

# Influence of lanthanides and thermal treatments on the morphology of Pd supported catalysts for methane combustion

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## Abstract

The morphology of Pd-based catalysts used on methane combustion was studied. The supports were prepared by combustion synthesis and the effects of the addition of cerium and lanthanum were analyzed. The morphology stability was followed by SEM. The micrographs revealed that the basic morphology of alumina is retained even after lanthanides addition. A process of grain separation was observed on both alumina and cerium-containing powder when treated at 1200 °C. Such a process is only significant at 1300 °C for the lanthanum loaded sample. A model in which CeO<sub>2</sub> small crystals are deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is suggested to describe the powder. Lanthanum compound seems to create a distinct phase with aluminum, which presents a slower grain separation process. The results also show that this process is catalyzed by Pd, which is located on the supports grains boundaries.

**Keywords:** Microstructure; combustion synthesis; Pd catalysts; methane combustion.

## Introduction

Catalytic combustion of methane has been extensively investigated over the past few years due to its outstanding advantages as a power generation technology (1,2). Low amounts of NO<sub>x</sub> emissions is firstly pointed out

as the combustion proceeds below 1400 °C. Nevertheless, when the catalysts are used in gas turbines operation temperatures as high as 1200 °C can be achieved (2) and, therefore, the use of thermostable catalysts is mandatory.

Several thermally stable systems have been studied and they are mainly based on hexaluminates (3) or alumina doped with lanthanides (4,5) since their stabilizer effect is well known (6,7). Ceramic oxides obtained by a high temperature process also arises as feasible materials to be used as catalysts supports. Indeed, the preparation of simple ceramic oxides via a route known as combustion synthesis has been gaining reputation as a straightforward process to produce homogeneous, very fine and crystalline powders (8,9). The synthesis explores an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts and a suitable organic fuel, which is ignited at a temperature much lower than the actual phase formation one. The major drawback of such a route is that it leads to low surface area materials. Moreover, previous results obtained by Greca (10) indicated that, despite the high temperature reached in the preparation of alumina via combustion synthesis, this oxide can undergo morphological changes when exposed to temperatures around 1200 °C.

This work focuses on the preparation of Pd-based catalysts used on the methane combustion whose supports were obtained by combustion synthesis. Alumina was taken as the reference support and the effects brought about by the addition of different lanthanides, namely La and Ce, and by the exposure to high temperature conditions on the catalyst morphology are reported. Scanning Electron Microscopy (SEM) was used to acquire some information about the morphology and surface structure of these systems.

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## Materials and Methods

A detailed description of the methodology used to prepare both supports and catalysts has been described elsewhere (11). Briefly, in the combustion synthesis the appropriate amounts of the cations precursors (nitrates) and an organic fuel (urea) dissolved in water were heated in a wide-mouth vitreous silica basin up to boiling and self-ignition. The basin was then transferred to a muffle furnace preheated at 600 °C and kept for 30 min producing a fragile foam that easily crumbles into powder.

The reactant proportions were calculated in order to obtain oxides with 12%wt. La or Ce and are listed in

Table 1. These supports will be denoted as Al12La and Al12Ce hereinafter. Pure  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$  and  $\text{CeO}_2$  were also synthesized to be taken as reference.

The catalysts were prepared by contacting the supports and an aqueous solution of  $\text{Pd}(\text{NO}_3)_2$  in a rotary evaporator for 8 h in order to achieve 1%wt. Pd. The solvent was then slowly evaporated under vacuum at 80 °C; the powder obtained was dried overnight at 110 °C and lastly calcined at 500 °C for 4 h in air. These samples will be referred in the same way as their parent supports preceded by Pd, e.g. PdAl12Ce.

All samples (catalysts, supports and reference oxides) were submitted to thermal treatments at 1100, 1200 and 1300 °C (8 °C/min) for 2 h in air.

Table 1 - Reactant proportions in order to obtain oxides with 12%wt. La or Ce by combustion synthesis.

Sample	$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	$\text{CO}(\text{NH}_2)_2$
Al	2.00	-	-	-	5.00
La	-	-	-	2.00	1.535
Ce3	-	1.00	-	-	1.325
Al12La	2.00	-	-	0.037	4.408
Al12Ce	2.00	0.068	-	-	4.474

The morphological changes induced by these treatments were evaluated by Scanning Electronic Microscopy (SEM) in a Zeiss Microscope DSM960. The samples were sprinkled over circular aluminium SEM stubs. The samples were sputter coated with a thin layer of carbon to avoid charging effects.

