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Optimization of structured cellular foam-based catalysts for low-temperature carbon dioxide methanation in a platelet milli-reactor

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ABSTRACT

Here, we present a preliminary study to choose a catalyst with enough catalytic activity at temperatures below 250 °C, in order to study heat transfer in a platelet milli-reactor (PMR) with an infrared camera and a commercial window inserted on the top of our reactor that only withstands a maximal temperature of 250 °C. The higher methane productivity of foam catalysts compared to powder catalysts was revealed. Foam catalysts, all impregnated with the same amount of active phase (Ni + Ru) and with different coatings, were compared to SiC only impregnated with Ni + Ru. The different coatings studied were: carbon nanofibers (CNF), ceria–zirconia (CZ) and the combination of both. Both CNF and CZ washcoats were able to increase the low specific surface area of the SiC foam. Moreover, the presence of ceria–zirconia was proven to be essential for ensuring high methane productivities. The catalyst combining both CNF and CZ showed the best results.

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1. Introduction

Carbon dioxide has always been present in the atmosphere in small quantities. There are natural sources responsible for its presence (breathing, fermentation, fires, volcanoes, decomposition of organic matter...), but also anthropogenic ones (combustion of fossil sources and biomass, industries, agriculture...), the contribution of which being massively and constantly increasing since the beginning of the industrial revolution. Carbon dioxide is one of the gases responsible for the greenhouse effect. In order to reduce the CO₂ production or its emission into the

atmosphere, a lot of research projects about capture and storage emerged [1].

Another pathway to reduce these emissions is the valorisation of CO₂ by transformation into valuable chemical compounds, like methane or longer hydrocarbon species, methanol, esters, ethers... [2].

The production of methane using CO₂ as a reactant is therefore a suitable way to contribute to the decrease of greenhouse gas emissions through chemical recycling. Using conventional electricity, made for example from fossil fuel, would be nonsense, contrary to the power-to-gas concept where the excess of energy mainly produced by wind parks or solar-electric generation is used. The hydrogen necessary for the methanation reaction is produced by water electrolysis and reacts with carbon dioxide to produce methane that can be directly injected into the natural gas grid. Few projects are already at the state of demonstration project, for example the ENERTAG

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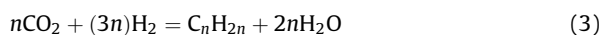
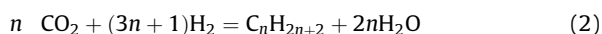
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project (2011) [3], which uses excess energy from wind parks to produce hydrogen combined with a biogas plant to produce biomethane, or Audi (2013) [4] with a power-to-gas facility of 6 MW to produce methane for their new gas powered cars.

The methanation reaction was discovered by Sabatier and Senderens in 1902 [5,6], who studied the hydrogenation reaction of CO and CO₂ on nickel or cobalt. Since then many studies on metallic elements of group VIII (Fe [7], Rh [8,9], Ru [10,11], Co [12] or Ni [9,13–19]) supported on oxides (TiO₂, CeO₂, ZrO₂, Al₂O₃, SiO₂, La₂O₃, La₂O₃/SiC [18]...) or mixed oxides [9,18–21] were published.

During the hydrogenation of carbon dioxide into methane (1), other side products like alkanes (2), alkenes (3), and CO through Reverse Water Gas Shift reaction (4) can be formed:



Most of the studies that can be found in the literature about this reaction were done using powder catalysts in a fixed-bed reactor. The use of cellular foam instead of powder in a fixed-bed has many advantages such as a high surface/volume ratio, low pressure drop, a better control of the reaction conditions and an intensification of mass and heat transfer [22–24]. The last one is very interesting for the intensification of the methanation reaction. Effectively, the exothermicity of this reaction is partly responsible for the catalyst deactivation by enhancing the sintering of metallic particles.

The cellular foams used in this work, made of β -SiC and provided by SICAT [25], are synthesized using a shape memory synthesis developed by Ledoux et al. [26]. The use of β -SiC foams have some advantages: SiC is chemically inert, has a good mechanical and thermal resistance and presents a high thermal conductivity for a ceramic matrix. β -SiC shows however one major disadvantage, its low specific surface area (approx. 20 m²·g⁻¹) which is due to its method of preparation that requires high temperatures. However, Édouard et al. [27] reported that by growing nanofibers on the foam's surface, the specific surface area can be increased up to 50 m²·g⁻¹.

