

# Effects of rhodium and platinum on the reactivity of lanthanum phases

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## Abstract

Rhodium and platinum catalysts were prepared by wet impregnation of Anedra lanthanum oxide. The polymorph forms of  $\text{La}_2\text{O}_2\text{CO}_3$  have also been prepared by an appropriate treatment of lanthanum compounds in carbon dioxide. The characterisation of the phases present in these solids was performed by XRD, FT-IR, LRS, TPD and TGA. One of the untreated supports (Aldrich) was  $\text{La}(\text{OH})_3$ , and the other (Anedra) consisted mainly of II- $\text{La}_2\text{O}_2\text{CO}_3$  with traces of type Ia oxycarbonate and lanthanum hydroxide. Catalysts with a low rhodium loading showed an increase of Ia- $\text{La}_2\text{O}_2\text{CO}_3$  already present on the support, whereas those with a low platinum loading would not modify the phases of the lanthanum solid. A different behaviour was observed in high metal loading catalysts. In this case, metals would catalyse the decomposition of type Ia polymorph and also prevent the hydration of the support. The treatment with  $\text{CO}_2$  provides additional information about the effect of the gas upon the metal containing solids. Pt would favour the carbon dioxide interaction with the support to form monoclinic polymorph (type Ia), while rhodium would prevent the further formation of the oxycarbonate phase. © 2004 Elsevier B.V. All rights reserved.

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## 1. Introduction

Numerous applications of lanthanum oxide have been recently found in various fields. In catalysis, it is used as support for metals active for different reactions. Due to its refractory nature, it is an important ingredient in the manufacturing of superconductors and ceramics.  $\text{La}_2\text{O}_3$  is also used in calcium lights, optical glass, and in the formation of ceramic cores for carbon arc electrodes [1].

The simple manipulation of lanthana in air induces its hydration and its carbonation in bulk. Therefore, carbonation should not be disregarded in the preparation of metal/ $\text{La}_2\text{O}_3$  solids. Lanthanum oxide carbonates exist in three crystalline modifications (I, Ia and II); the three polymorphs hold in an arrangement of  $(\text{La}_2\text{O}_2^{2+})$  layers separated by  $\text{CO}_3^{2-}$  ions. Type I has square layers and is tetragonal, while type Ia is described as a monoclinic distortion of form I [2]. II- $\text{La}_2\text{O}_2\text{CO}_3$  is completely indexed on the hexagonal unit cell. An exact description of this polymorph is given by Olafsen et al. [3]. Improved understanding of these materials is of importance in relation to the use of lanthanum oxides as catalyst supports in  $\text{CO}_2$ -containing atmospheres.

The incorporation of noble metals to the lanthanum oxide matrix induces phase transformations and catalytic chemical reactions between gas phase components and the solid.

On the other hand, it is well known that the physicochemical properties of the support strongly affect the catalytic behaviour of the metal on oxide materials [4,5].

The goal of this study was to characterise the structure of solids obtained when either Rh or Pt are supported on lanthanum oxide and are subjected to different heat treatments in the presence of several gas atmospheres. XRD, FT-IR, LRS; TPD and TGA were the main tools used to achieve this goal.

## 2. Experimental

### 2.1. Preparation methods

To prepare II- $\text{La}_2\text{O}_2\text{CO}_3$ ,  $\text{La}_2\text{O}_3$  (Anedra) was heated under flowing dry  $\text{CO}_2$  using a temperature program consisting of a linear  $5 \text{ K min}^{-1}$  ramp from 300 to 923 K, a linear  $2 \text{ K min}^{-1}$  ramp from 923 to 973 K, and finally an isothermal plateau at 973 K for 30 min [6]. The Ia- $\text{La}_2\text{O}_2\text{CO}_3$  was obtained from the Aldrich  $\text{La}_2\text{O}_3$  (99.99% Gold Label). The oxide was heated at  $10^\circ \text{ min}^{-1}$  from 298 to 773 K, under flowing He. The flow was then switched to dry  $\text{CO}_2$  and the temperature kept at 773 K for 1 h.

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Metal deposition on the oxide was performed by the conventional wet impregnation of  $\text{La}_2\text{O}_3$  (Anedra 99.99%) using  $\text{H}_2(\text{PtCl}_6) \cdot 6\text{H}_2\text{O}$  and  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  as precursor compounds. In all cases, the resulting suspension was then heated at 353 K to evaporate the water, and the solid material was dried in an oven at 383 K overnight. The catalysts were calcined for 6 h at 823 K.

## 2.2. X-ray diffraction (XRD)

The XRD patterns of the solids were obtained with an XD-D1 Shimadzu instrument, using  $\text{Cu K}\alpha$  radiation at 35 kV and 40 mA. The scan rate was  $1^\circ \text{min}^{-1}$  for values between  $2\theta = 10^\circ$  and  $80^\circ$ .

## 2.3. Laser Raman spectroscopy (LRS)

The Raman spectra were recorded with a TRS-600-SZ-P Jasco Laser Raman instrument, equipped with a CCD (charge coupled device) with the detector cooled to about 153 K using liquid  $\text{N}_2$ . The excitation source was the 514.5 nm line of a Spectra 9000 Photometrics Ar ion laser. The laser power was set at 30 mW.

## 2.4. FT infrared spectroscopy (FT-IR)

The IR spectra were obtained using a Shimadzu FT-IR 8101M spectrometer with a spectral resolution of  $4 \text{ cm}^{-1}$ . The solid samples were prepared in the form of pressed wafers (ca. 2 wt.% sample in KBr).