To evaluate Pd particles an alternative procedure was adopted for the catalysts. The samples were suspended in propanol and then a drop was deposited on a copper

support covered with a FORMVAR polymeric film. Such a procedure is commonly used in Transmission Electronic Microscopy (TEM).

## Results and Discussion

SEM micrographs of the synthesized reference oxides are displayed in Fig. 1.

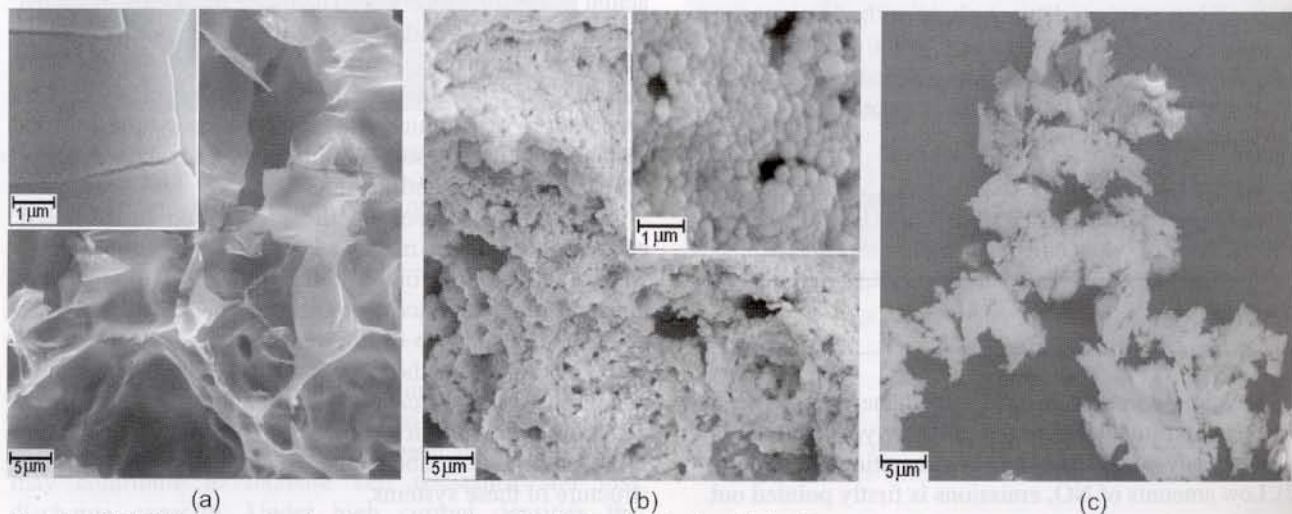


Fig. 1 – SEM Micrographs of reference oxides: (a)  $\text{Al}_2\text{O}_3$ ; (b)  $\text{CeO}_2$ ; (c)  $\text{La}_2\text{O}_3$ .

They reveal that the oxides have rather distinct morphological features. Alumina presents a plate-like morphology whereas  $\text{CeO}_2$  exhibits spherical grains with a

regular surface and lanthanum-based sample shows a typical aspect of an agglomerated powder.

SEM images of lanthanides-containing alumina as well as the Pd catalysts micrographs are presented in

Fig. 2 and it can be clearly seen that the basic morphology of alumina has been retained.

