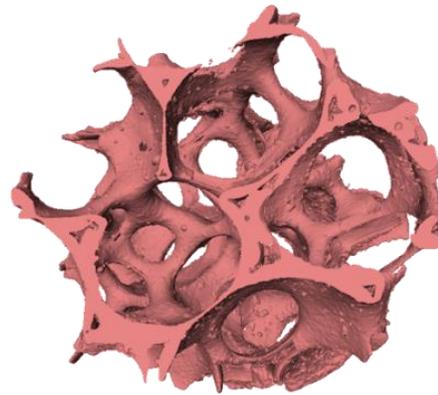


# Ceramic open cell foams as catalytic support for endothermic and exothermic reactions: Focus on lean methane combustion

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## Summary

The aim of this work is focused on the study of ceramic open cell foams (OCFs) as catalytic support for exothermic and endothermic reactions. In particular, focusing on the methane oxidation reaction under lean conditions. With projection toward process intensification, the research is dedicated to the analysis of the mass transfer effects occurring from the bulk gas phase to the external catalyst surface (external or interphase mass transfer) and within the catalyst layer (internal or intraparticle mass transfer) as well as to evaluate the different controlling regimes (kinetic, internal or external mass transfer) during  $\text{CH}_4$  oxidation on the coated OCF. In addition, this investigation also explores the heat transfer effects on foams.

In order to study the effects of mass transfer in the gas-solid reaction system, a theoretical low-dimensional model was used. Firstly, the model was applied to exothermic and endothermic reactions catalyzed in ceramic monolithic structures, since this substrate exhibits a much simpler geometry compared to that of OCFs. Specifically, the reactions of nitrous oxide ( $\text{N}_2\text{O}$ ) decomposition (*Paper I*) and  $\text{CH}_4$  steam reforming (*Paper II*) catalyzed on cordierite monolith were analyzed. Different

controlling regimes were identified by varying the operating conditions and the design parameters of the structured catalyst. Subsequently, the analysis of the OCFs was followed by first examining the steam and oxy-steam reforming reactions of biogas (*Paper III*) catalyzed in ceramic OCFs made of alumina of different pore density (20, 30 and 40 pore per inch). A thin catalytic layer was deposited on the structures via solution combustion synthesis (SCS) and wetness impregnation (WI) techniques. The coated OCFs were physically characterized by SEM/EDX, TEM, XRD, Helium Pycnometry, Stereoscopic measurement and adhesion test. Besides, pressure drop measurements were performed on all structures. Characteristic times and dimensionless numbers were calculated to analyze the mass transfer effects as well as to evaluate possible heat transfer limitations by varying the flow conditions. Stability tests were performed on both reactions over 200 h of time-on-stream (TOS).

For the intensification of CH<sub>4</sub> oxidation in lean conditions, 3 wt. % PdO/Co<sub>3</sub>O<sub>4</sub> catalyst was deposited on ceramic OCFs made of zirconia (Zir), alumina (Alu) and silicon carbide (SiC) with pore density of 30 ppi (*Paper IV*) using SCS and WI methods. Approximately the same amount of catalyst was deposited on each structure. The catalytic tests were performed at different flow conditions (WHSV of 30 NL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>, temperature range of 100-700°C, inlet CH<sub>4</sub> concentration of 0.5 and 1 vol. %) and lean conditions were ensured by maintaining a O<sub>2</sub>/CH<sub>4</sub> molar ratio of 8. In order to verify the stability of the catalyzed OCF, a catalytic test was performed on the best selected catalyst over about 250 h of TOS. All the coated OCFs were characterized by Raman spectroscopy, FESEM, N<sub>2</sub> physisorption, EDXS. In addition, adhesion tests were performed on all coated OCFs by ultrasonic treatment. The theoretical low-dimensional model was adapted to the OCF geometry taking into account the characteristic geometrical parameters: pore and strut diameter, specific surface area, tortuosity and open porosity. Thus, the operating regimes were analyzed by studying the evolution of the characteristic resistances as the process temperature varied. Furthermore, possible heat transfer limitations were evaluated using the Mears and Anderson criteria.

