Towards the scaling up of monolith- and foam-structured catalysts via *in-situ* combustion deposition for energetic applications

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Highlights

- Ceramic foams-monoliths (6.7-26.8 $cm^2 \cdot cm^{-3}$) as attractive catalyst supports.
- Thin-coated layers (8-30 µm) with high mechanical strength by facile combustion deposition.
- High activity and stability towards endothermic SR and OSR processes.
- High activity and stability towards exothermic CO_2 methanation reaction.

1. Introduction

Monoliths and foams have received growing attention as catalyst supports in both academic research and industrial applications due to their interesting specific properties (high geometric surface area, low pressure drops, high mass and heat transfer properties). Structured catalysts can operate at high space velocity, achieving a good contact between gas phase and surface reactions. All these characteristics are highly desirable for both exothermic (methanation reaction) and endothermic reactions (reforming processes) [1].
The solution combustion synthesis (SCS) method is a suitable procedure to deposit uniform, thin and high-strength catalytic layers on ceramic monoliths and foams [2,3]. In this work, the catalytic phase was *in-situ* deposited by the SCS on commercial cordierite monoliths (400-500 cpsi) and alumina foams (20,30,40 ppi). The activity and stability results were investigated towards Steam Reforming (SR) and Oxy-Steam Reforming (OSR) of different fuels (CH_4, biogas, n-dodecane) and CO_2 methanation reaction. Then, the catalyst scale-up was investigated to evaluate the goodness and the reproducibility of the coating method.

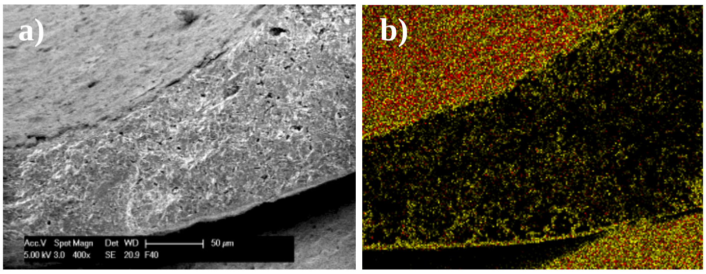

Figure 1. SEM image (a) and corresponding EDX mapping (b) of coated 40 ppi-foam.

2. Methods

The catalytic layers were deposited by the SCS at 600°C, dipping the supports in an aqueous solution containing metal precursors and urea as fuel [3]. The main morphological characteristics of monoliths (channel inner size and wall thickness) and foams (pore diameter and strut thickness) were examined with an optical microscope by means of the sizing techniques. Bed porosity was obtained by the He pycnometry. The geometric surface area (GSA) was calculated according to the Cybulski and Moulijn equation (monoliths) and the Buciuman and Kraushaar-Czarnetzki tetraidecahedrom model (foams). The pressure drops at different superficial velocities were determined by a water-filled U-tube manometer connected to a quartz tube open to the atmosphere. SEM technique was used to determine the coating thickness as well as the goodness of the deposition method. The adherence between the catalytic layer and the support walls was evaluated by ultrasonic treatment in isopropyl alcohol solution. Catalytic tests were carried out in a fixed-bed quartz reactor at atmospheric pressure; a detailed description of the experimental setup was provided in our previous publications [3,4].

3. Results and discussion

The catalyst load, calculated as the weight of catalytic layer (0.18 g) on the geometric surface area of supports, was ca. 22.8 (20ppi-foam), 15.5 (30ppi-foam), 11.8 (40ppi-foam), 6.0 (500cpsi-monolith) and 5.7 $mg \cdot cm^{-2}$ (400cpsi-monolith). Pressure drops of monoliths and foams well fitted the Hagen-Poiseuille and Lacroix theoretical calculation, respectively. Strong resistance to vibrations and mechanical shocks was revealed with negligible weight loss (< 1%) of the coated phase.
The combustion deposition method produced very reproducible coated layers homogeneously distributed on the support surface (Figs. 1,2). Uniform and thin coating tickness (8-30 μm, depending on the exposed GSA) were obtained (Figs. 2b,c,e). The magnifications of the coating layer confirmed the presence of a significant residual macro-porosity, related to the escaped gases during SCS steps (Fig. 2f). Homogeneous, thin and resistant coating was revealed scaling-up the supports from ca. 1 to 50 cm^3 (Fig. 2g).

