

La₂O₃ as primer for supporting La_{0.9}Ce_{0.1}CoO_{3 ± δ} on cordieritic honeycombs

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Abstract

To understand better the effect of La₂O₃ as primer for the preparation of honeycomb supported La_{0.9}Ce_{0.1}CoO_{3 ± δ} catalyst, some samples were prepared starting from different La-precursors. Physical and morphological properties of both the primer-coated honeycomb and its precursors (as-prepared and after thermal treatment at different temperature) have been investigated by TGA, TPD–MS, XRD and SEM. Calcination at high temperature brought about a rearrangement of both primer and active phase morphology. When La acetate was used as precursor, such a transformation seemed not to alter substantially the morphology of the primer layer, leading to a poorer anchoring to the support, with deep cracking and exfoliation of the La oxide platelets so formed. By contrast, when the primer precursor was La nitrate, the higher reactivity of the hydroxynitrates, forming during calcination, with respect to both the active phase and the honeycomb, led to a more uniform and compact La₂O₃ layer, anchoring much better the perovskite to the monolith support.

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1. Introduction

The abatement of gaseous pollutants such as NO_x, CO and un-burnt hydrocarbons is of ever-growing concern for environment protection. Perovskitic mixed oxides proved since long time to be a valuable alternative to the traditional noble metal based catalysts for many of these reactions, being cheaper, comparatively active and thermally stable, if properly prepared [1,2]. In particular, La_{0.9}Ce_{0.1}CoO_{3 ± δ} showed very active for the complete flameless combustion of hydrocarbons [3–5].

For practical application, structured catalysts are the most used, in order to reduce substantially the pressure drop across the catalyst bed. Usually structured catalysts are prepared by deposition of the active phase on cordieritic honeycomb monoliths. To favor the adhesion of the active

phase to the support, the latter is usually pre-coated with a primer, whose function is also to increase the surface area and to improve catalyst stability [6]. One of the most commonly used primer materials is γ-Al₂O₃, which however in some cases does not ensure a sufficient stability. The latter can be improved either by doping the alumina or by using different mixed oxides, such as Zr–Ce–Ti–Mg–O [7,8].

In a previous work [5] it was shown that La_{0.9}Ce_{0.1}CoO_{3 ± δ} cannot be firmly anchored onto a honeycomb monolith in the absence of a primer. Furthermore, alumina did not ensure a good thermal resistance to supported lanthanum cobaltites, due to the formation of LaAlO₃ or CoAl₂O₄, progressively leading to the destruction of the active phase during high temperature use of the catalyst. Moreover, alumina itself easily sinters, so reducing catalyst surface area. Finally, its different thermal dilation coefficient with respect to the cordieritic support can be very likely the main cause of the formation of deep cracks in the coating [5].

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Table 1
Catalyst composition

Sample	Primer precursor	wt.% of primer and of active phase	Calcination <i>T</i> of primer (°C)
La-N-500	La-nitrate	–	500
La-N-700	La-nitrate	–	700
La-Ac-500	La-acetate	–	500
La-Ac-700	La-acetate	–	700
H-N-500	La-nitrate	4% and 2%	500
H-N-700	La-nitrate	4% and 2%	700
H-Ac-500	La-acetate	2% and 2%	500
H-Ac-700	La-acetate	2% and 2%	700

A valid alternative primer for the present application showed La_2O_3 , which can be deposited from different precursors. A slightly higher activity was obtained with lanthanum oxide prepared from lanthanum acetate, but a much higher thermal resistance was observed using lanthanum nitrate as precursor [5].

The aim of the present work was to investigate the reason of the different behavior of these primer precursors. For this purpose, four honeycomb supported $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3 \pm \delta}$ samples were prepared, in which the La_2O_3 primer was prepared from either acetate or nitrate. Physical and morphological properties of primer, precursor and finished catalyst have been analysed by TGA, TPR–TPD–MS, XRD and SEM, before and after thermal treatment at different temperatures. At last the catalysts have been compared under identical reaction conditions for the catalytic flameless combustion (CFC) of methane, before and after several cycles of reaction/accelerated deactivation.

2. Experimental

2.1. Active phase preparation

$\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3 \pm \delta}$ was prepared by the flame hydrolysis (FH) technique. A detailed description of the apparatus can be found elsewhere [3]. Briefly, the preparation started from a 3% aqueous solution of precursors ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Aldrich, purity $\geq 99.99\%$; $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, ACROS, purity $\geq 99.50\%$; $\text{Co}(\text{NO}_3)_2$, Merck, purity $\geq 99.99\%$). Citric acid (Aldrich, purity $\geq 99.0\%$) was added both as complexing agent and as additional fuel to increase the flame temperature. The solution was nebulised into a $\text{H}_2 + \text{O}_2$ flame and the perovskite powder was collected by means of an electrostatic precipitator.

The high temperature (ca. 1600 °C) attained in the flame allowed to obtain a very high phase purity and satisfactory thermal resistance of both the powder and the supported catalyst. Moreover, the very short residence time within the flame [3,5] limited any extended sintering of the powder, leading to relatively high BET surface area (ca. 20 m²/g). SEM analysis showed clusters, 200–500 nm in size, made of highly uniform, nearly spherical particles, 20–80 nm in size.

2.2. Primer precursors treatment

Samples of La oxide from La nitrate and La acetate in powder form (La-N-500, La-N-700, La-Ac-500, La-Ac-700, Table 1) were obtained by calcination at either 500 °C or 700 °C for 1 h.

2.3. Primer and active phase deposition on honeycomb monoliths

For the wash-coat deposition of the primer from $\text{La}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$, which is scarcely soluble in water (0.17 g/l at 25 °C [9]), a stable suspension of 1.5 g of salt in 22.5 cm³ of distilled water was obtained by ball-milling for 2 h in a tumbling 50 cm³ cylindrical polypropylene jar with five zirconia balls ($D = 10$ mm).

The high solubility of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ allowed to prepare a clear and stable solution, by dissolving 3 g of salt in 22.5 ml of distilled water. The molar concentration of lanthanum (ca. 10^{−4} M) in the starting solution/suspension, allowed to obtain the deposition of up to 2 wt.% of La_2O_3 from acetate and 4 wt.% from nitrate, during each dip-coating step.

A detailed description of the apparatus and the conditions adopted for the dip-coating can be found elsewhere [5]. Briefly, a cylindrical monolith, 1 cm diameter \times 5 cm length, obtained from a commercial cordieritic honeycomb ($\text{Mg}_2\text{Al}_3(\text{AlSi}_5\text{O}_{18})$, 400 cpi = 62 cells/cm², wall thickness = 0.15 mm) was calcined at 500 °C for 1 h and weighed. The dip-coating was accomplished by means of a home made apparatus, so to dip and withdraw, at the desired constant speed, the honeycomb from the solution/suspension. Every dipping was followed by drying at room temperature for 10 min. After deposition of the primer precursors the samples were calcined at 500 or 700 °C in air for 1 h. The deposition of the active phase was carried out by dip-coating the primer-coated monolith with a suspension of the perovskite powder. The latter was obtained by ball-milling 0.8 g of the FH prepared $\text{La}_{0.9}\text{Ce}_{0.1}\text{CoO}_{3 \pm \delta}$ powder in 20 cm³ of distilled water for 4 h. Finally, the samples were calcined at 500 °C for 1 h.

Primer and active phase loading was expressed as weight percent referred to the final catalyst weight. The composi-

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