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## Development of a catalyst for oxidative coupling of methane in a gas-solid vortex reactor

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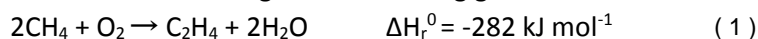
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### Highlights

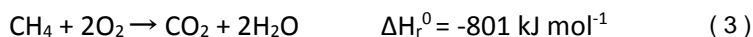
- Synthesis of a thermally and mechanically stable catalyst for OCM in a GSVR.
- First demonstration of oxidative coupling of methane in GSVR.
- Process intensification of OCM

### 1. Introduction

Oxidative coupling of methane (OCM) is a promising pathway for the direct synthesis of C<sub>2</sub> hydrocarbons from methane according to the following global chemical reactions.<sup>[1]</sup>

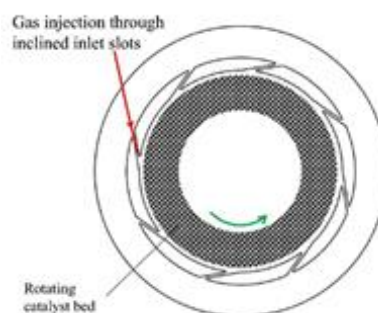


The presence of oxygen and the high reaction temperature can facilitate the overoxidation of reactants and products to CO and CO<sub>2</sub>, typically limiting the C<sub>2</sub> hydrocarbon yields to below 30%.<sup>[2]</sup>



The high reaction exothermicity moreover dictates the need for a suitable heat management strategy.

In a gas-solid vortex reactor (GSVR), a rotating fluidized bed of solids is obtained by the tangential injection of gas at high velocities (Figure 1).<sup>[3]</sup> In the bed, the centrifugal forces on the catalyst particles balance the drag forces, leading to a dense and uniform bed. The very high gas-solid slip velocities intensify interfacial transfer of mass, energy and momentum, allowing a reduction in gas phase residence time. Using extensive computational fluid dynamics (CFD) simulations, a gas-solid vortex reactor has been designed and commissioned at Ghent University<sup>[3]</sup>Error! Reference source not found.. The diameter of the reaction chamber is 80 mm, containing 8 inlet slots with a width of 1 mm (Figure 1).<sup>[3]</sup>Error! Reference source not found.



**Figure 1** . Top view and operation of a gas solid vortex reactor in static geometry

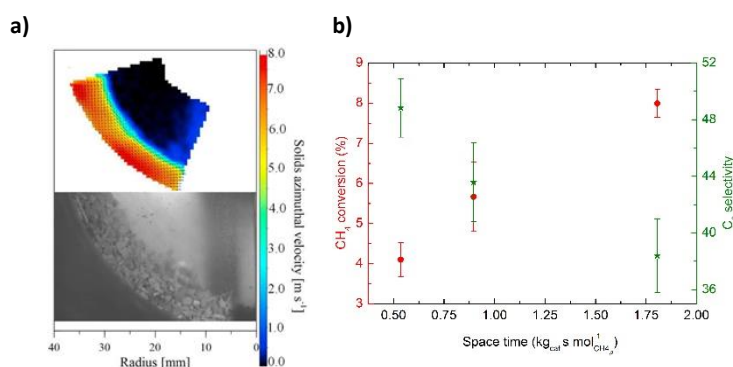
Using bifurcation analysis incorporating detailed microkinetic models, Vandewalle et al. <sup>[4]</sup> showed that the good thermal back mixing combined with limited species back mixing in the GSVR can potentially improve C<sub>2</sub> yields when the reactor is operated on an ignited branch close to the extinction state.<sup>[5]</sup>

The high reaction temperature, the high solid velocities, and the low space times in the GSVR at those conditions require the development of a novel catalyst with high attrition resistance, high

thermal stability, high activity, and proper size distribution. In this presentation, we report the development of such a supported catalyst, and compare its performance in a fixed bed reactor with that in the GSVR.

## 2. Results and Discussion

Cold flow experiments were performed in the GSVR with inlet gas flow rates in the range of 15-30  $\text{Nm}^3 \text{hr}^{-1}$ , and slot velocities exceeding  $100 \text{ m s}^{-1}$  to test the stability of the catalyst bed and its attrition resistance. Under these conditions, a stable bed of 10 g of catalyst material with a thickness of about 10 mm could be retained in the GSVR at room temperature for a duration of 1 hour (Figure 2a). Over the 1 hour experiment, less than 1% of the material was entrained. Similar experiments with conventional Sr/La<sub>2</sub>O<sub>3</sub> OCM catalyst pellets and with inert  $\alpha\text{-Al}_2\text{O}_3$  pellets resulted in rapid attrition and entrainment of the pulverised pellets with the gas stream. The



**Figure 2** a) Azimuthal velocity of solids in the GSVR [3] and b) CH<sub>4</sub> conversion and C<sub>2</sub> selectivity vs. space time for synthesized catalyst at 800 °C

gas flow rates and the catalyst material holdup in the GSVR correspond to very low space times of  $0.1 \text{ kg}_{\text{cat}} \text{s mol}^{-1}_{\text{CH}_4,0}$ . For these space times, the synthesized catalyst material was tested in a quasi-isothermal fixed bed reactor at 800 °C and for a O<sub>2</sub>:CH<sub>4</sub> inlet ratio of 4. A reasonable C<sub>2</sub> selectivity of 40-50% and a CH<sub>4</sub> conversion of 5-10 % were obtained for this high activity catalyst (Figure 2b). Typical OCM catalysts like Li/MgO and NaMnWO<sub>4</sub>/SiO<sub>2</sub> show essentially no CH<sub>4</sub> conversion for space times below  $5.0 \text{ kg}_{\text{cat}} \text{s mol}^{-1}_{\text{CH}_4,0}$ . [6] Next, the synthesized catalyst will be tested under reactive conditions in the GSVR. Based on detailed microkinetic simulations based on the fixed-bed experiments a methane conversion of 4% and a C<sub>2</sub> selectivity of 45% are expected.

## 3. Conclusions

A thermally and mechanically stable OCM catalyst material was synthesized, which forms a stable catalyst bed under the harsh conditions in the GSVR reactor. At the conditions and at low space times, the synthesized catalyst material displayed a methane conversion between 5 and 10 % and a C<sub>2</sub> selectivity around 50%. Detailed simulations indicate that a similar performance can be expected in the GSVR. These proof-of-concept experiments are currently scheduled and will be reported at the conference.

## References

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