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A Disruptive Innovation for Upgrading Methane to C3 Commodity Chemicals

Technical challenges faced by the C123 European consortium

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C123 is a €6.4 million European Horizon 2020 (H2020) integrated project running from 2019 to 2023, bringing together 11 partners from seven different European countries. There are large reserves of stranded natural gas waiting for a viable solution and smaller scale biogas opportunities offering methane feedstocks rich in carbon dioxide, for which utilisation can become an innovation advantage. C123 will evaluate how to best valorise these unexploited methane resources by an efficient and selective transformation into easy-to-transport liquids such as propanol and propanal that can be transformed further into propylene and fed into the US$6 billion polypropylene market. In C123 the selective transformation of methane to C3 hydrocarbons will be realised *via* a combination of oxidative conversion of methane (OCoM) and hydroformylation, including thorough smart process design and integration under industrially relevant conditions. All C123 technologies exist at TRL3 (TRL = technology readiness level), and the objectives of C123 will result in the further development of this technology to TRL5 with a great focus on the efficient overall integration of not only the reaction steps but also the required purification and separation steps, incorporating the relevant state-of-the-art engineering expertise.

Introduction

Methane market opportunities will keep emerging; most energy forecasts currently predict that natural gas will play an important future role in the global energy sector. Projected long-term growth rates for gas are around 2% per year and analysts are expecting natural gas to overtake coal in the global energy arena in the next two decades (1, 2). Security of supply is improving to meet this demand with the USA becoming a large liquid natural gas (LNG) export player in recent years as the price of natural gas continues to drop while liquid petroleum gas (LPG) and carbon exploitation associated costs increase. All these scenarios could also allow for economically viable opportunities for stranded gas and biomethane utilisation.

Sustainable exploitation is a key driver of natural gas consumption's future growth. The role of natural gas as a crucial stage strategy vector to reduce emissions could be supported

by carbon pricing policies with the development of low carbon technologies where natural gas is implemented. Sustainable gas sources combined with renewable energy applications and process efficiency innovations are all required to tackle global emissions. Some of these first and second generation lower carbon or fuel switch technologies are expected to merge and support future methane applications and opportunities (3–5).

An extensive technoeconomic and viability review paper was presented in parallel by the partners in C123, the reader is directed there for further details (6). In the present paper, technical progress and remaining challenges are reviewed.

Disruptive technologies need to evolve to support new challenges including biomethane composition (higher amounts of CO_2 in the gas), alternatives to natural gas flaring, transformations to easy-to-transport chemicals, hydrogen production and carbon capture, utilisation and storage (CCUS). Current stranded natural gas reserves opportunities include compressed natural gas (CNG), gas to liquids (GTL), gas to solids (GTS) (also known as solidified natural gas (SNG)) and gas to wire (GTW). GTL increases the ease of transport through a physical change of the natural gas into a liquid (7). Two additional state-of-the-art utilisation options include gas to polymers (GTP) and gas to olefins (GTO). For both GTO and GTP, natural gas is converted into syngas, which is used to produce methanol as the feedstock source for the methanol to olefins (MTO) process. The olefins, i.e. ethylene and propylene, are then converted into polymers, polyethylene and polypropylene.

C123 "Methane oxidative conversion and hydroformylation to propylene" is a €6.4 million European Union (EU) H2020 project running from 2019 to 2023. The consortium consists of 11 partners from seven different countries (Norway, Belgium, France, UK, Germany, Azerbaijan and The Netherlands) with six industrial partners, two research and technology organisations, two universities and one association, all of whom have extensive previous experience in national and international research and innovation projects. C123 will evaluate how to best valorise unexploited methane resources by an efficient and selective transformation into easy-to-transport liquids such as propanol and propanal. In C123 the selective transformation of methane to C3 products will be realised *via* a combination of OCoM and hydroformylation. The C123 process aims to validate the implementation in two energetically and economically relevant, complementary and

sustainable routes depending on the natural gas source exploited:

- Add-on route targeting propylene production as an add-on to large existing facilities (>140,000 tonnes year^{-1} of propylene – equivalent to >200,000 tonnes year^{-1} propanol)
- Modular route targeting decentralised modular production unit (~10,000 tonnes year^{-1}) of high value propanol or propanal that can be easily transported for further transformation into propylene or other products.

C123 will explore and evaluate the viability of this technology for biogas, associated gas and marginal gas fields, all with different challenges. Biogas is produced from organic matter such as sewage sludge, cow manure, agricultural waste and the organic fraction of municipal solid waste. Large concentrations of CO_2, about 36%, and impurities such as hydrogen sulfide (100–10,000 parts per million (ppm)) are usually found in biogas. Associated petroleum gas (APG), is a form of natural gas found with deposits of petroleum, either dissolved in the oil or above the reservoir. Associated gas is often wasted by flaring, under-utilised in low value applications such as onsite electricity generation or reinjection for enhanced oil recovery, or sold. Marginal fields are abandoned or non-developed fields that can have limited economic viability, unfavourable crude oil characteristics or high gas and low oil reserves. Marginal gas reserves account for approximately 15% of the world's proven gas reserves.

All C123 technologies exist at TRL3, and the objectives of C123 are their further development to TRL5 by an optimised integration of catalyst and process. The C3 commodity chemicals propanal and propanol can be transformed further into propylene and fed into the US$6 billion polypropylene market or transformed into other valuable chemical products. The breakthrough innovation is the replacement of propylene production *via* the very energy intensive steam cracking process with production by less energy demanding and more selective build-up from smaller molecules.

The C123 transformation of methane into C3 chemical building blocks will be developed through in the technical work packages (WPs) WP2, WP3 and WP4 described in **Figure 1**. The goal will be optimisation of the overall carbon and energy efficiencies and cost effectiveness of the integrated OCoM and hydroformylation processes through the application of a set of collaborative
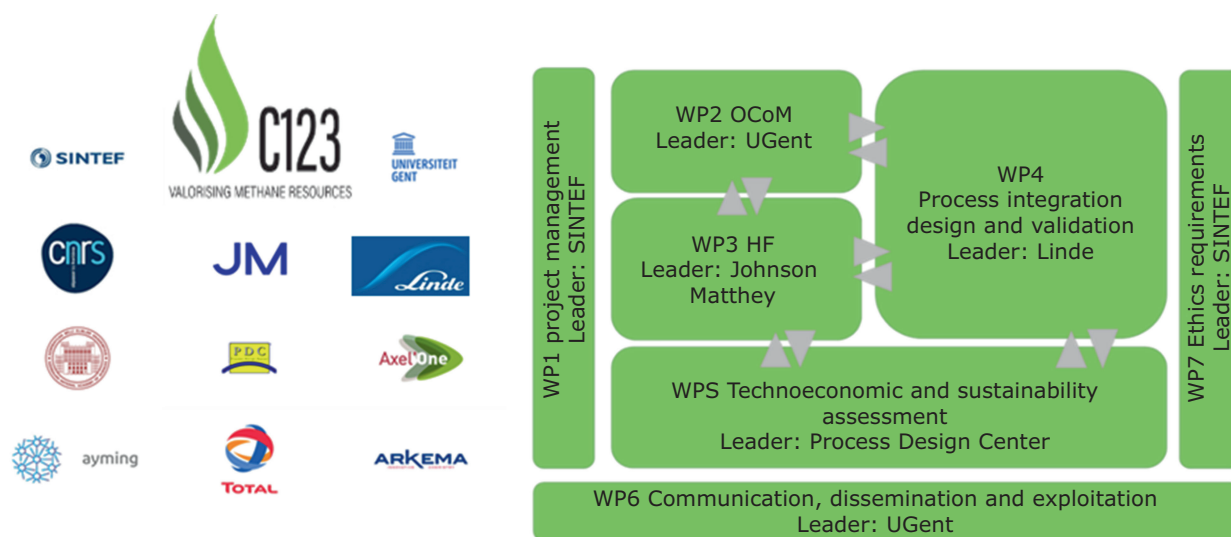
Fig. 1. C123 work package structure and consortium partners: Johnson Matthey, SINTEF, CNRS, Ghent University, Total, Linde, Axel'One, Process Design Center, Arkema, Ayming, and Azerbaijan Academy of Sciences

technologies involving both catalyst development and formulation and reactor design.