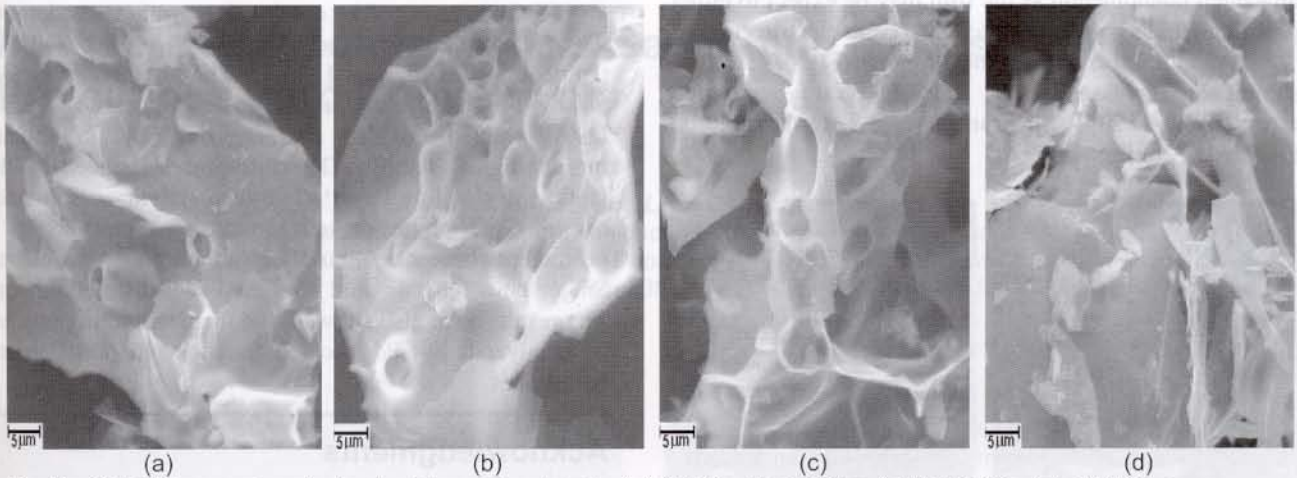


Fig. 2 – SEM Micrographs of mixed oxides and catalysts: (a) Al12Ce; (b) Al12La; (c) PdAl12Ce; (d) PdAl12La.

No segregation of La and Ce, which are present at relatively high concentrations, could be distinguished in the SEM micrographs. As XRD patterns of those mixed oxides showed only peaks corresponding to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase, it might suggest that all La and Ce are uniformly dispersed.

of CeO<sub>2</sub> crystals does not seem to disturb such a process, which might suggest that the CeO<sub>2</sub> does not react with aluminum during the preparation leading to a new phase. Therefore, a model in which CeO<sub>2</sub> small crystals are deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> could be taken to describe this support.

The samples studied revealed to be thermally stable, as far as their morphology is concerned, up to temperatures as high as 1100 °C. Nevertheless, the exposure of synthesized alumina to 1200 °C seems to slightly affect its morphology as small spherical isolated grains may already be distinguished. The onset of the grains separation is depicted in detail in Fig. 3a and indicates a morphological instability. A similar phenomenon is observed over the sample prepared with cerium (Al12Ce) (Fig. 3b). Indeed, this sample follows exactly the same trend as reference  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The presence

Lanthanum-based powder, on the other hand, did not exhibit any significant morphological change when submitted to that temperature. The process of grain separation could only be observed at 1300 °C (Fig. 3c). The grains formed under this condition can be described as small tubes, rather distinct from the Al<sub>2</sub>O<sub>3</sub> and Al12Ce powders. Such a particular behavior might suggest that the lanthanum compound forms a distinct crystalline phase with aluminum, which presents a slower grain separation process.