A new kind of platelet milli-reactor (PMR), shown on Fig. 1, has been developed by our institute for the intensification of catalytic processes like the dehydration of methanol into dimethylether [28,29], the oxidative dehydrogenation of ethane and ammoxidation of propane [30] and the Fischer–Tropsch synthesis [31]. But, up to date, no industrial processes have been reported using microreactors or PMR despite their advantages compared to conventional reactor. The PMR used in this study is composed of a metallic host structure where a cellular β -SiC foam with or without carbon nanofibers (CNF), impregnated with a catalyst, is inserted into a central channel (18 mm × 5 mm × 24 mm), as shown in Fig. 1. This PMR is used in order to enhance the methanation reaction

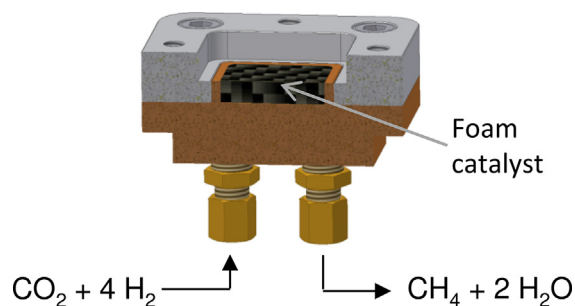


Fig. 1. (Color online.) Drawing of the platelet milli-reactor (PMR) developed for this study with a single central channel of 18 × 5 × 24 mm.

by combining the advantages of milli-reactors and β -SiC foam support.

The final objective of our work is to study the heat transfer of the highly exothermal carbon dioxide methanation reaction. In order to study the heat transfer, an infrared camera will be used and a commercial window inserted on the top of the PMR. The window used only stands a maximal temperature of 250 °C. Therefore, in this paper, we will present the preliminary studies made to choose a catalyst with enough catalytic activity at temperatures below 250 °C (10–20%). First, catalytic tests in a fixed-bed were made on powder catalyst, then on fragments of impregnated β -SiC foam, in order to choose which active phase will be deposited on the foams that will be tested in the PMR.

Nickel-based catalysts were chosen because they are efficient for CO₂ methanation in term of activity and selectivity [9,21], and are less expensive than ruthenium-based catalysts also used for methanation. A ceria–zirconia support, that has already been studied by our institute [32,33] and proven to show high conversion rates, methane selectivity and stability, was employed. Two powder catalysts impregnated with 10 wt% of Ni and 0.1 wt% of Ru were compared: CZ_p (CZ being Ce₂Zr₂O₈) and SiC_p. Six SiC foam-based catalysts (cell size 2700 μ m, strut size 226 μ m, window diameter 1146 μ m, porosity 0.9), whose detailed compositions are summarized in Table 1, were also studied. The first one, SiC_f, was a SiC foam impregnated with 10 wt% of Ni and 0.1 wt% of Ru and was compared to SiC_p catalyst to investigate the difference between foam and powder catalysts regarding the catalytic activity. The second one, 27CZ_f, was a SiC foam with 27 wt% loading of ceria–zirconia and 2.5 wt% of Ni and 0.025wt% of Ru to have the same Ni/CZ ratio (1/9) than powder catalyst CZ_p. It will allow us to investigate the difference between foam and powder catalysts regarding the catalytic activity in the case of ceria–zirconia-based catalysts. The amount of active phase was set to 2.5 wt% of Ni and 0.025 wt% of Ru, to compare the foam catalysts studied. The third catalyst studied, SiC_f, was a SiC foam only loaded with the Ni and Ru active phases. The fourth catalyst studied, 15CNF_f, was a SiC foam with 15 wt% loading of carbon nanofibers to study the influence of those CNF on the catalyst's activity. A SiC foam with 1 wt% of CZ was also synthesized, 1CZ_f, to compare the effect of CNF and a ceria–zirconia-based catalyst with lower CZ content.

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