad de Zaragoza - CSIC), Zaragoza, Spain

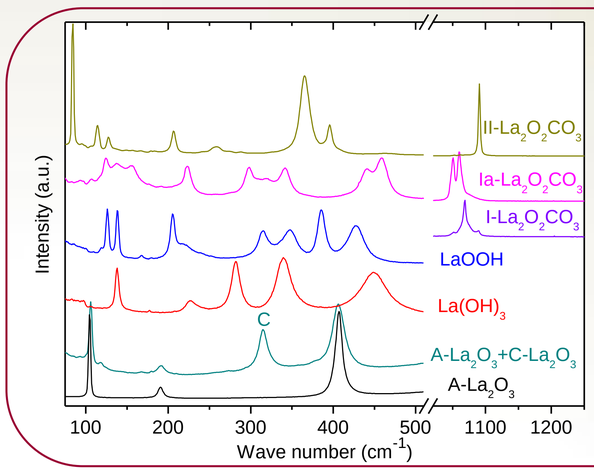
Introduction

- Lanthanum oxide takes part in a great variety of solids with technological interest, mainly as **support of catalysts for hydrocarbon oxidation**.
- The presence of $La_2O_2CO_3$ together with La_2O_3 is beneficial to the catalytic activity [1]. Besides, CO_2 and H_2O are byproducts in these catalytic reactions, so they play an important role in the process.
- **La_2O_3-related materials used in catalysis may undergo significant changes during reaction.**
- A great effort has been made in establishing the **thermal evolution** of La_2O_3, $La(OH)_3$ and La carbonates in varying atmospheric conditions, whit the aim of:
  - predict the aging behavior of the catalysts
  - test the conditions yielding the best performance
- We present a Raman study of La_2O_3-based materials focusing on the identification of phase content and thermal mechanisms involving **hydration** and **carbonation effects**.

Experimental

- La_2O_3 converts to $La(OH)_3$ when exposed to air. So it has been use as starting material for our studies.
- Raman spectra were recorded in a Dilor XY microspectrometer with a CCD detector.
- A Linkam TS1500V stage was used for high temperature measurements.

Experiments in different atmospheres were performed to check the temperature range of each phase



Phase Identification

To begin with, Raman spectra of the main derivatives of $La(OH)_3$ have been identified.

Attempts to synthesize pure tetragonal oxycarbonate I-$La_2O_2CO_3$ were unsuccessful, the Ia phase being always present.

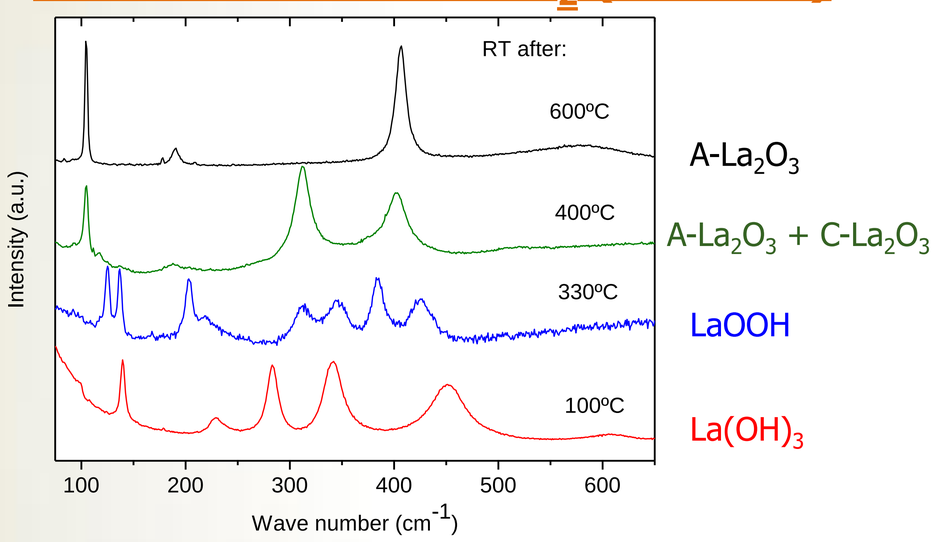
All these phases have been verified by XRD.

Fig. 1 Raman spectra of La_2O_3 based materials.

Phase Formation and Stability in different atmospheres

Heating-Cooling Cycles

Evolution Without CO_2 (Vacuum)



$A\text{-}La_2O_3$

$A\text{-}La_2O_3 + C\text{-}La_2O_3$

$LaOOH$

$La(OH)_3$

Fig. 2 Thermal evolution of $La(OH)_3$ under vacuum.

Dehydration of $La(OH)_3$ in two steps is observed, yielding a mixture of C and A La_2O_3 that evolve to the hexagonal phase as temperature is increased.

$$La(OH)_3 \rightarrow LaOOH \rightarrow C\text{-}La_2O_3 + A\text{-}La_2O_3 \rightarrow A\text{-}La_2O_3$$