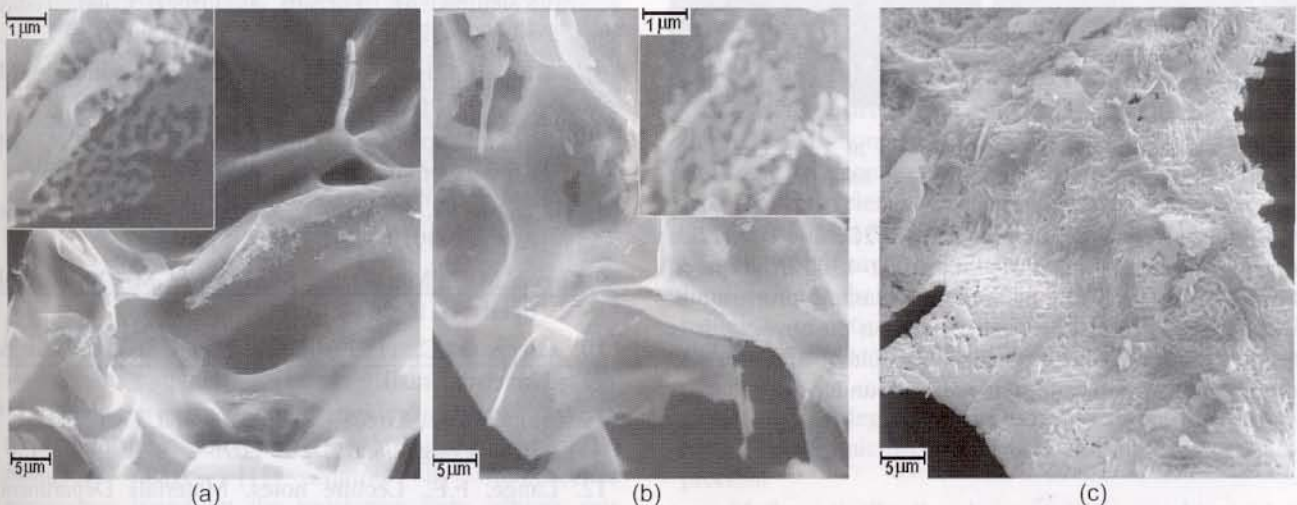


Fig. 3 – De-sintering process observed on: (a) Al<sub>2</sub>O<sub>3</sub> at 1200°C; (b) Al12Ce at 1200°C; (c) Al12La at 1300°C.

The morphological instability characterized by the separation of grain pairs is also observed over polycrystalline fibers and films (12), whose break-up is an unwanted phenomenon as the film may be expected to either protect an underlying substrate or carry an electric current.

The addition of Pd on the supports (Fig. 4) led to a significant increase in the rate of grain separation especially at 1300°C. Such an increase is remarkable on the PdAl<sub>12</sub>Ce (Fig. 4a).

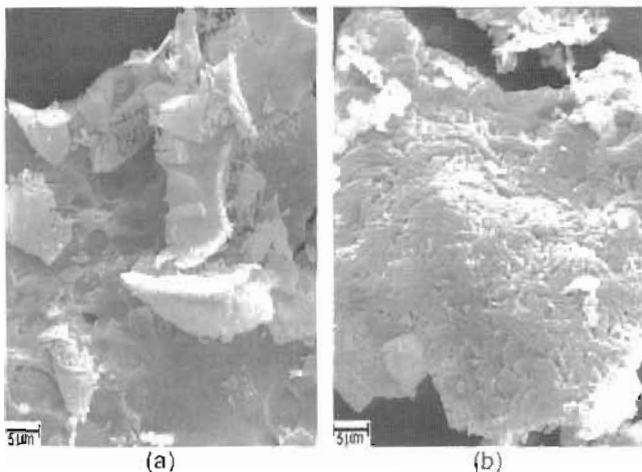


Fig.4 - De-sintering process observed at 1300°C on: (a) PdAl<sub>12</sub>Ce; (b) PdAl<sub>12</sub>La

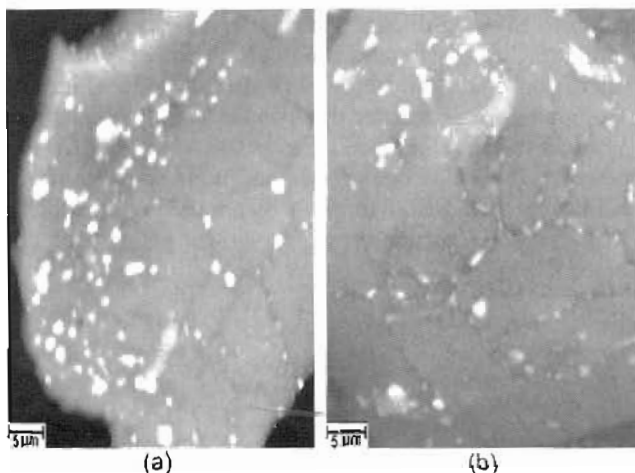


Fig.5 - De-sintering process observed at 1300°C on: (a) PdAl<sub>12</sub>Ce; (b) PdAl<sub>12</sub>La both prepared as in TEM.

Fig. 5 depicts the images of PdAl<sub>12</sub>Ce and PdAl<sub>12</sub>La obtained with the catalysts treated at 1300°C prepared according to the TEM methodology sample preparation. The Pd particles can be clearly seen on the support. It is worth outlining that such particles are located preferentially on the supports grains boundaries.

## Conclusions

Alumina prepared by combustion synthesis undergoes slight morphological changes when exposed to temperatures as high as 1200 °C. The addition of Ce did not modify such behavior whereas La appears to form a La/Al mixed oxide characterized by a higher morphological stability. The differences induced by the lanthanides will probably affect the catalytic performance as the CeO<sub>2</sub>-phase present on alumina can act as a promoter whereas a mixed La/Al compound would no longer be a La-promoted alumina but a distinct support. The results have also showed that the de-sintering process is catalyzed by Pd located on the supports grains boundaries.

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