The expected major advancements in WP2 OCoM with respect to the state-of-the-art are the achievement of a higher methane conversion per pass, simpler heat management, higher energy efficiency, better carbon utilisation and an optimum product stoichiometry for an efficient hydroformylation process. The latter will be realised by tuning the output of the OCoM process to provide the optimal C_2H_4:CO ratio. Some hydrogen, required for hydroformylation and also processes downstream of the hydroformylation step, will be formed during OCoM, but optimising the amount of hydrogen is not part of the overall targets of OCoM. Any extra hydrogen for the overall process will be supplied externally. The hydroformylation step will need to tolerate CO_2 in the reactor feed, as that is provided by both the feed gas and the byproduct recycle. C123 will thus improve the atom economy and will circumvent the bottlenecks of the state-of-the-art oxidative coupling of methane (OCM) process which optimises only the ethylene production.

The goal of WP3 is production of the liquid C3 intermediates propanol and propanal through the development of a heterogeneous hydroformylation catalyst and process optimised for conversion of the OCoM effluent. This is advantageous for transportation and can be used for on-demand production of propylene by dehydration of propanol,

or for further conversion of propanal to valuable downstream chemicals propionic acid. While industrial hydroformylation is a homogeneous process, a heterogeneous catalyst for the C123 hydroformylation is envisaged, allowing simplified separation and global process integration with OCoM.

WP4 will comprehensively develop and optimise process concepts from the simultaneous tuning of the catalyst properties, the operating conditions and the reactor configuration. It includes an innovative integrated reactor design that optimises heat management and transfer, mass transfer and recycling, thus improving energy and carbon efficiency, as well as achieving high product yields. This requires an optimal combination of the two processes, including possible equalisation of the operating pressure (around 10 bar) of both OCoM and hydroformylation in order to minimise the costs of pressurisation and improve reactor integration efficiency. Further, the additional reaction steps, the hydrogenation of propanal and dehydration to propylene, as well as appropriate purification and separation steps need to be efficiently included. The C123 process innovation is expected to result in an increase in carbon efficiency of at least 25%. Overall, at least 30% of fossil fuel consumption can be saved, and this can potentially increase up to 100% when any external hydrogen required by the overall process is electrolytically generated with electricity from renewable energy sources.

Oxidative Conversion of Methane

For about four decades, i.e., since the pioneering work of Keller and Bhasin, (8) OCM into ethylene has been a goal of the petrochemical industry. It has made scientists and industrials dream of converting a low-value feedstock fuel, such as natural gas or methane into ethylene, i.e., the base chemical with the highest global production volume. The promising perspectives offered by this reaction came with severe challenges. Indeed, methane oxidative coupling products such as ethane and ethylene are more easily activated than the reactant methane by the

typically employed metal oxide catalysts, such as Li/MgO, Sr/La_2O_3 and $NaWMn/SiO_2$ (9). Basicity was recognised as an interesting catalyst property to reduce the interaction between ethylene and the catalyst. Nevertheless, C2+ yields seldomly exceeded 20% not to mention 30% which, at times, was considered as a minimum threshold value for commercial viability, see **Figure 2**. The oxidative character of the reaction comes with a pronounced exothermicity, rendering temperature control difficult and triggering parasitic phenomena at the high reaction temperatures, i.e., 800°C or higher, such as wall effects in the case of improper reactor material selection.
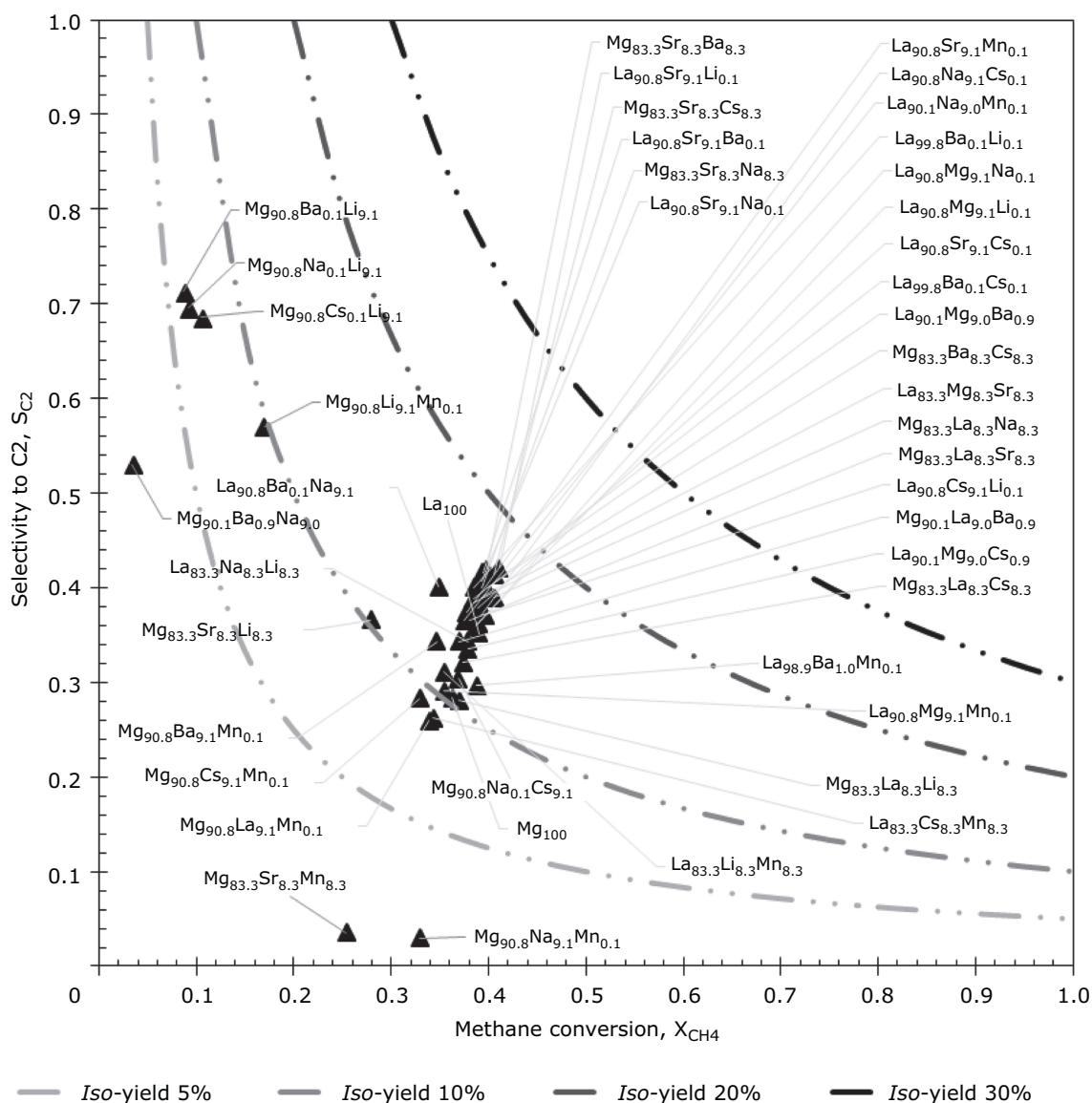

Fig. 2. C2 selectivity as a function of the methane conversion for the OCM catalyst library gathered by Kondratenko *et al*. Image reprinted from (9), Copyright 2014, with permission from Elsevier / Republished with permission of Royal Society of Chemistry, from (10)

Almost the entire periodic table has been probed for finding the best suited elements to be included in OCM catalysts (11). Li/MgO and its tin promoted version belonged to the first generation of investigated catalysts and provided good perspectives, despite shortcomings with respect to stability. La_2O_3 and SrO_2 were other catalysts that resulted in high activities at the expense of the C2 selectivity. More recently, NaWMn on SiO_2 has been identified as a more moderately active but more selective catalyst. These catalysts have been studied in a series of European integrated projects, including, among others, 'Towards Optimised Chemical Processes and New Materials Discovery by Combinatorial Science' (TOPCOMBI) and 'Oxidative Coupling of Methane followed by Oligomerization to Liquids' (OCMOL), and within C123 they constitute the benchmark materials (12, 13). In addition to a better understanding of these catalysts in these projects, the perception arose that no adequate combination of catalyst and operating conditions was available to allow an economically viable, single-pass conversion of methane into ethylene *via* oxidative coupling with a sufficiently high selectivity. It became clear that, rather, an entire process concept would be required to meet this purpose, an aspect which was also recognised by Siluria Technologies, USA, who were the first to implement OCM technology at the pilot scale.