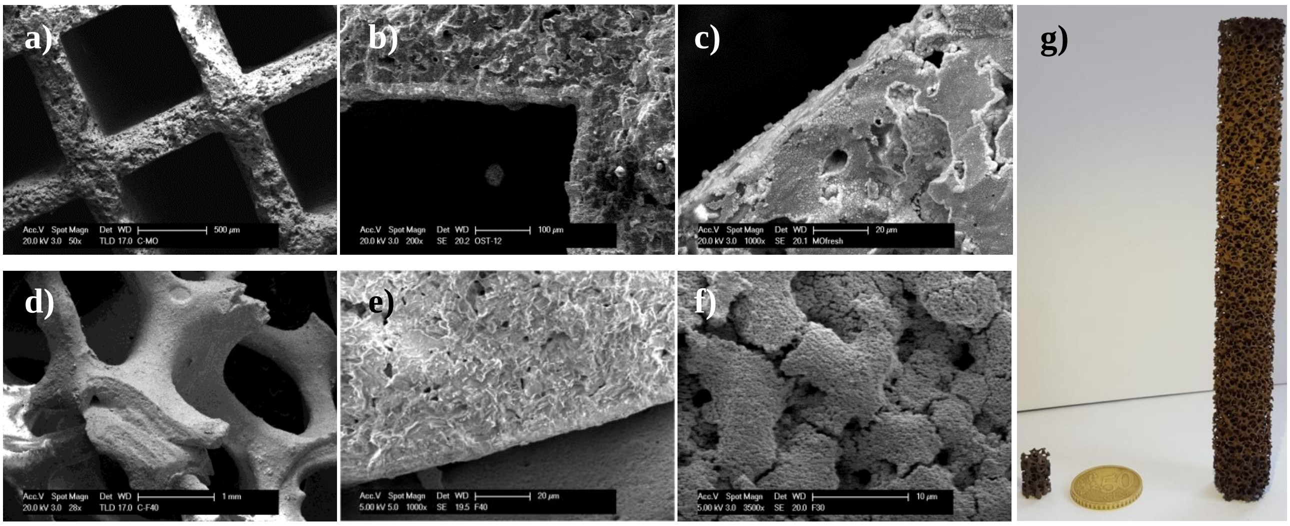

Figure 2. SEM images at different magnifications of coated monoliths (a-c) and foams (d-f); photograph of foam scale-up (g).

High catalytic activity was observed for both reforming and methanation processes, following the order 400cpsi-monolith ≈ 500cpsi-monolith < 20 ppi-foam < 30 ppi-foam ≈ 40 ppi-foam. Excellent long-term stability was observed over 200 h of time-on-stream (TOS) towards SR and OSR processes carried out a very stressful conditions (900°C, 140,000 $Nml \cdot g_{cat}^{-1} \cdot h^{-1}$): almost total methane conversion was obtained in both processes, while H_2 concentration of 64.7% to 58.2% (dry and N_2-free basis) was revealed for SR and OSR, respectively. Besides, stable activity results both in term of CO_2 conversion and products composition were obtained during CO_2 methanation for 200 h of TOS (400°C, 200,000 $Nml \cdot g_{cat}^{-1} \cdot h^{-1}$).

4. Conclusions

The *in-situ* combustion deposition was an easy, fast and cheap method to synthesize structured catalysts by self-sustained strongly exothermic reactions. The obtained results represented a promising advance in the process intensification leading to smaller, less costly and more efficient reactors.

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Keywords
Structured supports; Foam; Monolith; Combustion deposition.