## 2.5. Temperature-programmed desorption (TPD)

TPD measurements were carried out on the calcined and the  $\text{CO}_2$  treated samples at 773 K. The temperature was increased at  $10 \text{ K min}^{-1}$  from 300 to 1073 or 1173 K. In either case the final temperature was kept constant for 2 h. The evolved gases were analysed by a Leybold quadrupole mass spectrometer able to monitor 10 components simultaneously as a function of temperature/time.

## 2.6. Thermogravimetric analysis (TGA)

They were performed on the calcined and  $\text{CO}_2$  treated catalysts in a Mettler Toledo TGA/SDTA (Model 851) system. The solids (usually 10 mg) were heated at  $10 \text{ K min}^{-1}$  to 1173 K under flowing air ( $90 \text{ ml min}^{-1}$ ).

## 3. Results

### 3.1. Lanthanum phases

#### 3.1.1. The support

The XRD pattern of the Aldrich support exposed to ambient conditions indicates that  $\text{La}(\text{OH})_3$  is the only phase present in this solid (Fig. 1a). Two phases,  $\text{La}(\text{OH})_3$  (ASTM

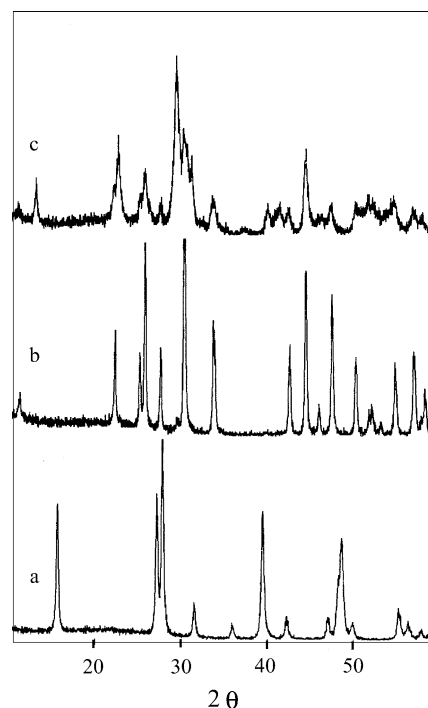


Fig. 1. X-ray diffraction patterns of lanthanum compounds: (a) Aldrich support; (b) Anedra support treated in  $\text{CO}_2$  at 973 K; (c) Aldrich support treated in  $\text{CO}_2$  at 773 K.

No. 6-585) and  $\text{La}_2\text{O}_2\text{CO}_3$  (ASTM No. 37-804), were identified in the lanthanum oxide used as support (Anedra).

Table 1 shows the IR band assignments. The FT-IR spectrum of  $\text{La}_2\text{O}_3$  (Aldrich) is shown in Fig. 2a. A sharp band at  $3608 \text{ cm}^{-1}$  (not shown) and a broad band at  $643 \text{ cm}^{-1}$  are observed. They are characteristic of stretching and bending OH vibrations of lanthanum hydroxide, respectively [7]. The bands at 1462, 1384 and the weak one at 855 correspond to the vibration of  $\text{CO}_3^{2-}$  groups in hydrated  $\text{La}_2(\text{CO}_3)_3$  [7]. Bands observed in the  $2950\text{--}2200 \text{ cm}^{-1}$  region (not shown) could be assigned to the combination and overtone vibrations of carbonate [8]. The Raman spectrum of Aldrich support (not shown) exhibits four bands at 284, 339, 447 and  $597 \text{ cm}^{-1}$ . The frequencies of these bands are in agreement with those reported for crystalline  $\text{La}(\text{OH})_3$  [9].

$\text{La}_2\text{O}_3$  (Anhedra) FT-IR spectrum (Fig. 2b) also exhibits the bands characteristic of OH vibrations,  $3608$  and  $643 \text{ cm}^{-1}$ , while the  $\text{CO}_3^{2-}$  vibrations appear at 1462, 1086, 855 and  $749 \text{ cm}^{-1}$ . These bands correspond to type II- $\text{La}_2\text{O}_2\text{CO}_3$  [2]. The shoulder at  $1364 \text{ cm}^{-1}$  reveals the presence of the monoclinic type (Ia).

#### 3.1.2. Type Ia- $\text{La}_2\text{O}_2\text{CO}_3$

The diffraction pattern of the Aldrich  $\text{La}(\text{OH})_3$  treated with carbon dioxide at 773 K reveals the major peak of monoclinic Ia- $\text{La}_2\text{O}_2\text{CO}_3$  (Fig. 1c). Traces of type II are also present. Besides, the FT-IR spectrum also corresponds to Ia- $\text{La}_2\text{O}_2\text{CO}_3$  (Fig. 2d). The  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  modes show

Table 1  
FT-IR and Raman data of lanthanum compounds

Solid	Crystalline phases (DRX)	Raman 250–700 cm <sup>-1</sup> region	FT-IR wavenumbers of CO <sub>3</sub> <sup>2-</sup> (cm <sup>-1</sup> ) vibration			
			$\nu_3$	$\nu_1$	$\nu_2$	$\nu_4$
Ia-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	Ia-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	297, 315, 340, 358, 388, 437(sh),450	1504, 1470, 1367	1093	863	740
II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	358, 384	1508, 1465	1087	856	747
Rh(0.2%)	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub>	358, 384	1504(s), 1467, 1370	1087	856	747
Rh(0.6%)	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub>	358, 384	1504(s), 1467, 1370	1087	856	747
Rh(2%)	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub>	358, 384	1470, 1388	1087	856	747
Pt(0.93%)	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub> , La <sub>2</sub> O <sub>3</sub>	358, 384, 426, 443	1495, 1465, 1370(s)	1087	856	747
Pt(3.8%)	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub>	297, 326, 358, 387, 403, 429	1470	1087	856	747
Anedra support	II-La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub> , La(OH) <sub>3</sub>	284, 358, 384, 447	1504(s), 1467, 1370(s)	1087	856	747
Aldrich support	La(OH) <sub>3</sub>	284, 339, 447, 597	1462, 1384	–	855	–

threefold splitting, due to more than one CO<sub>3</sub><sup>2-</sup> type [2].

