



## Research Paper

# Oxidative coupling of methane on cordierite monoliths coated with Sr/La<sub>2</sub>O<sub>3</sub> catalysts. Influence of honeycomb structure and catalyst-cordierite chemical interactions on the catalytic behavior



Brenda M. Sollier, Leticia E. Gómez, Alicia V. Boix, Eduardo E. Miró\*

*Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE, Universidad Nacional del Litoral, CONICET, Facultad de Ingeniería Química, Santiago del Estero, 2829-3000, Santa Fe, Argentina*

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## ABSTRACT

When powder Sr/La<sub>2</sub>O<sub>3</sub> catalysts are deposited on the walls of cordierite monoliths, an important increase in both, methane conversion and C<sub>2</sub> yield, takes place. In this work, it is shown that this improved catalytic behavior is due to a combination of physical and chemical factors. This conclusion was drawn after performing a systematic study in which several structured formulations were catalytically evaluated and characterized using different techniques (EDX, XRD, BET, XPS, LRS), which helped us to rationalize the experimental observations. It is suggested that the honeycomb structure provides a more homogeneous gaseous flow as compared with the powder catalyst. This fact results in a better contact between reactant and catalyst surface, which in turn results in an increase of the overall reaction rate. Furthermore, it is demonstrated that the catalytic layer enrichment with Mg and Si, coming from the cordierite structure, greatly contributes to the improved catalytic behavior.

## 1. Introduction

Natural gas production is expected to expand dramatically in the next few years [1]. Advances in exploration and development of new extracting methods have made it possible to reach to shale deposits previously deemed uneconomical to exploit. One of the biggest natural gas supplies is located in Argentina. According to the latest studies performed in Vaca Muerta region, these deposits would have a potential similar to that of the most productive deposits across the globe [2]. The second biggest natural shale gas reserve and the fourth largest petroleum reserve in the world are located in this region.

Therefore, special interest exists in the opportunity of using these natural supplies and exploiting them to their maximum potential. Today, due to difficulties in transportation, natural gas has been used as a commodity or wasted in the oil wells, causing profound environmental damage. Moreover, methane (main natural gas component) is a greenhouse gas with a global warming potential 20 times that of CO<sub>2</sub> [3].

The abundance of natural gas, the need for its transportation, and environmental concerns are factors that challenge researchers to find and develop better ways of exploiting this resource. Therefore, the conversion of methane into ethane and ethylene via the oxidative coupling of methane (OCM) is an attractive alternative [4,5]. This

reaction enables obtaining more valuable products like chemicals or fuels.

The development of the OCM technology is performed by Siluria Technologies. The aim of this company is to reduce costs, energy and environmental emissions in the production of ethylene. At present, a demonstration plant has been built by Siluria to demonstrate the feasibility of this technology [6].

Among the catalysts reported in literature for the OCM reaction, rare earth metal oxides are probably the most widely studied. For example, La<sub>2</sub>O<sub>3</sub>-based catalysts exhibit an excellent catalytic activity and thermal stability [7–10]. Choudhary et al. [11] studied a series of Sr-doped rare earth metal oxides (La, Ce, Pr, Ne, Sa, Eu, Ga, Dy, Er, and Yb), and they found that the Sr-doped La<sub>2</sub>O<sub>3</sub> catalysts exhibited the best catalytic performance. Baidya et al. [12] claimed that La<sub>2</sub>O<sub>3</sub> or samarium (III) oxide catalysts doped with Ca, Sr, or Ba were the most active OCM catalysts of the irreducible metal oxide catalysts. An important characteristic of these oxides is that they have very complex structural features. For example, they interact with CO<sub>2</sub> and H<sub>2</sub>O from ambient air creating carbonated and hydrated species [13]. These species are also present under OCM reaction conditions. As a matter of fact in our previous study, we detected the presence of LaOOH, La(OH)<sub>3</sub> and La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> by in situ LRS. While hydroxide prevailed at low temperature, the presence of oxycarbonates started to be relevant when the

\* Corresponding author.

E-mail address: [emiro@fiq.unl.edu.ar](mailto:emiro@fiq.unl.edu.ar) (E.E. Miró).

reaction took place at temperatures around 400 °C, and above 700 °C all lanthanum species decomposed into La<sub>2</sub>O<sub>3</sub> [14].

In order to contribute to the development of new technologies for exploiting methane reserves, it is important to study the methodology of scaling from lab to plant conditions more deeply. Therefore, under industrial conditions, high flows should be used at relatively high temperatures. Monolithic catalysts could be a good option to study, because they provide lower pressure drop, smaller diffusion resistance and better mass and heat transfer than powder catalysts [15–17]. In a recent work we evaluated several structured catalysts (monoliths and foams) as substrates for different Sr/La<sub>2</sub>O<sub>3</sub> formulations [14]. We concluded that, among the catalysts studied, a cordierite monolith washed with Sr (5 wt.%)/La<sub>2</sub>O<sub>3</sub> was the best option, because of its significant C<sub>2</sub> yield and high mechanical stability. Interestingly, we found that this structured catalyst was more active than the powder one, and that at 800 °C, C<sub>2</sub> yield progressively increased from around 18.0% to 22.5% during 70 h of time-on-stream.

In this work, a systematic experimental study was designed to understand physical and chemical aspects involved in the above described behaviors. To this end, we evaluated a series of catalytic systems in which the physical effects of the honeycomb structure and the chemical interactions between the catalytic layer and cordierite were analyzed separately. A characterization of selected systems through Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS) and Laser Raman Spectroscopy (LRS), were also performed to further support our hypothesis.