The necessity of a proper process concept was already recognised. The OCMOL project proposed the integration of OCM with (dry) methane reforming, mainly to recuperate the heat provided by OCM, see **Figure 3**.

The resulting syngas was subsequently valorised by methanol synthesis and MTO conversion. Whereas each of the individual process steps could be designed in a competitive manner, the needs imposed on the separation proved to go significantly beyond the state of the art. Moreover, only about 10% of the carbon in the end products was the result of oxidative coupling, while 90% was incorporated by the conventional syngas route. Siluria Technologies took advantage of the presence of non-negligible amounts of ethane in shale gas to accommodate a post-bed ethane cracking zone in their process concept, which of course imposes constraints on the feedstocks that should be processed.

Considering the lessons learned from the work on OCM, the following C123 hypotheses and constraints were put forward:

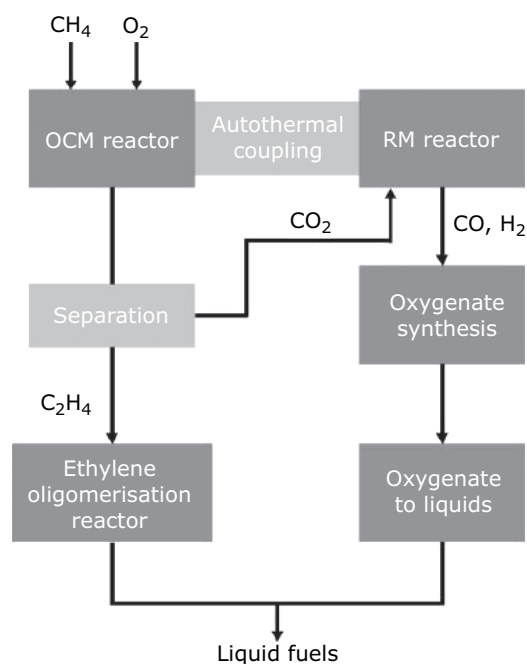- OCM remains an interesting route for methane upgrading

Fig. 3. Simplified process flow sheet for the OCMOL process concept Reprinted from (12), Copyright 2011, with permission from Elsevier

- Exploration of OCM catalysts and operating conditions has not resulted in an outstanding combination and is unlikely to do so in the near future, if at all
- The key towards economic viability is situated in an adequate process concept, provided that separation efforts can be properly tailored.

As an answer to the above, the concept of the OCoM was conceived, still critically relying on OCM, yet potentially embodying a variety of alternative methane conversion routes not just to maximise the C2 yield, but to produce an effluent suitable for hydroformylation. Apart from an OCM reactor, the OCM process will also take advantage of methane conversion *via* reforming and partial oxidation and by incorporating a water-gas shift reactor. The heat produced by OCM can still drive the reforming reaction as was the case in the OCMOL project; however, the goal in C123 is to mix the effluents into an adequate proportion for hydroformylation rather than perform difficult separations. Achieving full oxygen conversion in the OCM reactor will be key to achieve this goal. The CO_2 produced can be recycled to the OCM reactor for CO_2 induced OCM or to the reforming reactor for dry reforming. Ethane formed can be dehydrogenated oxidatively or by interaction with CO_2. Subsequent hydroformylation to propanal and propanol efficiently combines

products formed in relatively high amounts, i.e., carbon monoxide and ethylene, which would, otherwise, require difficult separation steps.

In order to establish a proper C123 process implementation, research advances are required along various directions. A suitable combination of catalytic material and operating conditions is required. However, this time the goal is not to maximise the per pass ethylene yield but to produce the most promising product spectrum: hydrogen, carbon monoxide and ethylene for subsequent hydroformylation. As a result, an innovative process concept is required for the efficient conversion of methane into a hydroformylation feedstock (14). The common denominator, serving both challenges, is the fundamental modelling of the reaction and transport phenomena involved, both at the catalyst pellet and the reactor scale, see **Figure 4**. Such a fundamental model is the mathematical translation

of the experimental insight into the investigated system. The goal is not to prove the model, but rather to indicate when the model (hypothesis) is not adequate and, hence, it is an extremely useful tool to assess the potential validity of model assumptions.

Within C123, the activities on OCoM are, hence, focused along three lines: (a) further catalyst development and operating conditions screening; (b) microkinetic modelling of the OCoM reactions; and (c) process concept development. As evident from the above, the further catalyst development and operating conditions screening mainly serves the need of providing the relevant information for evaluating various alternative process concepts and, of course, as a basis for the training of the OCoM microkinetic model. Three benchmark catalysts, i.e. two Sr/La_2O_3 catalysts and one $NaWMn/SiO_2$ catalyst, have been shared among
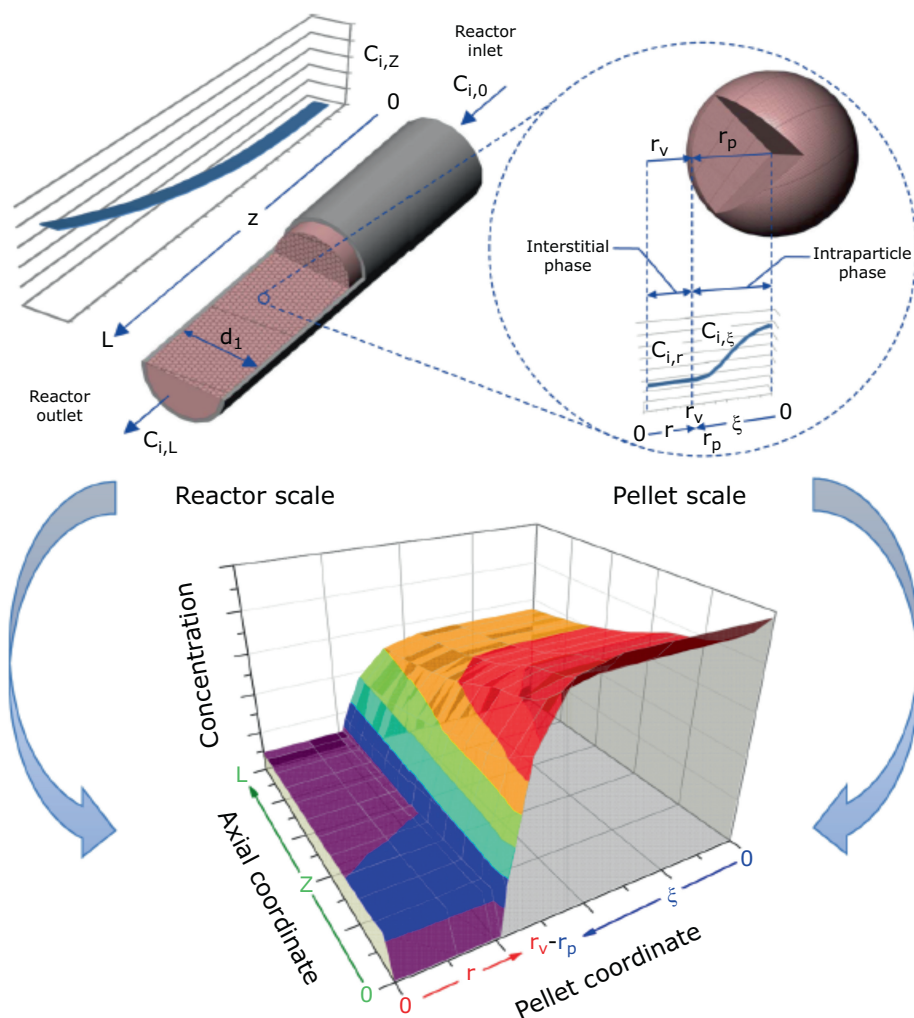

Fig. 4. Scheme of the heterogeneous reactor model accounting for transport limitations. Reprinted (adapted) with permission from Kechagiopoulos *et al*. Copyright (2014) American Chemical Society (14)

the project partners by Johnson Matthey, UK. A crucial aspect for a proper performance evaluation is the pretreatment of the catalyst samples. Bosch *et al*. (13, 15) specifically focused on the crystal phases obtained in nanoparticle catalysts and identified some interesting differences as a function of the calcination atmosphere, i.e. whether or not it contained oxygen, see **Figure 5**.