The Raman spectrum presents several overlapped peaks at 297, 315, 338, 358, 388 and 437(sh), 450 cm<sup>-1</sup>. Multiple splitting is observed in the 700–1600 cm<sup>-1</sup> region Fig. 3a and 4g). The strongest band appears at 1060 cm<sup>-1</sup>. It was previously assigned to type Ia polymorph [10] by comparison with the FT-IR spectrum.

### 3.1.3. Type II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>

After treating the Anedra support in a flow of dry CO<sub>2</sub> at 973 K, the XRD technique reveals the presence of the hexagonal La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (type II, ASTM No. 37-804) (Fig. 1b). Only traces of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> type I or Ia appear in this solid. The FT-IR bands at 3608 and 643 cm<sup>-1</sup> and the shoulder at 1364 cm<sup>-1</sup> vanish, indicating that no lanthanum hydroxide is present (Fig. 2c).

The Raman spectrum of this solid shows three peaks in the 250–800 cm<sup>-1</sup> region, at 358, 384, and 747 cm<sup>-1</sup>. Besides, a

strong band at 1086 cm<sup>-1</sup> and weak ones at 1408, 1415 and 1450 cm<sup>-1</sup> are seen (Figs. 3b and 4h). In a previous work we assigned those bands to type II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [10], since no Raman data for lanthanum oxycarbonates were found in the literature.

### 3.2. The catalysts

The XRD patterns of all the metal supported solids showed the presence of II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La(OH)<sub>3</sub> phases. La<sub>2</sub>O<sub>3</sub> signals were also detected on the Pt(0.93%) catalyst. No XRD reflections associated with either Rh or Pt compounds were detected in the calcined catalysts, not even in those solids with high metal loading (Rh(2%) and Pt(3.8%) (not shown)).

The FT-IR spectra of the calcined catalysts are presented in Fig. 5. FT-IR spectra of solids with high metal loading (Fig. 5a and b, respectively) present bands at 1504(s), 1462, 1384, 1086, 855 and 749 cm<sup>-1</sup>, pertaining to type

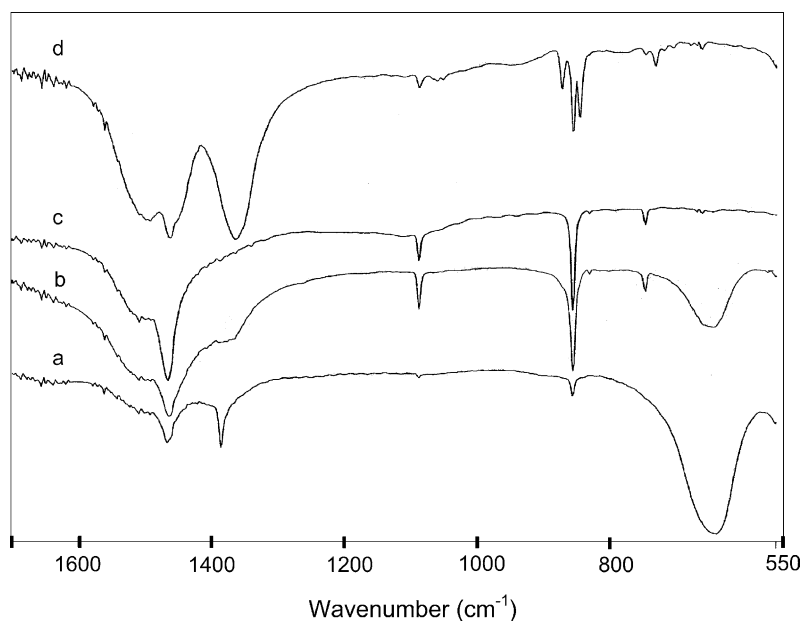


Fig. 2. FT-IR spectra of lanthanum phases: (a) Aldrich support; (b) Anedra support; (c) Anedra support treated in CO<sub>2</sub> at 973 K; (d) Aldrich support treated in CO<sub>2</sub> at 773 K.