## 2. Experimental

### 2.1. Structured catalyst preparation

Honeycomb monoliths made of cordierite (Corning, 400 cpi, 0.1 mm wall thickness) were used as substrates. The cordierite composition was 2MgO·5SiO<sub>2</sub>·2Al<sub>2</sub>O<sub>3</sub>. The preparation method was based on the deposition of powder catalyst Sr(5 wt.%)/La<sub>2</sub>O<sub>3</sub> previously prepared by wet impregnation onto cordierite honeycomb monoliths [14]. This was accomplished by immersing the substrates during 30 s in 20 cm<sup>3</sup> of Sr(5 wt.%)/La<sub>2</sub>O<sub>3</sub> slurry prepared in distilled water with a solid concentration of 20 wt.%. Besides, 1 wt.% of colloidal silica was added to improve adherence. After each immersion, the pieces were blown with air in order to remove the slurry excess and then they were dried at 120 °C for 90 min. Special care was taken in the blowing step procedure, because it is important to obtain a homogeneous catalytic layer. The improvement in this preparation step resulted in a catalytic behavior slightly different from that obtained in the previous work [14], C<sub>2</sub> selectivity being higher and methane conversion somewhat lower. This immersion-blowing-drying cycle was repeated as many times as necessary to achieve the desired catalyst loading. Then, the samples were calcined at 850 °C during 4 h. This sample was denoted as SrLaM.

In order to study the effect of honeycomb structures on the catalytic behavior, the monolithic catalyst SrLaM was milled, and denoted as SrLaM-milled. Another powder catalyst was also prepared, by loosely mixing Sr(5 wt.%)/La<sub>2</sub>O<sub>3</sub> and milled cordierite, denoted as SrLa + M-milled. To further analyze the chemical interactions between Sr and cordierite, catalysts without lanthanum were prepared. This was done by impregnation of the monolith with a 0.47 M Sr(NO<sub>3</sub>)<sub>2</sub> solution, reaching 5 wt.% of Sr. This catalyst was calcined at 850 °C during 4 h and it was denoted as SrM.

### 2.2. Catalytic tests

The experiments were conducted in a fixed-bed flow quartz reactor at atmospheric pressure. The reactor design was described in a previous work [14]. The system was heated with a furnace to reach the desired

temperatures. The exiting gases from the reactor were conducted through a condenser in order to eliminate H<sub>2</sub>O from the flow. Finally, the exiting flow was measured using a gas chromatograph (GC-2014 Shimadzu) with thermal conductivity detector (TCD) equipped with two columns, Zeolite 5A and Hayesep D. The carbon balance was always higher than 97%. The catalytic tests were repeated several times over SrLaM and powder samples, showing quite reproducible results.

The reaction mixture consisted of 64 vol.% CH<sub>4</sub>, 8 vol.% O<sub>2</sub> and 28 vol.% He. The catalyst weigh/total flow ratio was 0.166 mg cm<sup>-3</sup> h. The catalysts were tested in a wide temperature range (300–800 °C).

Methane conversion, C<sub>2</sub> selectivity and C<sub>2</sub> yield were calculated as follows:

Methane conversion (%) = (moles of methane reacted/moles of methane in feed) × 100

C<sub>2</sub> selectivity (%) = 2(moles of C<sub>2</sub>/moles of methane reacted) × 100

C<sub>2</sub> yield (%) = methane conversion (%) × C<sub>2</sub> selectivity (%) × 1/100

### 2.3. Catalysts characterization

#### 2.3.1. Textural properties

N<sub>2</sub> adsorption and desorption isotherms were obtained at –196 °C with an ASAP 2020 Physisorption, Micromeritics instrument. Prior the measurement, the samples were degassed under vacuum at 250 °C for 4 h. The BET equation was used for obtaining the specific surface area, and average pore size was calculated using the Gurvich rule (dp (nm) = 4 Vp Sg<sup>-1</sup> 10<sup>3</sup>). The results were referred to powder weight in the case of Sr/La<sub>2</sub>O<sub>3</sub> and to total weight (cordierite + powder) in the case of monolithic catalyst.

#### 2.3.2. X-ray diffraction

The patterns of powder and monolithic catalysts were measured on a Shimadzu XD-D1 instrument with monochromator using Cu-Kα radiation at a scanning rate of 2° min<sup>-1</sup>.

#### 2.3.3. Laser Raman Spectroscopy (LRS)

Raman analyses were performed in a Horiba JOBIN YVON Lab RAM HR instrument. The excitation source was the 514.5 nm line of Spectra 9000 Photometrics Ar ion laser with its power set at 30 mW.

#### 2.3.4. Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometer (EDS)

The morphology of the catalytic coatings was examined with a scanning electron microscope SEM, Phenom ProX operated at an adjustable acceleration voltage range between 4.8 and 15 kV imaging and analysis mode. Pieces of different samples were observed in order to study the inner channel walls and cross-sections.

The elemental chemical analysis was performed using a Phenom ProX microscope with a fully integrated EDS detector and software. Results were obtained by the theoretical quantitative method (SEMIQ) which does not require standards. The distribution of the different elements in the catalytic layer was evaluated with the Element Identification (EID) software package and a specially designed and fully integrated Energy Dispersive Spectrometer (EDS). The apparatus was equipped with a Silicon Drift Detector Thermoelectrically cooled (LN<sub>2</sub> free). Samples were studied using a charge reduction sample holder and it was not necessary to coat them.

#### 2.3.5. X-ray photoelectron spectroscopy

The structured and powder catalysts were characterized by means of a multi-technique system (SPECS) equipped with a dual Mg/Al X-ray source. The analyzer was PHOIBOS 150 and it was operated in the fixed analyzer transmission (FAT) mode. The pass energy was of 30 eV and the Al Kα X-ray source was operated at 200 W and 12 kV. The XPS measurements were performed on the monolithic catalysts with an

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