The microkinetic model, see **Figure 4**, accounts for intraparticle gradients for reactants, products, radicals and surface species. Particularly for the most reactive radicals and surface species, significant gradients were found to develop, even if reactant and product concentrations had a negligible gradient. According to the model, methane is mainly activated by oxidised sites on the catalyst surface. Practically no methane activation occurs in the interstitial phase, i.e. outside of the catalyst particles. The coupling steps, on the other hand, do proceed homogeneously, both in the catalyst pores (intraparticle phase) and between the catalyst pellets (interstitial phase). Highly porous catalyst materials appear to hold a lot of promise, on the conditions that sufficient surface sites remain for the methane activation. More particularly within C123, the impact of CO_2 in the feed on the catalyst performance is assessed. Limited experimental information is available and, at present, both positive and negative impacts are reported. Hence, additional experimentation at intrinsic kinetics conditions will be performed to elucidate the true behaviour. In the meantime, preliminary simulations have already been performed to probe the capability of the available microkinetic model to account for the effects induced by CO_2. Indeed, CO_2 formation is included already in this model, see **Table I** for the considered elementary steps.

However, now that CO_2 is assuming the role of the oxidant, there may be a need for tailoring the rate coefficients of the already included steps involved in the production and consumption of CO_2 and incorporation of additional reaction steps. For the time being, a moderating effect on the methane conversion has mainly been observed after including CO_2 in the considered feedstock.

Awaiting more detailed results from catalyst development, operating conditions screening and microkinetic modelling, the process concept development has already been started by making a stoichiometric analysis. The minimum amount of methane for producing a maximum amount of hydroformylation feedstock is determined from stoichiometric considerations and idealistic conversion scenarios. Such a scenario will serve as a benchmark for comparing actual implementations in a later stage of the project, initially based on literature reported kinetics, later based on microkinetics developed as part of C123.

Hydroformylation of Ethylene into C3 Commodities

Hydroformylation is the catalytic synthesis of an aldehyde from an alkene and a synthesis gas mixture. Aldehydes are convenient building blocks for a large range of organic compounds, including alcohols, carboxylic acids and amines, making hydroformylation a commercially attractive synthesis process (16). The reaction mechanism proceeds through a series of fundamental organometallic reactions, including ligand exchange, alkene insertion, oxidative addition and reductive elimination (17). Rhodium complexes are the most active catalysts, and although more
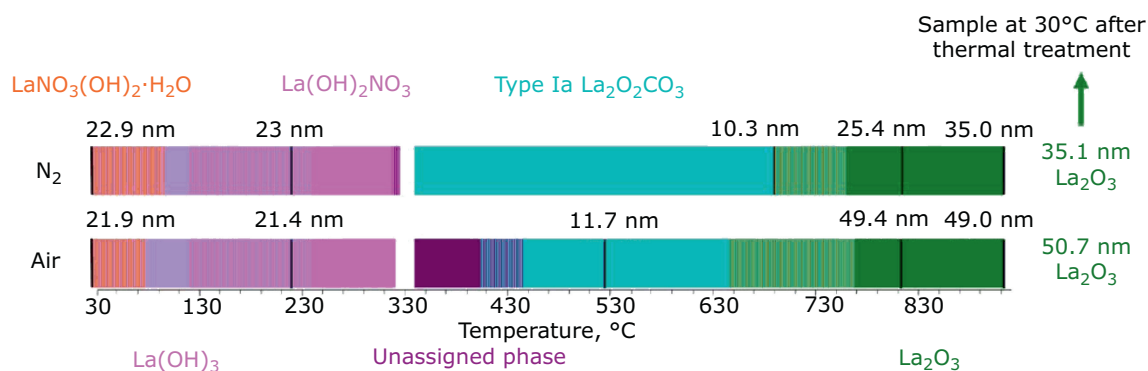

Fig. 5. *In situ* X-ray diffraction analysis for lanthanum oxide with increasing temperature under a nitrogen or air atmosphere

Table I Elementary Reaction Steps Contained in the Oxidative Coupling of Methane Microkinetic Model		
Gas phase reactions		
$CH_4+O_2 \leftrightarrows CH_3 \bullet+HO_2 \bullet$	$CHO \bullet+M \leftrightarrows CO+H \bullet+M$	$C_2H_4+CH_3 \bullet \leftrightarrows C_2H_3 \bullet+CH_4$
$CH_4+H \bullet \leftrightarrows CH_3 \bullet+H_2$	$CHO \bullet+O_2 \leftrightarrows CO+HO_2 \bullet$	$C_2H_3 \bullet+M \leftrightarrows C_2H_2+H \bullet+M$
$CH_4+O \bullet \leftrightarrows CH_3 \bullet+OH \bullet$	$CO+HO_2 \bullet \leftrightarrows CO_2+OH \bullet$	$C_2H_3 \bullet+O_2 \leftrightarrows C_2H_2+HO_2 \bullet$
$CH_4+OH \bullet \leftrightarrows CH_3 \bullet+H_2O$	$C_2H_6+H \bullet \leftrightarrows C_2H_5 \bullet+H_2$	$C_2H_3 \bullet+O_2 \leftrightarrows CH_2O+CHO \bullet$
$CH_4+HO_2 \bullet \leftrightarrows CH_3 \bullet+H_2O_2$	$C_2H_6+OH \bullet \leftrightarrows C_2H_5 \bullet+H_2O$	$C_2H_5 \bullet+CH_3 \bullet \leftrightarrows C_3H_8$
$CH_3 \bullet+O_2 \leftrightarrows CH_3O \bullet+O \bullet$	$C_2H_6+CH_3 \bullet \leftrightarrows C_2H_5 \bullet+CH_4$	$C_3H_8+H \bullet \leftrightarrows C_3H_7 \bullet+H_2$
$CH_3 \bullet+O_2 \leftrightarrows CH_2O \bullet+OH \bullet$	$C_2H_5 \bullet+HO_2 \bullet \leftrightarrows CH_3 \bullet+CH_2O+OH \bullet$	$C_2H_4+CH_3 \bullet \leftrightarrows C_3H_7 \bullet$
$CH_3 \bullet+ HO_2 \bullet \leftrightarrows CH_3O \bullet+OH \bullet$	$C_2H_5 \bullet+M \leftrightarrows C_2H_4+HO_2 \bullet$	$C_3H_7 \bullet \leftrightarrows C_3H_6+H \bullet$
$CH_3 \bullet+CH_3 \bullet+M \leftrightarrows C_2H_6+M$	$C_2H_5 \bullet+O_2 \leftrightarrows C_2H_4+HO_2 \bullet$	$O_2+H \bullet \leftrightarrows OH \bullet+O \bullet$
$CH_3O \bullet+M \leftrightarrows CH_2O+H \bullet+M$	$C_2H_4+O_2 \leftrightarrows C_2H_3 \bullet+HO_2 \bullet$	$O_2+H \bullet+M \leftrightarrows HO_2 \bullet+M$
$CH_2O+OH \bullet \leftrightarrows CHO \bullet+H_2O$	$C_2H_4+H \bullet \leftrightarrows C_2H_3 \bullet+H_2$	$HO_2 \bullet+HO_2 \bullet \leftrightarrows O_2+OH \bullet+OH \bullet$
$CH_2O+HO_2 \bullet \leftrightarrows CHO \bullet+H_2O_2$	$C_2H_4+OH \bullet \leftrightarrows C_2H_3 \bullet+H_2O$	$H_2O_2+M \leftrightarrows OH \bullet+OH \bullet+M$
$CH_2O+CH_3 \bullet \leftrightarrows CHO \bullet+CH_4$	$C_2H_4+OH \bullet \leftrightarrows CH_3 \bullet+CH_2O$	$HO_2 \bullet+HO_2 \bullet \leftrightarrows O_2+H_2O_2$
Catalytic reactions		
$O_2+*+* \leftrightarrows O*+O*$	$CH_3 \bullet+O* \leftrightarrows CH_3O*$	$C_2H_3O*+O* \leftrightarrows CH_2O*+CHO*$
$CH_4+O* \leftrightarrows CH_3 \bullet+OH*$	$CO_2+* \leftrightarrows CO_2*$	$H_2+O* \leftrightarrows H \bullet+OH*$
$C_2H_6+O* \leftrightarrows C_2H_5 \bullet+OH*$	$CH_3O*+O* \leftrightarrows OH*+CH_2O*$	$OH \bullet+O* \leftrightarrows O \bullet+OH*$
$2OH* \leftrightarrows H_2O*+O*$	$CH_2O*+O* \leftrightarrows CHO*+OH*$	$H_2O+O* \leftrightarrows OH \bullet+OH*$
$H_2O* \leftrightarrows H_2O+*$	$CO*+O* \leftrightarrows CO_2*+*$	$H_2O_2+O* \leftrightarrows HO_2 \bullet+OH*$
$C_2H_5 \bullet+O* \leftrightarrows C_2H_4+OH*$	$CO+* \leftrightarrows CO*$	$CH_3O \bullet+O* \leftrightarrows CH_2O+OH*$
$HO_2 \bullet+O* \leftrightarrows O_2+OH*$	$C_2H_4+O* \leftrightarrows C_2H_4O*$	$CH_2O+O* \leftrightarrows CHO \bullet+OH*$
$HO_2 \bullet+* \leftrightarrows OH \bullet+O*$	$C_2H_4O*+O* \leftrightarrows C_2H_3O*+OH*$	$CHO \bullet+O* \leftrightarrows CO+OH*$
$C_2H_4+O* \leftrightarrows C_2H_3 \bullet+OH*$	–	–

expensive, they have generally replaced less active and selective cobalt catalysts. Both linear and branched aldehydes are produced from all C3+ alkenes, and the linear:branched ratio can be controlled *via* the reaction conditions, particularly the phosphine ligands bound to rhodium. Linear aldehydes are generally the preferred products.