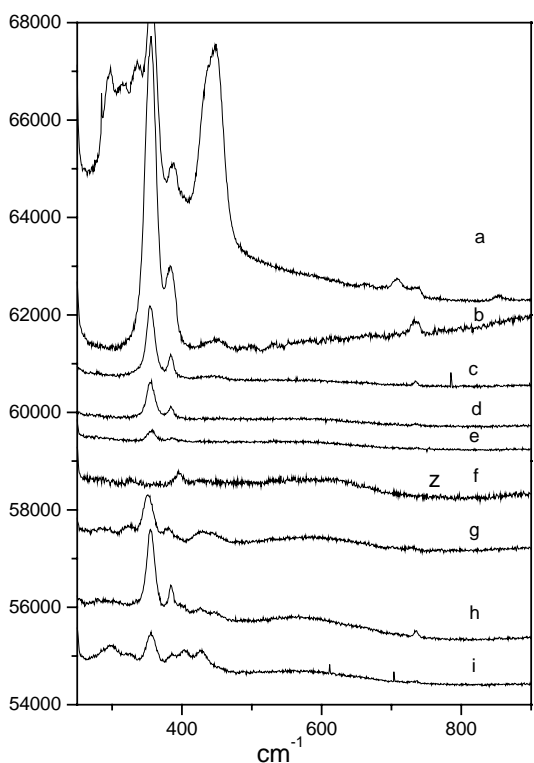


Fig. 3. Laser Raman spectra of lanthanum oxycarbonates and metal supported solids in the 250–900  $\text{cm}^{-1}$  region: (a) Ia- $\text{La}_2\text{O}_2\text{CO}_3$ ; (b) II- $\text{La}_2\text{O}_2\text{CO}_3$ ; (c) Rh(0.2%); (d) Rh(0.6%); (e) Rh(2.0%); (f) Rh(2.0%) calcined at 1073 K; (g) Pt(0.9%) treated in  $\text{CO}_2$  at 773 K; (h) Pt(0.9%); (i) Pt(3.8%).

II- $\text{La}_2\text{O}_2\text{CO}_3$  and the carbonate. The spectra of low metal loading catalysts show bands at 1504(s), 1467, 1087, 856 and 747  $\text{cm}^{-1}$  coinciding with those of the hexagonal (type II) structure of  $\text{La}_2\text{O}_2\text{CO}_3$  [11]. In addition, a signal at 1368  $\text{cm}^{-1}$  points out the presence of monoclinic (type Ia)

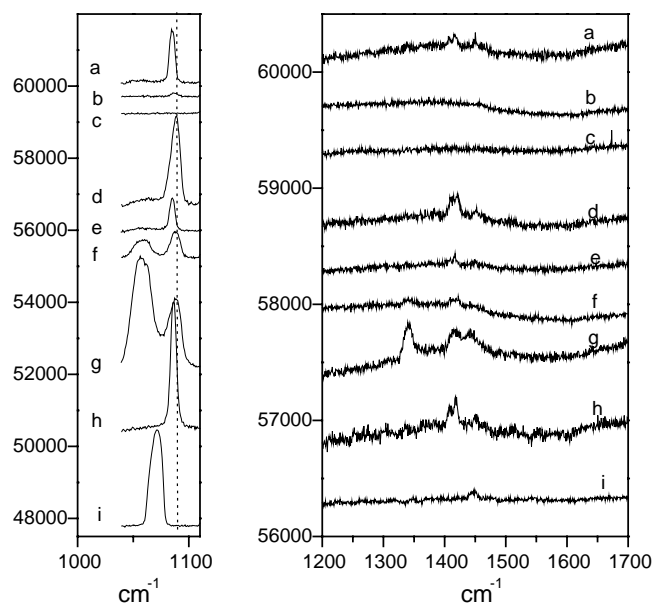


Fig. 4. Laser Raman spectra of lanthanum oxycarbonates and metal supported solids in the 1000–1600  $\text{cm}^{-1}$  region: (a) Rh(0.2%); (b) Rh(2.0%); (c) Rh(2.0%) calcined at 1073 K; (d) Pt(0.9%) treated in  $\text{CO}_2$  at 773 K; (e) Pt(0.9%); (f) Pt(3.8%); (g) Ia- $\text{La}_2\text{O}_2\text{CO}_3$ ; (h) II- $\text{La}_2\text{O}_2\text{CO}_3$ ; (i)  $\text{SrCO}_3$ .

or tetragonal polymorph (type I) in rhodium solids (Fig. 5c). Some slight splitting of those bands would indicate that the Ia phase is present. On the other hand, the Pt(0.93%) spectrum shows only a shoulder at 1368  $\text{cm}^{-1}$  (Fig. 5d). The spectra of the same Pt solid treated with pure  $\text{CO}_2$  at 773 K is shown in Fig. 5e. The shoulder at 1364  $\text{cm}^{-1}$  grows in an intense band while signals in the 2800–2900  $\text{cm}^{-1}$  region almost vanish. This would indicate the development of type I or Ia- $\text{La}_2\text{O}_2\text{CO}_3$  and the disappearance of carbonates and the lanthanum hydroxide. The splitting observed in the oxycarbonate bands favours the predominance of the Ia

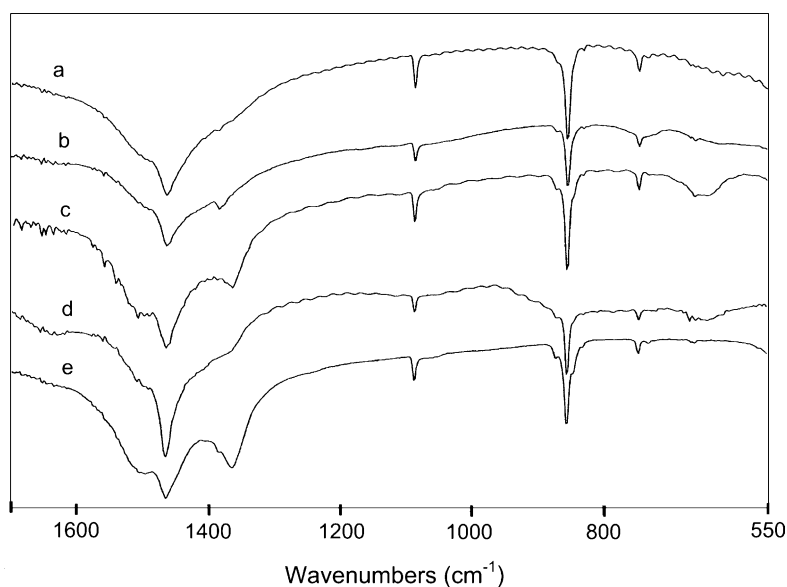


Fig. 5. FT-IR spectra of metal supported solids: (a) Pt(3.8%); (b) Rh(2.0%); (c) Rh(0.6%); (d) Pt(0.9%); (e) Pt(0.9%) treated in  $\text{CO}_2$  at 773 K.

polymorph. Bands of rhodium-based catalysts do not show any change after treating the solid with CO<sub>2</sub>.