CURRICULUM VITAE

A. PERSONAL INFORMATION

Italiano Cristina
Researcher (ORCID, 0000-0001-6118-653X)
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B. EDUCATION

2013	***PhD in “Chemical Technologies and Innovative Processes”**, April 29, 2013* Faculty of Science - Department of industrial chemistry and materials engineering - University of Messina - Italy Thesis titled: “Synthesis, Characterization and Testing of Highly Effective MnO_x-based Oxidation Catalysts”, PhD Supervisor: Prof. Francesco Arena
2008	***Master Degree in Industrial Chemistry summa cum laude*** (110/110 cum laude), December 22, 2008 Faculty of Science - Department of industrial chemistry and materials engineering - University of Messina - Italy Thesis titled: “Development of Catalyst for the Partial Oxidation of Methane to Formaldehyde (MPO): Effect of Doping on the Catalytic Activity of the FeO_x/SiO_2 System”.

C. CURRENT POSITION

2013-Today	Researcher at CNR-ITAE - National Research Council, Institute of Advanced Technologies for Energy, Messina, Italy

The scientific activity addresses the development of materials and technologies for hydrogen production by i) reforming processes and ii) solar water splitting. Particularly, the current research interests concern the design and characterization of catalysts obtained in pellets or structured form (monoliths, foams) for fossil fuels (natural gas, LPG, diesel) and renewable fuels (biogas, bio-ethanol) reforming processes (Steam, Partial Oxidation, Autothermal, Oxy-Steam and Tri-reforming). In the field of water splitting, the research activities aim at discovering new materials/solution for solar energy capture, highlighting the correlations between physico-chemical properties, band-gap energy and photocatalytic activity.
Other activities are correlated with the development of catalytic systems for CO_2 methanation (Sabatier reaction) and porous solid materials for gas stream cleaning (CO_2 and H_2S separation from biogas).
Parallel to the development of materials, the research activity regards also the design and realization of small scale Fuel Processor Systems based on reforming processes of fossil and renewable fuels, finalized to syngas production and/or integration with Fuel Cell systems for mobile and stationary applications.

D. RESEARCH ACTIVITIES

- Author and co-author of **23 publications** (P1-P23)**, 1 book chapter** (B1)**, 6 conference proceedings** (C1-C6), many technical reports for national and international projects.
- Participation to many national and international **conference and symposia**, presenting scientific results in poster and oral communications.
- ***Referee*** for several international scientific journals (Applied Catalysis B: Environmental, Journal of Catalysis, Journal of Nanomaterials, International Journal of Hydrogen Energy, Applied Surface Science).

Messina, October 3, 2017

- Relevant scientific **awards:**

2016 Poster Presentation Award;
Title of the work: "Structured catalysts for hydrogen production by biogas steam and tri-reforming processes at high flow-rates"; A. Vita, **C. Italiano**, L. Pino, C. Fabiano, S. Specchia; IMPRES 2016, Taormina, Italy.

2015 Best Presentation;
Title of the work: "Syngas production by biogas steam and oxy steam reforming processes on Rh/CeO_2 catalyst coated on ceramics monolith and open foams"; A. Vita, M.A. Ashraf, **C. Italiano**, C. Fabiano, L. Pino, S. Specchia; 2015 AIChE Annual Meeting, Salt Lake City, UT.

2014 Award at Young Scientists Symposium for the scientific results;
Title of the work: "Bio-hydrogen production by oxidative steam reforming of biogas over nanocrystalline Ni/CeO_2 catalysts"; **C. Italiano**, A. Vita, C. Fabiano, M. Laganà, L. Pino; WHEC 2014, Gwangju Metropolitan City, Korea.

2014 Best Presentation;
Title of the work: "Biogas steam and oxy-steam reforming reactions over Me/CeO_2-based (Me = Rh, Pt, Ni) structured cordierite monoliths"; A. Vita, G. Cristiano, **C. Italiano**, L. Pino, S. Specchia; 2014 AIChE Annual Meeting, Atlanta.

E. PUBLICATIONS

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P2. "$Ce_{0.70}La_{0.20}Ni_{0.10}O_{2-\delta}$ catalyst for methane dry reforming: Influence of reduction temperature on the catalytic activity and stability", L. Pino, **C. Italiano**, A. Vita, M. Laganà, V. Recupero, *Appl. Catal. B* 218 (2017) 779-792.

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F. BOOK CHAPTER

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