The reaction parameters have been well established for nearly all alkenes, in particular propylene, since the hydroformylation product from propylene, *n*-butyraldehyde, is so industrially important. However, the literature is rather scarce on the conditions for the hydroformylation of ethylene, a simpler molecule with no stereoselectivity issues (18–21).

As discussed above, coupling a robust heterogeneous ethylene hydroformylation process with OCoM could disrupt the current technology. Benefits include a more circular economic process, responsible use of stranded, flared or biogas and improved transport in the value chain. The OCoM step is a high temperature (650–900°C), atmospheric pressure reaction. When tuned properly, this OCoM process will provide an optimised feedstock of ethylene and carbon monoxide for the hydroformylation process, which operates around 100°C and 20–40 bar pressure in the current industrial, homogeneous processes. A suitable heterogeneous catalyst will keep both processes in the gas phase, reduce precious metal losses during operation and address corrosion issues associated with solvent use. In addition to a tuned feedstock for hydroformylation, another operational goal is the reduction of the pressure difference between the two parts of the process (i.e. OCoM and hydroformylation). A detailed understanding of the reaction variables for homogeneous ethylene hydroformylation will guide catalyst and process development of a heterogeneous version of the reaction and the overall C123 process scheme.

The integrated process will attempt to avoid interstage purifications and pressure switches between each step. That means that the OCoM will have to operate under pressure, but also that the hydroformylation might have to operate at lower pressure than usual, and in a stream that contains

CO_2, water and other impurities from previous stage such as residual methane and ethane. The hydroformylation C123 WP goals are development of stable heterogeneous hydroformylation catalysts, development of an integrated engineering concept for hydroformylation and demonstration of the process in an industrial environment at TRL5.

A screening study, involving both batch scale and high-throughput experiments, was carried out to determine the optimum catalyst and reaction parameters for the homogeneous ethylene hydroformylation. 11 different rhodium catalysts and 13 different phosphines with varying electronic and steric profiles (see **Table II**) were screened under two different $CO:C_2H_4:H_2$ feed gas compositions, several different pressures, different feed gas:catalyst ratios, a range of excess phosphine molar ratios and with argon or CO_2 as diluent gas. In all cases, only propanal was detected as product. No propanol was detected, even at higher pressures and with an excess of hydrogen in the feed gas.
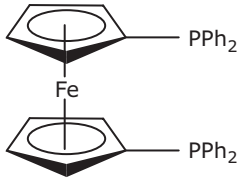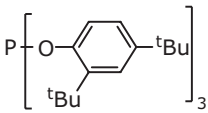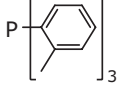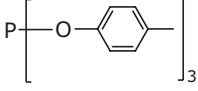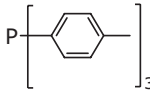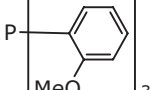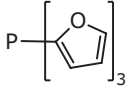
As shown in **Figure 6**, the best catalysts are the known hydroformylation catalysts $Rh(CO)H(PPh_3)_3$, **1**, and $Rh(CO)(acac)PPh_3$. A 10–20 fold excess of phosphine proved optimal, at least when PPh_3 was used. The high throughput screening studies showed that a 10-fold excess of the π-accepting

phosphite ligands $P(Otol)_3$, $P(O-tBu_2Ph)_3$ and $P(2-fur)_3$ gave activities on par with the benchmark ligand PPh_3, but a definitive activity ranking of phosphines was difficult because of the high overall catalyst activity.

To verify the high throughput results and investigate both the effect of CO_2 and the catalyst loading on activity, a series of batch studies were performed, and the results are given in **Table III**. As can be seen from the first six entries in **Table III**, there is very little difference in the turnover number (TON) for propanal formation, regardless of ligand, feed gas pressure or diluent gas. At least for the modest pressures and low C_2H_4:Rh ratios, CO_2 does not have an adverse effect on propanal TON. The enhanced effect of the π-acid ligands is most pronounced with the highest C_2H_4:Rh ratios. While $P(Otol)_3$ gives slightly higher TON than PPh_3 with the highest ratios (compare entries 8 and 9 with entries 11 and 12), the effect of the ligand $P(2-fur)_3$ is dramatic, with this ligand giving TONs 2.5 times greater than those with PPh_3 (compare entries 8 and 9 with entries 17 and 18).

The high selectivity of the hydroformylation reaction to propanal is an important factor for the process design and impact of C123. Propanol is the preferred product over propanal since it is easier to transport and requires only a dehydration step to the valuable C3 product propylene. The

Table II Phosphines Screened in Batch Scale and High Throughput Studies

| Name (abbreviation)	Structure	Name (abbreviation)	Structure
Triphenylphosphine (**PPh₃**)	$P(C_6H_5)_3$	Tris(pentafluorophenyl)-phosphine (P(Ph_f)$_3$)	$P(C_6F_5)_3$
1,1'-Ferrocenediylbis-(diphenylphosphine) (**Fcdpp**)		Tris(2,4-di-*tert*-butylphenyl) phosphite (P(O-*t*Bu₂Ph)₃)	
Tri(*o*-tolyl)phosphine (**P(*o*-tol)₃**)		Tri(*p*-tolyl)phosphite (P(Otol)₃)	
Tri(*p*-tolyl)phosphine (**P(*p*-tol)₃**)		Tris(2-methoxyphenyl)-phosphine (P(MeOPh)₃)	
Tri-*n*-butylphosphine (**P(*n*Bu)₃**)	$P(CH_2CH_2CH_2CH_3)_3$	Tri-*n*-butylphosphite (P(O*n*Bu)₃)	$P(OCH_2CH_2CH_2CH_3)_3$
Tris(2-furyl)phosphine (**P(2-fur)₃**)		Tricyclohexylphosphine PCy₃	
Tris(diethylamino)-phosphine (**DEAP**)	$P[N(CH_2CH_3)_2]_3$	–	–
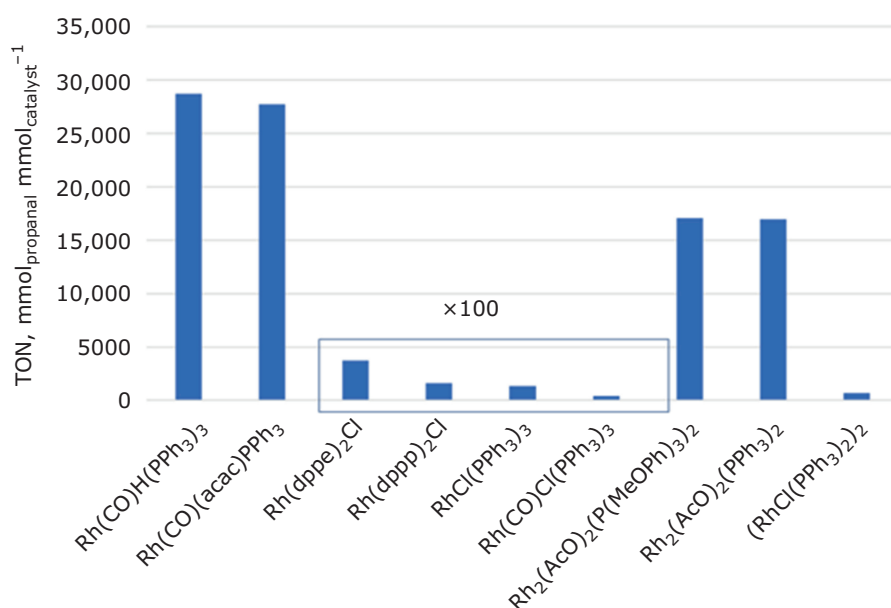
Fig. 6. TON values ($mmol_{propanal}$ $mmol_{catalyst}^{-1}$) for nine different rhodium catalysts compared during the screening process using 1:1:1 H_2:CO:C_2H_4, 20 bar, 100°C and 1.5 h at 1000 rpm and 5 mg of catalyst in 5 ml of toluene