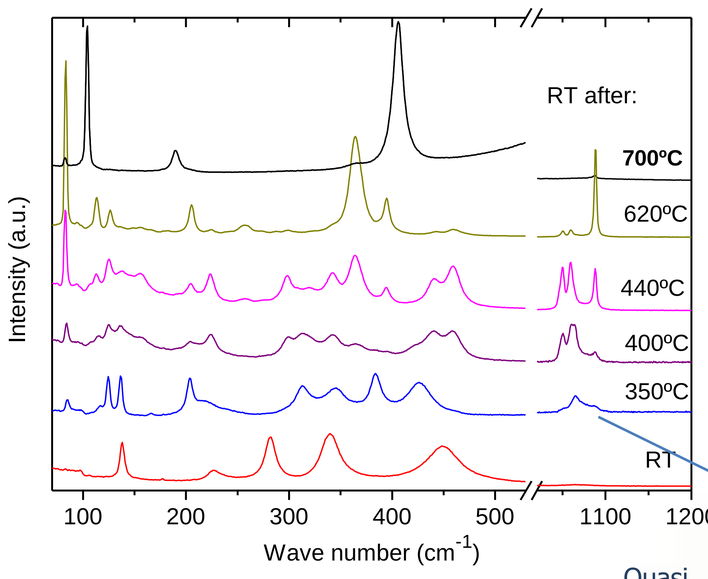
Cubic phase needs a complete crystallization of the **LaOOH** intermediate phase and $A\text{-}La_2O_3$ phase forms preferably from $La(OH)_3$.

Evidence of a relation between the symmetry of the starting material and the type of product obtained.

Evolution With CO_2 (Air)

When CO_2 is present, as in catalytic reactions involving hydrocarbons, the scenario is very different:

Phase content depends on the thermal history of the sample:
- ❑ Purity of the starting material
- ❑ Retention times at each temperature
- ❑ Flow of gas



Slow heating rates and long retention times have been employed in order to achieve quasi-equilibrium.

$A\text{-}La_2O_3$

$II\text{-}La_2O_3CO_3$

$Ia+II\text{-}La_2O_3CO_3$

$I+Ia\text{-}La_2O_3CO_3$

$LaOOH + La_x(OH)_y(CO_3)_z$

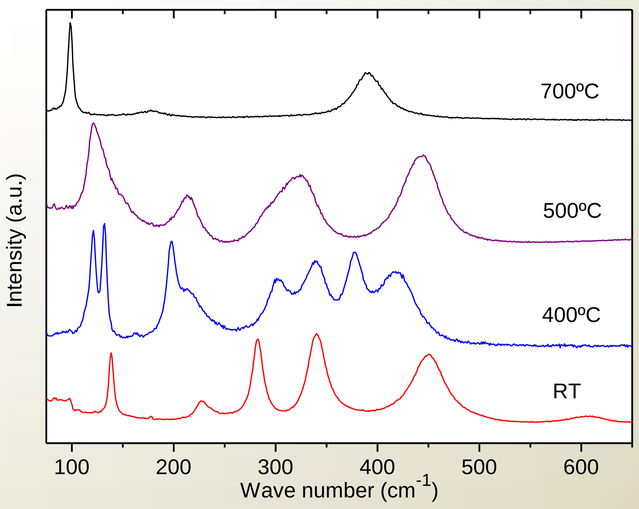
$La(OH)_3$

Fig. 3 Thermal evolution of $La(OH)_3$ in air.

Quasi amorphous hydroxycarbonates might be a transient phase between $La(OH)_3$ and $II\text{-}La_2O_2CO_3$. [2]

In-Situ Heating experiments

Fast heating minimizes carbonation effects (only type $Ia\text{-}La_2O_2CO_3$ is detected) and favors dehydration to $A\text{-}La_2O_3$.



$A\text{-}La_2O_3$

$Ia\text{-}La_2O_3CO_3$

$LaOOH$

$La(OH)_3$

Fig. 4 Thermal evolution of $La(OH)_3$ in air heating at 10ºC/min.

Summary

Different temperature phase evolution have been observed depending on atmosphere and dynamic:

$La(OH)_3$ →
- $LaOOH \rightarrow I\text{-}La_2O_3CO_3 \rightarrow Ia\text{-}La_2O_3CO_3 \rightarrow II\text{-}La_2O_3CO_3 \rightarrow A\text{-}La_2O_3$
- $LaOOH \rightarrow Ia\text{-}La_2O_3CO_3 \rightarrow A\text{-}La_2O_3$
- $[La_x(OH)_y(CO_3)_z] \rightarrow II\text{-}La_2O_3CO_3 \rightarrow A\text{-}La_2O_3$
- $LaOOH \rightarrow C\text{-}La_2O_3 + A\text{-}La_2O_3 \rightarrow A\text{-}La_2O_3$ **No CO_2**

Conclusions

- ✓ **Raman spectroscopy allows the observation of surface effects that are extremely important in catalysis processes.**
- ✓ **Raman spectrum of $La(OH)_3$, LaOOH, A and C-La_2O_3, I, Ia and II-$La_2O_2CO_3$ have been identified.**
- ✓ **The occurrence of one or another phase among the list of La_2O_3-derived phases and their thermal evolution depends upon several factors:**
  - **Purity of the starting material**
  - **Environmental conditions**
    - **Humidity**
    - **Atmosphere**
  - **Surface effects: Grain size**
  - **Thermal history**
    - **Heating rates**
    - **Retention times and T**
- ✓ **If no CO_2 is present, $La(OH)_3$ dehydrates to LaOOH and then to a mixture of C- and A-La_2O_3 until, upon further heating, only A-La_2O_3 phase remains.**
- ✓ **In air a competition occurs between dehydration from LaOOH to the oxide and carbonation to oxycarbonates.**

References:
- [1] Taylor R.P.; Schrader G.L., Ind. Eng. Chem. Res. 1991, 30, 1016-1023.
- [2] Bernal S.; Botana F.J.; García R.; Rodríguez-Izquierdo J.M., Termochim. Acta 66, 1983, 139-145

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