The Raman spectra of the Rh catalysts are shown in Figs. 3 and 4. All the solids treated at 823 K exhibit peaks at 358, 384, 747 and 1086 cm<sup>-1</sup> assigned to type II lanthanum oxycarbonate. The high loading solid calcined at 1073 K shows no peak at 1086 cm<sup>-1</sup>, which is in agreement with the disappearance of the features in the region 250–800 cm<sup>-1</sup>. Only two very weak bands appear between 300 and 400 cm<sup>-1</sup>. The band at 400 cm<sup>-1</sup> could correspond to lanthanum oxide [4].

For the platinum low loading catalyst (Figs. 3h and 4e), the Raman spectrum is similar to those recorded for the Rh solids, with weak bands at 426, 446, and 1060 cm<sup>-1</sup>. These features correspond to type Ia oxycarbonate. After the treatment with CO<sub>2</sub>, those bands become well defined (Figs. 3g and 4d).

In the case of the Pt(3.8%) material, new features are observed at 297, 326, and 403 cm<sup>-1</sup> (Fig. 4f). The band at 446 cm<sup>-1</sup> does not appear suggesting that the Ia oxycarbonate is not present. Bands at similar frequency were previously [9] assigned to the presence of LaOCl in Pd/La<sub>2</sub>O<sub>3</sub> catalysts. In those solids, it appeared that part of the chlorine originally associated with PdCl<sub>2</sub> may react with La(OH)<sub>3</sub> during calcinations to form LaOCl. A similar reaction could occur in the platinum catalysts. This observation is supported by TPR data. The TPR profile of Pt/La<sub>2</sub>O<sub>3</sub> (not shown) is symptomatic of the oxychloride species.

### 3.3. TPD

The main gaseous products obtained in the desorption experiments carried out in calcined solids were CO<sub>2</sub> and H<sub>2</sub>O. Phases II and Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> profiles (Fig. 6c and d) revealed only one peak of CO<sub>2</sub> desorption at 1070 and 1150 K, respectively. Type I oxycarbonate desorption was carried out at 1173 K and then kept at this temperature for 1 h. The decomposition temperature of type II oxycarbonate is in agreement with the value previously reported by Taylor and Schrader [6], even though the gas phase composition was a mixture of carbon dioxide, methane, helium and oxygen.

Fig. 6 shows the 44 amu profile for Rh(0.6%) and Pt(0.93%) solids (a and b, respectively). The rhodium solid profile displays two peaks, the first at 1070 K and the second and more important one appearing along the 1073 K isotherm. The platinum solid profile also presents two peaks at temperatures similar to those of the Rh(0.6%), but in this case both peaks have a similar intensity. Experiments carried out from 298 to 1173 K confirm the existence of these two peaks for all the solids. The 18 amu profile (not shown) exhibits one peak at 650 K due to lanthanum hydroxide decomposition.

After treatment with CO<sub>2</sub> at 773 K, a very slight increase in the second peak area is observed in the Rh(0.6%) 44 amu profile (Fig. 7a). The Rh(0.2%) (Fig. 7b) shows a similar

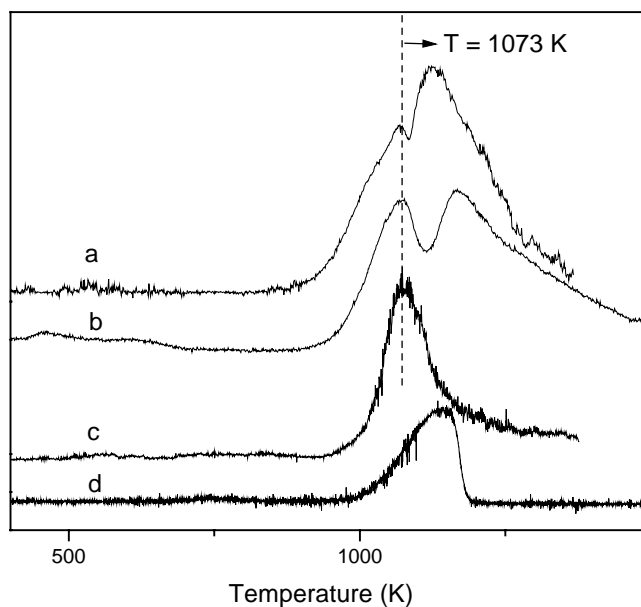


Fig. 6. TPD profiles of CO<sub>2</sub> obtained over: (a) Rh(0.6%); (b) Pt(0.9%); (c) II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>; (d) Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.

