C123: from methane to value-added C3 chemicals via ethylene

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Introduction

Natural gas is and will remain emerging as key player in the global energy sector. The conversion of natural gas beyond flaring, hydrogen production and capture, and technologies such as gas-to-liquids is thus critical to achieve a more sustainable chemical industry. Here a breakthrough innovation for upgrading methane to C3 commodity chemicals is presented in the H2020 C123 project[1]. Methane is firstly converted to a mixture of ethylene and synthesis gas to be further converted to C3 chemicals. The first step is denoted as the Oxidative Conversion of Methane (OCoM) while the second step is the well-known hydroformylation of ethylene to propanal which can be further converted to, e.g., propanol and propylene.

Oxidative Conversion of Methane

OCoM is a process comprising several reactions built around and critically relying on the Oxidative Coupling of Methane (OCM). While ethylene production from natural gas *via* OCM is already investigated for almost 40 years, its commercial implementation is held back due to low C2/C2+ yields, remaining below 30%, and the economic viability remains a dream. To overcome these challenges C123 aims at the conversion of methane to an equimolar mixture of ethylene and synthesis gas, rather than optimizing the ethylene yield. The mixture is subsequently converted to C3 species in the hydroformylation step, see below, ensuring a high atom efficiency in the C3 product while bypassing the challenging ethylene yield maximization.

For OCM, almost the entire periodic table has been probed as potential elements for catalytic materials. Metal oxide catalysts have shown promising results, yet the $NaWMn/SiO_2$ has recently gained attention[2] and is considered the C123 benchmark catalyst. Next to OCM additional reactions to increase the ethylene yield as well as ensure the equimolarity of the synthesis gas and ethylene mixture are considered, with post bed ethane cracking, (dry) methane reforming and (CO_2 induced) oxidative dehydrogenation of ethane to ethylene as the most promising ones. The OCoM process proposal is visualized in Figure 1. The feed is first converted to ethylene, CO and H_2, with CO_2 and water as side products, in the OCM reactor at 700-800°C. The ethylene yield is further increased in the PBC unit, where ethane is thermally cracked to ethylene. Such a configuration allows running the PBC on the heat generated by OCM and generates a stream enriched in ethylene (and H_2) at a temperature of 600°C. Finally, in the CO_2-ODH reactor, the ethylene yield is further increased while CO_2 generated during OCM, or present in a feedstock such as biomethane, is converted to CO. If required, additional synthesis gas can be generated *via* methane dry reforming, which then operates in parallel to the three reactions discussed above. To produce the most suited ethylene hydroformylation feed challenges on every scale are addressed, with fundamental modelling as the main tool to achieve the project goal.

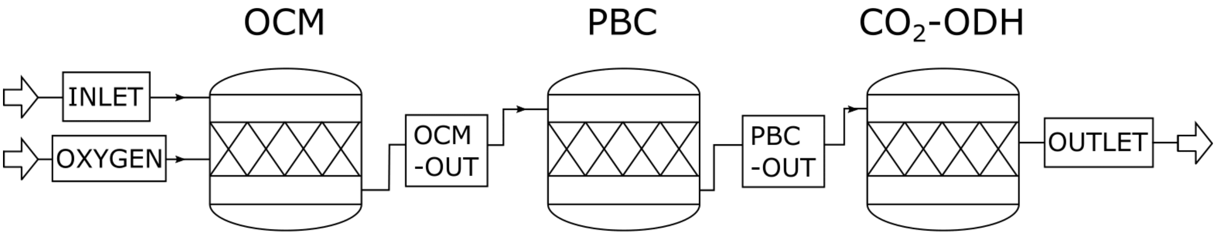

Figure 1: OCoM process configuration consisting of an Oxidative Coupling of Methane (OCM) reactor followed by a post bed cracker (PBC) and a CO_2 assisted oxidative dehydrogenation (CO_2-ODH) reactor.