Table III	Effect of Changes in Diluent Gas, Feed Gas Pressure, Catalyst Loading and Phosphine on Turnover Number to Propanal				
Entry	**Phosphine[a]**	**Pressure, bar[b]**	**Diluent gas[c]**	**Ethylene:rhodium ratio[d]**	**TON[e]**
1	PPh_3	10	CO_2	185	128
2	PPh_3	10	Argon	115	130
3	PPh_3	20	CO_2	360	233
4	PPh_3	20	Argon	370	268
5	$P(Otol)_3$	20	CO_2	260	219
6	$P(Otol)_3$	20	Argon	295	221
7	PPh_3	40	Argon	970	260
8	PPh_3	40	Argon	16,800	4835
9	PPh_3	40	Argon	49,400	12,700
10	$P(Otol)_3$	40	Argon	970	250
11	$P(Otol)_3$	40	Argon	16,800	6000
12	$P(Otol)_3$	40	Argon	49,400	13,200
13	$P(O\text{-}t\text{Bu}_2Ph)_3$	40	Argon	970	320
14	$P(O\text{-}t\text{Bu}_2Ph)_3$	40	Argon	16,800	5700
15	$P(O\text{-}t\text{Bu}_2Ph)_3$	40	Argon	49,400	10,700
16	$P(2\text{-fur})_3$	40	Argon	970	425
17	$P(2\text{-fur})_3$	40	Argon	16,800	13,900
18	$P(2\text{-fur})_3$	40	Argon	49,400	31,500

Note: all reactions run with **1** as catalyst, at 100°C for 2 h under static pressure and 8–11 equivalents of the indicated phosphine

[a]Refer to **Table II**
[b]Feed gas 1:1:2 CO:C_2H_4:H_2
[c]Diluent gas at 10 bar
[d]Based on ideal gas law calculation at 100°C
[e]Determined as $mmol_{propanal}$ $mmol_{Rh}^{-1}$

economic and sustainability impact of an extra hydrogenation process step for the conversion of propanal to propylene will need to be evaluated. On the other hand, the selectivity for propanal even with excess hydrogen will lessen the need for hydrogen from the OCoM step, which may favour the OCoM process development.

Importantly, the production of only propanal in the homogeneous reaction does not guarantee that the gas phase, heterogeneous hydroformylation reaction will show the same selectivity. These results will regardless be very valuable in the design of the heterogeneous catalyst that will be developed in the next phase of the project, in addition to supporting the modelling work at Ghent University (UGent), Belgium, and in building a set of experimental data for the hydroformylation process optimisation and the WP4 process integration toolbox.

As indicated above, a gas phase hydroformylation reaction is preferred for the C123 process. While there are some examples of heterogeneous hydroformylation catalysts (19–22) the development of such a catalyst with the same activity and selectivity as the widely-used homogeneous ones remains a challenge. The C123 approach for development of a heterogeneous hydroformylation catalyst will therefore involve a more traditional funnelling strategy. First generation catalysts will be synthesised by tethering appropriate organometallic rhodium complexes in porous supports. Testing and iterative synthesis will provide a set of innovative, heterogeneous hydroformylation catalysts that will achieve the key performance indicators (KPIs) for TRL4. Second generation hydroformylation catalysts will be developed from the first generation catalysts by using relatively well-established shaping residence time distribution (RTD) protocols to select one or two catalysts that meet the KPIs for TRL5. For the hydroformylation catalysts, a part of the risk management strategy will be the use of homogeneous catalysts as backup, while still pursuing project work.

Heterogeneous Material Synthesis Strategy Proposed

Johnson Matthey will functionalise high surface area silica surfaces with phenyl phosphine groups, and ultimately with rhodium complex catalysts, to form heterogeneous hydroformylation catalysts. Suitable organosilanes can interact with silica displacing surface silanol groups, creating a covalent bond. Two approaches have been selected for this functionalisation using ethoxy and methoxy silane organic precursors to anchor organic groups over the original silanol. Fumed silica, silicagel and templated mesoporous MCM-41 will be used to compare the effect of pore and surface area in the silica functionalisation.

The first approach will use an amine as an anchor group to then react the basic ligand with a rhodium salt, as shown in **Figure 7**. Aminopropyl trimethoxy silane grafted silicas have been widely reported in the literature as they can selectively remove acid molecules such as CO_2 and hydrogen sulfide (23). Direct impregnation techniques can attach propyl amines to silica, but there is evidence of more ordered surface coverages and optimisation through a toluene excess silane reflux approach over dehydrated silica. Surface secondary amines can then react with phenyl phosphine groups, attaching rhodium organometallic complexes such as Wilkinson's catalyst or **1** to the silica surface (24–26).

The second, more ambitious approach involves incorporation of a larger monophosphine organosilane precursor, 2-(diphenylphosphino) ethyl-triethoxysilane on silica, as shown in **Figure 8**. The surface anchored phosphine can then be coupled to rhodium salts such as $[(COD)Rh(\mu\text{-}Cl)]_2$ (COD = 1,5-cyclooctadiene), $[(NBD)Rh(\mu\text{-}Cl)]_2$ (NBD = norbornadiene) or $[(COT)_2Rh(\mu\text{-}Cl)]_2$ (COT = cyclooctene) that can selectively incorporate other phosphines by sequential reaction with, for example, bis(diphenylphosphino)ethane dppe.

The goal of the SINTEF, Norway, approach is to synthesise a metal organic framework (MOF) based material that has a large number of phosphines decorating the pores of the MOF. The idea is that, after introduction of rhodium to the material, a traditional organometallic reaction mechanism can be accessed, in that the rhodium has access to an abundance of phosphine moieties to both steer the fundamental reaction steps and prevent instability and leaching. This effect of this concept was illustrated by the incorporation of **1** into a (PTA)-MIL-1010(Cr) MOF (PTA = phosphotungstic acid). The PTA immobilised the rhodium complex within the MOF pores, yet provided homogenous catalyst-like selectivities in the hydroformylation of 1-octene in toluene (27).
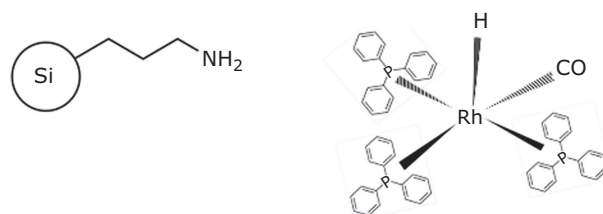

Fig. 7. Example of possible interaction of a hydroformylation catalyst with amino propyl triethoxy silane functionalised silica. Silicas typically are functionalised with around 1 mmol g^{-1} amine groups (26)
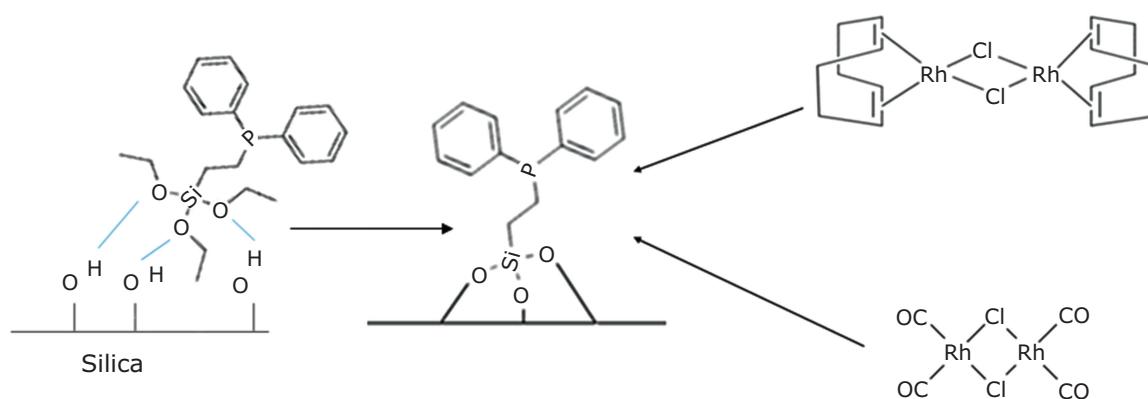
Fig. 8. Organosilane silica phenyl phosphine functionalisation followed by reaction with traditional rhodium coordination complexes to prepare a tethered hydroformylation catalyst