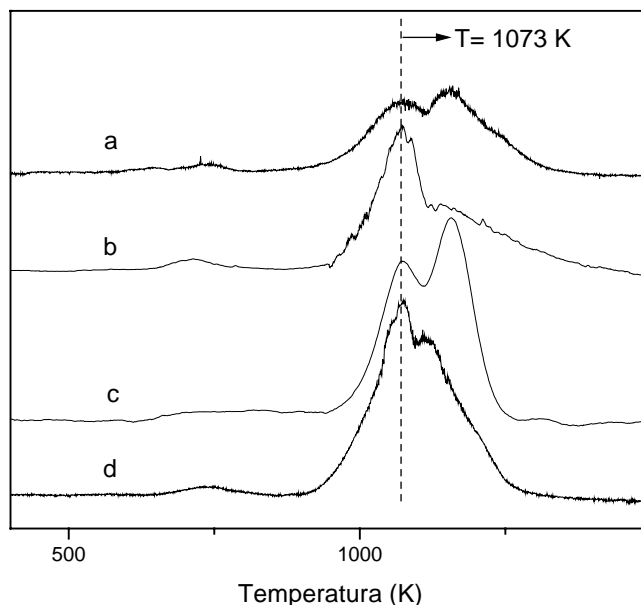


Fig. 7. TPD profiles of 44 amu of the solids treated in CO<sub>2</sub> at 773 K: (a) Rh(0.6%); (b) Rh(0.2%); (c) Pt(0.9%); (d) Anedra support.

behaviour. The small peaks at 633 K could be assigned to decomposition of carbonate, since no peaks in the 18 amu profile are detected for both solids at this temperature. On the other hand, after treating Pt(0.93%) with carbon dioxide, the CO<sub>2</sub> desorption profile shows a significant increase in the area of the second peak (Fig. 7c). In the case of the support treated with CO<sub>2</sub> (Fig. 7d), the second peak appears only as a shoulder.

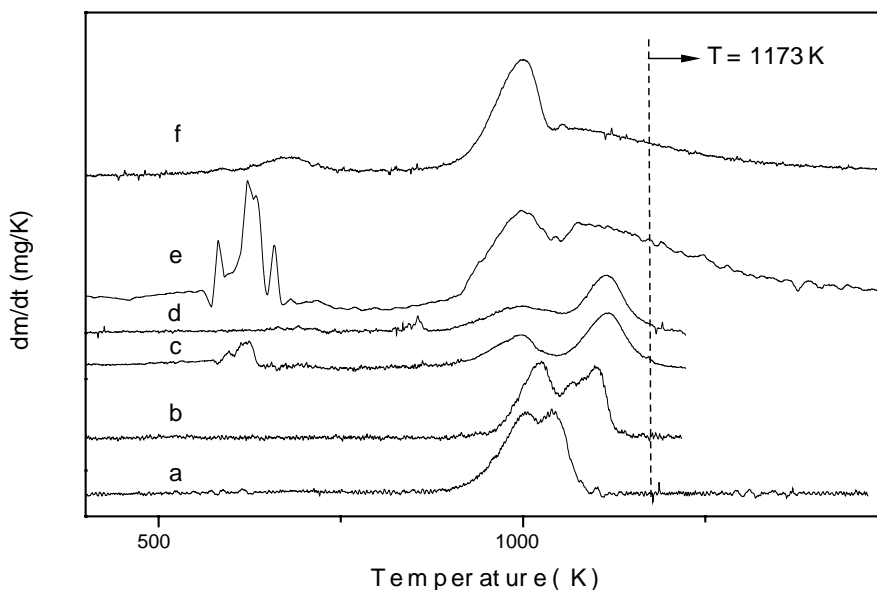


Fig. 8. DTG analysis of the prepared solids: (a) Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>; (b) II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>; (c) Rh(0.6%); (d) treated in CO<sub>2</sub> at 773 K; (e) Pt(0.9%); (f) Pt(0.9%) treated in CO<sub>2</sub> at 773 K.

### 3.4. TGA

Fig. 8 shows calcined and CO<sub>2</sub> treated solids weight changes during TGA experiments. Taking into account the TPD results for the calcined solids, the mass loss in the temperature range from about 550 to 670 K could be due to the decomposition of lanthanum hydroxide. This peak appears in all calcined solids and the fresh Anedra support. The oxycarbonate decomposition in type Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> (a) starts at 900 K and takes place in two steps with maximums at 1000 and 1040 K (the temperature program went up to 1173 K, followed by an isothermal step at this temperature). Type II oxycarbonate profile (b) shows also two peaks with maxima at 1030 and 1100 K. For both solids the weight loss corresponds to the total decomposition of the oxycarbonate.

The Rh(0.6%) catalyst (c) presents two well-defined peaks, the first with a maximum at 1000 K and the second one at 1110 K. The Rh(0.2%) solid behaves alike (not shown). After treating these solids with CO<sub>2</sub>, no major changes in the TGA profile are observed (d). After treating the Pt(0.93%) with carbon dioxide, on the other hand, there is a significant increase in the first peak area (e and f). The low temperature peak (680 K) could be due to the lanthanum carbonate formed during the CO<sub>2</sub> treatment.

## 4. Discussion

### 4.1. Lanthanum phases

A variety of compounds may coexist with the lanthanum oxide exposed to different gases. The actual composition of the solid depends on the preparation method and the pretreat-