Ethylene Hydroformylation

The produced mixture of ethylene and synthesis gas is subsequently converted to propanal *via* hydroformylation. Propanal as such is an interesting building block with applications such as, but not limited to, propanol and propylene and is furthermore easy to store and transport[3]. Currently, industrial-scale hydroformylation is a homogeneously catalyzed process because of the high ethylene conversion and even higher propanal selectivity that can be achieved using Rh complexes. Even though these catalysts are (much) more expensive than the cobalt catalysts, the catalyst selection is justified by the high propanal yield that is achieved. To reduce (precious) metal losses and facilitate product separation heterogeneously catalyzed hydroformylation is envisaged. To achieve these goals the homogeneously catalyzed ethylene hydroformylation is investigated and the most promising heterogeneous hydroformylation catalysts are designed by tethering the best performing complexes in porous supports.

Material and process design and optimization

Despite most, if not all, of the technologies considered within the project are already (well) established, the development of an integrated C123 process is not straightforward. The OCoM step is ideally operated at temperatures in the range between 650 and 900°C and at atmospheric pressure, while the hydroformylation step is ideally performed at 100°C and a total pressure between 20 and 40 bar. To ensure a smooth transition between these steps and keep all components in the gas phase, a heterogeneously catalyzed hydroformylation step is developed, see also above. To achieve these goals experimentation and (micro)kinetic modeling are performed for both the OCoM and the hydroformylation step. In the OCoM step the focus is on the effect of CO_2 and exploring the performance when operating above atmospheric pressure. In the hydroformylation step the effect of CO_2 as well as the potential to operate at a lower total pressure and a higher temperature are investigated. In this way, both steps will ultimately be brought as close as possible to each other.

The heterogenization of the hydroformylation catalyst is another challenging step in the envisaged C123 process and multiple approaches are considered, such as functionalization of silica surfaces, synthesis of a metal organic framework based material and the development of novel porous organic polymers, which can be further functionalized with, e.g. Rh. The latter is a promising heterogenization procedure that was recently discovered by Canivet et al.[4]. Following this novel synthesis method the active complex is integrated in the framework of the heterogeneous catalyst rather than attached to it. All strategies are supported by microkinetic modeling: the quantitative insights in terms of kinetic and catalytic descriptors obtained from modeling the homogeneously catalyzed hydroformylation are transferred to the heterogeneously catalyzed one, allowing for assessment the determining factors to optimize the catalyst selectivity in particular and the C123 process in general.

Conclusions and perspectives

A breakthrough technology to upgrade natural gas to propanal is presented. The process consists of OCoM, rather than OCM, where ethylene and synthesis gas are formed, and the heterogeneously catalyzed hydroformylation of ethylene to propanal. C123 is closing the gap between the operating conditions of both process steps as much as possible using a model supported multiscale approach and will ultimately develop a unified catalyst and process at TRL 5.

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References

1. Amieiro Fonseca, A.; Heyn, R. H.; Frøseth, M.; Thybaut, J. W.; Poissonnier, J.; Meiswinkel, A.; Zander, H.-J.; Canivet, J., A Disruptive Innovation for Upgrading Methane to C3 Commodity Chemicals. *Johnson Matthey Technology Review* **2020**.
2. Gordienko, Y.; Usmanov, T.; Bychkov, V.; Lomonosov, V.; Fattakhova, Z.; Tulenin, Y.; Shashkin, D.; Sinev, M., Oxygen availability and catalytic performance of NaWMn/SiO2 mixed oxide and its components in oxidative coupling of methane. *Catalysis today* **2016,** *278*, 127-134.
3. Dubois, J.-L.; Nieder-Heitmann, M.; Letoffet, A.; Vleeming, H., C123–Methane oxidative conversion and hydroformylation to propylene. *Johnson Matthey Technology Review* **2020**.
4. Wisser, F. M.; Mohr, Y.; Quadrelli, E. A.; Canivet, J., Porous Macroligands: Materials for Heterogeneous Molecular Catalysis. *ChemCatChem* **2020,** *12* (5), 1270-1275.