Rather than incorporating the necessary phosphine moieties during the demanding MOF synthesis, we will investigate a post-synthetic modification approach called solvent-assisted ligand incorporation (SALI) (28). In particular, it has been shown that a range of ligands with pendant carboxylic acid and phosphoric acid groups can react with the μ_3-OH functionalities of MOFs built up with $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(H_2O)_4(OH)_4$ nodes. There are a wide range of MOFs with varying pore sizes and shapes that are built up from this inorganic building block, such as NU-1000, the UiO series and MOF-808 (29). Our hypothesis is that full incorporation of phosphine ligands with an appropriate tether within a zirconium MOF, followed by addition of an appropriate fraction of a rhodium complex such as **1**, will provide a heterogeneous version of a homogeneous hydroformylation catalyst (see **Figure 9**).

Our initial attempt to make a suitably tethered PPh_3 variant, specifically $(PPh_3)_2P(p\text{-}C_6H_4CH=CHCOOH)$ (see Equation (i)), provided instead the phosphine oxide **2**. Reaction of **1** with the MOF NU-1000 provided evidence for incorporation of the tethered ligand into the MOF. Appropriately tethered ligands based on phosphites should be less prone to oxidation and have been synthesised.

(i)
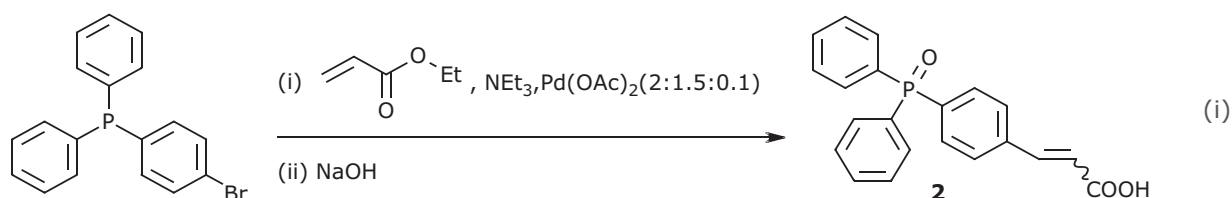
The concept of porous macroligands, i.e. a porous solid acting as the organic ligand of a molecular complex, has been introduced and used recently by Canivet *et al.*, at the National Centre for Scientific Research (CNRS) in Lyon, France, for the heterogenisation of active molecular catalysts to combine the advantages of high activity and versatility of molecular catalysts and sustainability of easy to separate and easy to recycle heterogeneous catalysts (30). Following this strategy Canivet's team at CNRS will develop novel porous organic polymers which will embed efficient organometallic hydroformylation catalysts (31–33). Porous organic polymers formed from
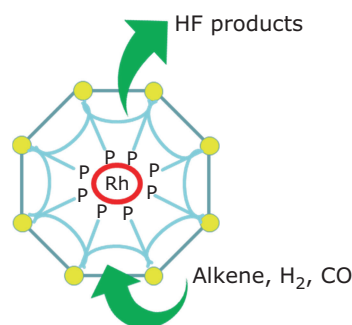

Fig. 9. Schematic representation of a catalytic rhodium complex immobilised within a MOF with an excess of phosphine ligands within the pores

functionalised PPh$_3$ and biphephos have already been used as supports for the rhodium-catalysed hydroformylation of 1-octene in toluene and ethylene, propylene and 1-butylene in fixed bed reactor. Here, easily accessible phosphine or bipyridine based vinyl monomers will be used in controlled radical polymerisation leading to solid porous organic matrix with high surface area and pore accessibility (**Figure 10**). Further functionalisation with cobalt or rhodium precursors will give access to heterogenised and site-isolated hydroformylation catalyst within stable microporous structures.

The high versatility of porous organic polymers will be used to advantageously tune the hydrophilic/hydrophobic balance of the hosting pore as catalytic nanoreactor, and the confinement within the micropore will play a crucial role by influencing transport, reaction rate and product selectivity. Moreover, the intrinsic swelling behaviour of porous organic polymers will ensure that the solubilised gaseous species will reach the active site while larger aldehydes or alcohols produced will freely transfer to the reaction medium.

Two microkinetic models will be developed for the hydroformylation of ethylene, i.e. one dedicated to the homogeneous and one to the heterogeneous process. The kinetic parameters will be determined *via* regression of the models to a comprehensive set of intrinsic kinetic data, i.e. data acquired in the absence of mass and heat transfer limitations. By performing such a detailed model construction, i.e. no rate determining steps are assumed, for homogeneous hydroformylation the critical steps in the selective conversion of ethylene to propanal can be unraveled. A distinction will be made between catalyst descriptors (for example, adsorption parameters) and kinetic descriptors (such as activation energy). Preliminary simulations using the model developed for homogeneous hydroformylation have shown that the increase of the propanal yield with the total pressure is nicely captured by the model.

Following the same principles a microkinetic model will be developed for heterogeneously catalysed hydroformylation, and similar relationships in terms of catalyst and kinetic descriptors will be established. This will allow the unravelling of the determining factors to optimise the heterogeneous catalyst activity and selectivity, and the models will be further used in the reactor design.

WP2 and WP3 will work in close collaboration with continuous exchange between both WPs as well as with WP4 in order to ensure overall integration. WP3 focus will be on the optimisation of the reaction and process conditions for maximised product yield and ethylene conversion, as well as achieving more active and more stable catalysts
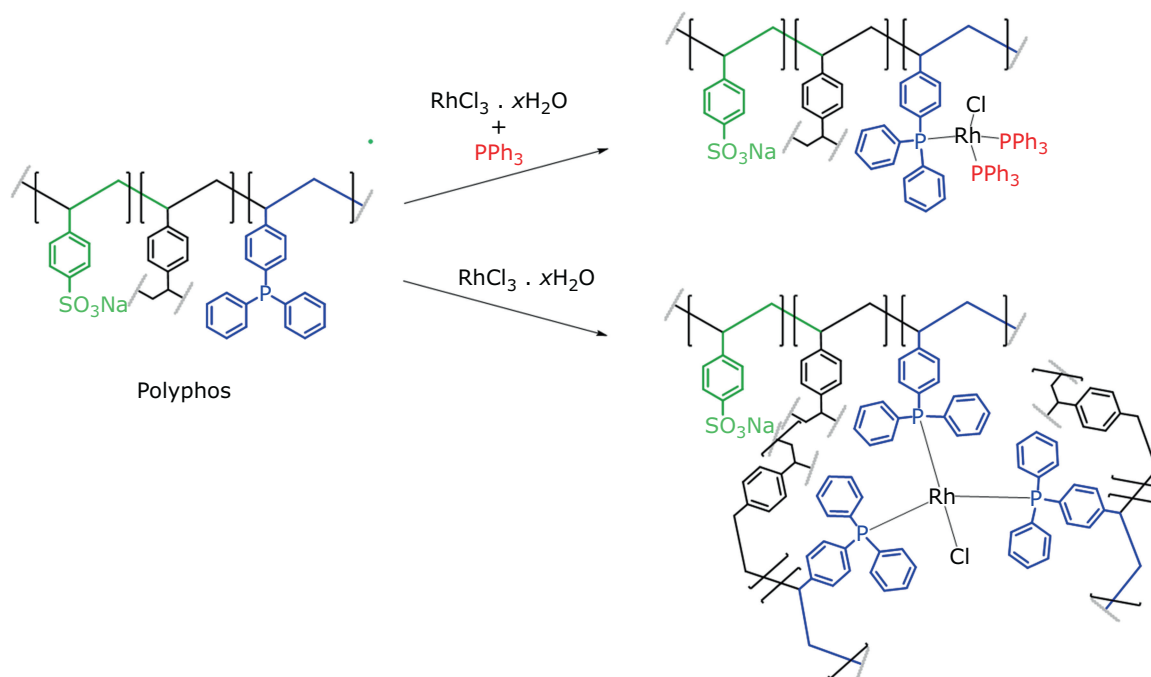

Fig. 10. Synthetic strategies using phosphine-rich porous polymer Polyphos as macroligand for rhodium-based catalysts

that can be operated at higher temperatures without deactivation and at lower pressures (close to those for OCoM) without decreasing conversion. This will be achieved through the combined development of heterogeneous catalysts optimised for operation in fixed reactor beds and maximum selectivity toward propanol with competitive performance with homogeneous catalysts and reactor design.