ment. There is also a particular sensitivity to the presence of H<sub>2</sub>O and CO<sub>2</sub> in the gas phase [12]. La<sub>2</sub>O<sub>3</sub> was shown to undergo hydration and carbonation. This latter process was found to involve the formation of a hydroxycarbonate material on the outer layers of the bulk oxide. Fleisch et al. [13] found that on exposure to atmospheric water and CO<sub>2</sub>, the lanthanum oxide completely transforms into carbonated hydroxide in less than 24 h. Bernal et al. [12] showed that the only diffraction lines observed in the oxide aged in air are those of La(OH)<sub>3</sub>. Klingenberg and Vannice [8] examined the influence of purity on La<sub>2</sub>O<sub>3</sub> samples. The XRD patterns for samples of 99.9 and 99.99% revealed that they are crystallized as La(OH)<sub>3</sub> whereas for the sample of 99.999% the pattern of La<sub>2</sub>O<sub>3</sub> is prominent and only a small amount of La(OH)<sub>3</sub> is present. In our case, both oxides are 99.99%, but in the Aldrich sample the only diffraction lines are those of the La(OH)<sub>3</sub> (Fig. 1a). This is confirmed by the corresponding Raman and FT-IR spectrum (Fig. 2a); the latter has strong bands at 3608 and 643 cm<sup>-1</sup> assigned to the hydroxyl groups. The FT-IR data also reveal the presence of a small amount of carbonated species (bands at 1462, 1384, and a weak one at 855 cm<sup>-1</sup>). As the XRD patterns do not show the presence of any bulk carbonate, it is assumed that the carbonate groups visible in the FT-IR spectra are located at the surface or in the subsurface region of the layered oxide structure.

In the Anedra sample, II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> is the main phase and only a small amount of lanthanum hydroxide is present (Table 1, Fig. 2). This is in agreement with data reported by Moggia et al. [11] for the support. In addition, a shoulder observed around 1360 cm<sup>-1</sup> in the FT-IR spectrum reveals the presence of traces of I-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> [2]. This shoulder could be hiding the surface carbonate species vibration found by Moggia et al. [11].

The treatment of the Aldrich sample in dry  $\text{CO}_2$  to 773 K and the cooling in the same atmosphere results in the transformation of  $\text{La}(\text{OH})_3$  to poorly crystalline Ia- $\text{La}_2\text{O}_2\text{CO}_3$ . (Fig. 1c). Small signals of type II polymorph are also detected. The splitting observed for bands in the FT-IR and Raman spectra of the sample (Figs. 2d and 3) confirm the presence of the monoclinic polymorph (type Ia).

Exposing  $\text{La}_2\text{O}_3$  Anedra to a flow of dry  $\text{CO}_2$  from room temperature to 973 K yielded the hexagonal (type II) polymorph of oxycarbonate (Figs. 1b, 2c, and 3). A tiny reflection at  $d = 3.02 \text{ \AA}$  in the DRX pattern, corresponding to the most intense signal of monoclinic Ia oxycarbonate, reveals the presence of traces of this phase.

Turcotte et al. [2] found that for La, where the mixture of type I and type II was attainable, both types decomposed at the same temperature to give the A sesquioxide, with a slight indication that type I decomposed at a faster rate than type II. Several papers deal with lanthanum carbonate and oxycarbonates decomposition but none of these studies make reference to the three different polymorphic forms of lanthanum oxycarbonate. Hussein and Ismail [14] reported that  $\text{La}_2\text{O}_2\text{CO}_3$  decomposition takes place endothermally between 973 and 1023 K to form the hexagonal structure of  $\text{La}_2\text{O}_3$ . Studying  $\text{La}_2(\text{C}_2\text{O}_4)_3$  decomposition, Vanhoyland et al. [15] identified the presence of lanthanum oxycarbonate in the 800–873 K temperature range. The thermal analysis of  $\text{La}_2(\text{CO}_3)_3$  decomposition in nitrogen atmosphere showed that the decarbonisation process of  $\text{La}_2\text{O}_2\text{CO}_3$  took place at 1043 K [16]. In  $\text{La}_2(\text{C}_2\text{O}_4)_3$  and  $\text{La}_2(\text{CO}_3)_3$  decomposition, proceeding via intermediate oxycarbonates, the mechanism was not sensitive to the atmosphere [15,16]. On the other hand, Shirsat et al. [17] reported that the oxycarbonate decomposed at 1000 K in air, but when the decomposition was carried out in  $\text{CO}_2$ , the  $\text{La}_2\text{O}_3$  formation was observed at 1223 K.

In the present work, type I and type II decompositions were found to be dependent on the atmosphere. In helium, the hexagonal form (type II) decomposed at a lower temperature than type I (Fig. 6), both in one step, while in dry air, the two oxycarbonates decomposed in more than one step. Turcotte et al. have reported that the transformation of type I to type II- $\text{La}_2\text{O}_2\text{CO}_3$  occurred at temperatures higher than 823 K and is greatly affected by the presence of carbon dioxide [2]. This transformation gave no indication of reversibility, type II being more stable than the type I.

Note that the air used in our TGA experiments can contain up to 500 ppm  $\text{CO}_2$ . During these experiments type Ia could partially transform into II- $\text{La}_2\text{O}_2\text{CO}_3$  at temperatures between 823 and 873 K, in the absence of weight change due to the polymorphic nature of the transformation. To confirm this reaction, FT-IR and Raman spectra (not shown) were taken after heating in flowing air both type Ia and type II oxycarbonates, from room temperature to 873 K. For II- $\text{La}_2\text{O}_2\text{CO}_3$  no changes were detected. However, for Ia- $\text{La}_2\text{O}_2\text{CO}_3$  the peak intensities decrease comparatively to the bands corresponding to type II, indicating that the trans-

formation has occurred. The presence of two or more peaks could be assigned to the decarbonisation of the different oxycarbonate types formed during the heating in flowing air.

These studies show that the initial phase composition as well as heating treatment and atmosphere are crucial in determining the reactivity of lanthanum solids.