The effect of the catalyst content on the catalytic performance and on the various operating regimes during CH<sub>4</sub> combustion were also evaluated (*Paper V*). For this purpose, Zir-OCF of 30 ppi was used as catalytic support. Different catalyst loading (C<sub>load</sub><sup>100</sup>, C<sub>load</sub><sup>150</sup> and C<sub>load</sub><sup>250</sup> corresponding to 6.1, 8.2 and 13.7 mg<sub>cat</sub> cm<sup>-2</sup><sub>OCF</sub>) and flow conditions were investigated (0.5 and 1.0 vol.% inlet CH<sub>4</sub> concentration, O<sub>2</sub>/CH<sub>4</sub> molar ratio 8, temperature range of 100-700°C and WHSV of 30, 60 and 90 NL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). Pore and strut dimensions were individuated using SEM and X-CT images. A correlation that describes the mass transfer in coated OCFs at low Reynolds numbers was derived. Finally, a combination of coated (3 wt. % PdO/Co<sub>3</sub>O<sub>4</sub>) SiC/Zir OCF (of 30 ppi) were tested for CH<sub>4</sub> combustion under lean conditions (*Paper VII*). In each combination, the SiC-OCF was placed inside the reactor on the inlet side of reactive gases followed by the Zir-OCF. The catalytic performance,

mass and heat transfer effects were evaluated at different flow conditions (0.5 and 1.0 vol.% inlet CH<sub>4</sub> concentration, O<sub>2</sub>/CH<sub>4</sub> molar ratio 8, temperature range of 100-700°C and WHSV of 30, 60 and 90 NL h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). Operating regimes of each catalytic combination were evaluated in terms of characteristic resistances using the adapted theoretical model for OCFs. In addition, heat transfer effects were studied by evaluating the Mears and Anderson criteria. The temperature difference between the bulk gas phase and the catalyst surface was also determined theoretically. Lastly, the values of Nusselt number and volumetric heat transfer coefficients were estimated and compared with those obtained in previous work on individual foams.

Zirconia, alumina and silicon carbide OCFs of 30 and 45 ppi were fully characterized by X-ray computed microtomography (*Paper VI*). Characteristic geometrical dimensions such as pore size, length and diameter of strut, node diameter, open porosity and specific surface area were extracted from both 2D slices and 3D foam reconstruction. In addition, the experimental specific surface area values were compared with theoretical models proposed in the literature. Finally, an empirical expression to determine the specific surface area in ceramic OCFs was derived.

Microporosity, dense grains and circular hollow strut were the most relevant characteristics present in the skeletons of all the ceramic OCFs studied. The increase in OCF pore density led to a higher specific surface area. Excellent adhesion of the catalyst to the ceramic foams was found with weight losses below 5%, even at high catalyst contents. All coated alumina foams showed high catalytic activity in the following order 20 ppi < 30 ppi ≈ 40 ppi. Zir-OCF exhibited full CH<sub>4</sub> conversion at the lowest temperatures compared to Alu and SiC supports for all flow conditions investigated. At low temperatures, all coated OCFs operated in a kinetic regime independently of the structure material. The diffusion effects within the catalyst become more important at lower temperatures for coated foams with higher thermal conductivity and lower specific surface area in the following order Zir < Alu < SiC. For all flow conditions studied, the best catalytic performance in terms of CH<sub>4</sub> conversion and mass transfer was found for the catalyst loading of 6.1 mg<sub>cat</sub> cm<sup>-2</sup><sub>OCF</sub>. The SiC1.5Zir1.5 catalytic combination showed a promising catalytic performance for complete CH<sub>4</sub> oxidation in lean conditions, where the CH<sub>4</sub> light-off curve was shifted toward lower temperatures than those obtained for individual OCF. According to Anderson's criteria, no temperature gradients were present within the catalytic layer. Nevertheless, the structures could operate in an unstable zone for external heat transfer depending on the structure's nature, caused by the strong exothermicity and fast combustion reaction. The PdO/Co<sub>3</sub>O<sub>4</sub> catalyst coated on Zir-OCF resulted highly stable after approximately 250 hours of operation.