#### 4.2. Metal effect on lanthanum phases

The most commonly used procedure to prepare lanthanum supported metal catalysts involves impregnation of the oxide with aqueous solutions of the metal precursor salt followed by calcination in air. Since  $\text{La}_2\text{O}_3$  is a highly active phase against water, the preparation of metal supported solids would involve strong chemical and structural rearrangements in the support. As a result of the intense carbonation phenomena induced on lanthana by the preparation procedure, the actual nature of the support phases would depend on the impregnation method and the gas treatments of the impregnated samples [12]. Ruckenstein and Hu [18] reported that the phase composition of  $\text{Ni}/\text{La}_2\text{O}_3$  solids depends on the nature of the Ni precursor used in the preparation and on the treatment condition employed. Different phases are formed when  $\text{Ni}/\text{La}_2\text{O}_3$  is calcined in  $\text{O}_2$  or He because the different calcining gases change the equilibrium between oxygen and the compounds containing Ni, La and O.

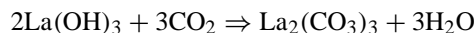
For  $\text{Rh}/\text{La}_2\text{O}_3$ , Gallaher et al. [19] reported that the as-received support and the support following impregnation were  $\text{La}(\text{OH})_3$ .  $\text{LaOOH}$  was formed after treating these solids in  $\text{H}_2$  at 400 °C, but the exposure of the catalyst to room air overnight results in conversion of  $\text{La}_2\text{O}_3$  and  $\text{LaOOH}$  to  $\text{La}(\text{OH})_3$  and  $\text{La}_2(\text{CO}_3)$ . They found that, in a reducing atmosphere, Rh catalysed the decomposition of the carbonate species on the support. On the other hand, carbonate species were found to be very stable on the surface of  $\text{LaRhO}_3$  oxide [20].

Our air calcined solids with low rhodium loading (0.2 and 0.6%) show an increase in type Ia polymorph (Figs. 2b and 5b and c) which was already present in the support. The FT-IR and Raman spectra of  $\text{Ni}(2\%)/\text{La}_2\text{O}_3$  solid (not shown) also revealed an increase in Ia- $\text{La}_2\text{O}_2\text{CO}_3$ . Platinum, on the other hand, would not modify the phases of the lanthanum oxide (Figs. 2b and 5d). The  $\text{CO}_2$  desorption profiles in flowing He show two peaks at 1030 and 1130 K. By comparison with the profiles of reference phases, they can be assigned to the decomposition of type II and type Ia oxycarbonates, respectively. The profile for  $\text{Rh}(0.6\%)$  solid indicates the presence of a higher proportion of type Ia.

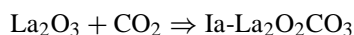
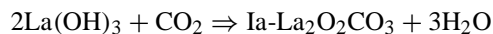
The treatment with  $\text{CO}_2$  provides additional information about the effect of the gas upon the metal containing solids.  $\text{Pt}(0.93\%)$  exposed to  $\text{CO}_2$  shows an important increase in the proportion of Ia- $\text{La}_2\text{O}_2\text{CO}_3$  as observed from FT-IR, Raman and TPD results. (Figs. 3g, 4d, 5e and 7c). The lanthanum phases in rhodium solids were slightly modified after exposure to  $\text{CO}_2$  at 773 K.

During the CO<sub>2</sub> treatment at 773 K, the lanthanum hydroxide and the oxide could react with carbon dioxide producing Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and/or La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>. Type II would form at temperatures higher than 973 K.

For the Rh solids, the following reaction could occur:



and in the case of platinum



Guo et al. [21], found that due to CO<sub>2</sub> adsorption on La<sub>2</sub>O<sub>3</sub>, type Ia oxycarbonate was mainly formed in the LaNiO<sub>3</sub> perovskite used in the dry reforming of methane. In Ni/La<sub>2</sub>O<sub>3</sub> solids, Verykios [22] reported the formation of stable La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> species due to a strong interaction between CO<sub>2</sub> and lanthanum oxide. According to our results, Pt would favour the carbon dioxide interaction with the support to form monoclinic polymorph (type Ia), while rhodium would prevent the further formation of the oxycarbonate phase. In Rh solids, type Ia transformation into II-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> would not occur during the TGA experiments, since two well-defined peaks are observed.

Rh/La<sub>2</sub>O<sub>3</sub> catalysts were found to be active and stable in the CO<sub>2</sub> reforming of methane at low temperature (823 K). However, the activity of Pt/La<sub>2</sub>O<sub>3</sub> solid falls after 50 h on stream. The deactivation of Pt catalysts has been ascribed to Pt sintering favoured by a strong metal–support interaction [5,23]. The lanthanum support could enhance the activation of carbon dioxide adsorbed on basic sites, facilitating the reforming reaction.

A different phase composition could be observed in solids with high metal loading. Type I polymorph, present in the support, was not detected in the Rh(2%) and Pt(3.8%) solids (Fig. 5a and b, respectively; XRD not shown). Besides, the disappearance of vibrations in the OH region indicates that these solids were almost completely dehydroxylated. It seems that the high metal loading would catalyse the decomposition of type Ia and prevent the hydration of the lanthanum oxide. This is in agreement with Zhang and Verykios [24], who found that fresh Ni/La<sub>2</sub>O<sub>3</sub> catalysts, with 17 wt.% metal loading, consist only of Ni phases and lanthanum oxide.

## 5. Conclusions

- The initial phase composition as well as the heating treatment and atmosphere are crucial in determining the reactivity of lanthanum solids.

- A low rhodium loading would increase the amount of type Ia polymorph on the support, whereas a low platinum loading would not modify those phases.
- A high metal loading would catalyse the decomposition of type Ia-La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and prevent the hydration of the lanthanum support.
- Pt would favour the carbon dioxide interaction with the support to form monoclinic polymorph (type Ia), while rhodium would prevent the further formation of oxycarbonate phase.

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