The results from OCoM (WP2) and hydroformylation (WP3) catalyst development and reactor design will be transferred into WP4 for the integrated process design and validation in relevant environment (TRL5) for both the modular and the add-on routes, to allow a conceptual design of the fully integrated units with all process steps, and the development of a possible scheme for an integrated commercial process.

Process Tuning and Integration

The process design of the C123 technology is characterised by the combination of several reactions which are performed under different conditions and the integration of required purification and separation steps. In addition to the OCoM and hydroformylation reactions described before as novel core elements, a hydrogenation and a dehydration reaction also have to be included in the process. Furthermore, purifications and separations need to be implemented. Although these are in principle based on state-of-the-art technologies, at this point improved or innovative concepts and solutions have to be taken into account. Only by consideration of the interaction and optimal integration of all steps and process operations can an efficient and sustainable approach matching the efficiency and sustainability targets of the C123 project be achieved. Accordingly, this chapter is focusing on the base considerations and key aspects of process design for an implementation on technical scale and under industrially relevant conditions.

Methane shows a lower reactivity towards oxygen than higher hydrocarbons and olefins are more reactive than paraffins. Therefore, it is no surprise that OCoM reactions suffer from low selectivity at high conversion. Only at low conversion are highly selective reactions, for example to ethane and ethylene, feasible, although the difficult separations and high recycle ratios have an overwhelming impact on process economics.

In conventional approaches of OCoM (9, 10), carbon monoxide is considered an undesired byproduct, requiring additional effort in process design for separation, further conversion and recycling. Siluria Technologies, for example, based its technology on methanation and recycling of carbon oxides in order to increase the overall process efficiency (34). In contrast, C123 is taking advantage from the carbon monoxide production; by allowing the reaction to produce equimolar amounts of ethylene and carbon monoxide, propanal can be further produced by hydroformylation. Subsequent hydrogenation to propanol and dehydration yields propylene as final product. Propylene is very important chemical key intermediate, and propanal and propanol could be potential value products.

The challenge of a process design is the number of subsequent reaction steps which have completely different demands on conditions, which makes the process complex and requires compromises and optimisation.

The OCoM reactor is under strong kinetic control (8, 35). Thermal runaways leading to total oxidation are always possible and need to be avoided by a careful reactor design. A low pressure helps to push back the typically unselective gas phase reactions. Nevertheless, the reaction heat release is tremendous and requires a very effective cooling. Also, temperatures and heat recovery are challenging. While it looks attractive to use endothermic ethane dehydrogenation to recover high temperature heat after the OCoM reactor, providing the respective ethane stream requires cryogenic distillation. The process limitations affect the reactor design and *vice versa*.

Reaction thermodynamics already indicate the required reaction conditions for the subsequent steps. In addition, certain vapour-liquid-equilibria (VLE) separations require a high pressure. As the OCoM pressure is low, the pressure staging of the overall process is accordingly also subject to an optimisation.

The hydroformylation reaction (14, 36) has an equilibrium limitation at high temperature and low pressure, (**Figure 11**) and is therefore usually performed at 15 bar or more, i.e. significantly above the OCoM pressure. While in conventional hydroformylation the reaction partners are the main components in the gas phase, for the C123 process the overall equilibrium conversion is further reduced by inert gases, as the partial pressure of the educts is decreased by inert dilution (including especially methane, ethane, CO_2). Hence the process design has an impact on the maximum achievable hydroformylation
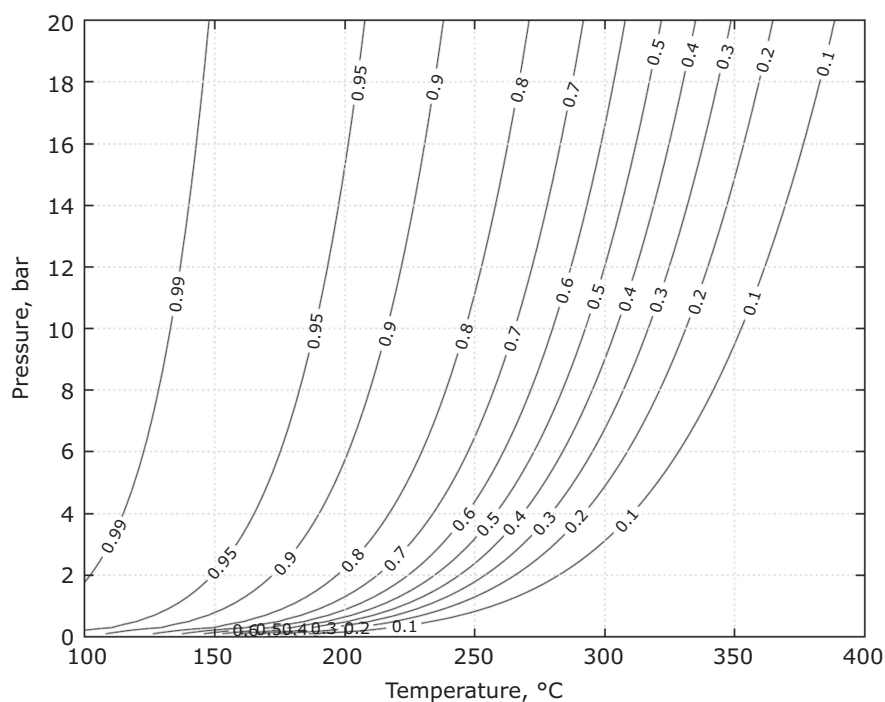
Fig. 11. Equilibrium conversion of the hydroformylation reaction

conversion. The hydroformylation as targeted in the C123 project is designed as a heterogeneous system. In contrast to a homogeneous system, the catalyst is immobile and remains in the reactor avoiding dedicated efforts for catalyst separation and recycling.

The propanal hydrogenation is again an equilibrium limited reaction performed at elevated but still limited temperature. In order to maximise the conversion, sufficient pressure is required (**Figure 12**). To provide the overall hydrogen demand for both steps (hydroformylation and hydrogenation) an external hydrogen source needs to be considered which is preferably based on renewable resources or energy.

The dehydration is preferably performed at lower pressure and elevated temperature (**Figure 13**). Next to a beneficial increase of reaction rates and equilibrium conversion, typical catalysts for this reaction require a minimum temperature of >250°C. The endothermic dehydration from propanol to propylene can be performed in a heated reactor (for example, tube bundle fixed bed reactor) or in an adiabatic multi-stage reactor with intermediate cooling.

Although the intention of the C123 project is to minimise the intermediate separation and purification effort, a minimum set of such process operations will be required (such as separation, drying). Due to different temperatures of the specific reactions, heat exchangers need especially to be implemented accompanied by the respective pressure drop.

The light unconverted gases hydrogen, carbon monoxide and ethylene, but also byproducts such as ethane, need to be separated from the hydroformylation product. Cryogenic separations themselves already require significant technical effort and equipment and are therefore expensive. If cryogenic separation cannot be avoided the effective removal of water and CO_2 using, for example, adsorptive removal and drying over molecular sieves are mandatory and further increase the technical and financial effort. Accordingly low temperatures are preferably avoided to maintain the process efficiency. Further, to minimise the cryogenic effort a minimum pressure is also required for these steps. The column design requires the detailed knowledge of the column feed stream and therefore of the performance of all reactors. Again, the separation efficiency also defines the reactor feed streams. The C2/C3 separation gives a C3 product stream with low gas impurities. The overhead fraction contains different light molecules including some uncondensed C3. At this point of the process an extractive distillation can for example be used to separate a gas recycle from the C3 product, avoiding a cryogenic process step. A further separation of this gas recycle stream is not possible without a cryogenic process. Again, the OCoM selectivities highly impact the process design: if this stream cannot be sent to combustion or if some species shall be recovered due to other reasons, this stream could be either recycled to an existing petrochemical plant or the cryogenic
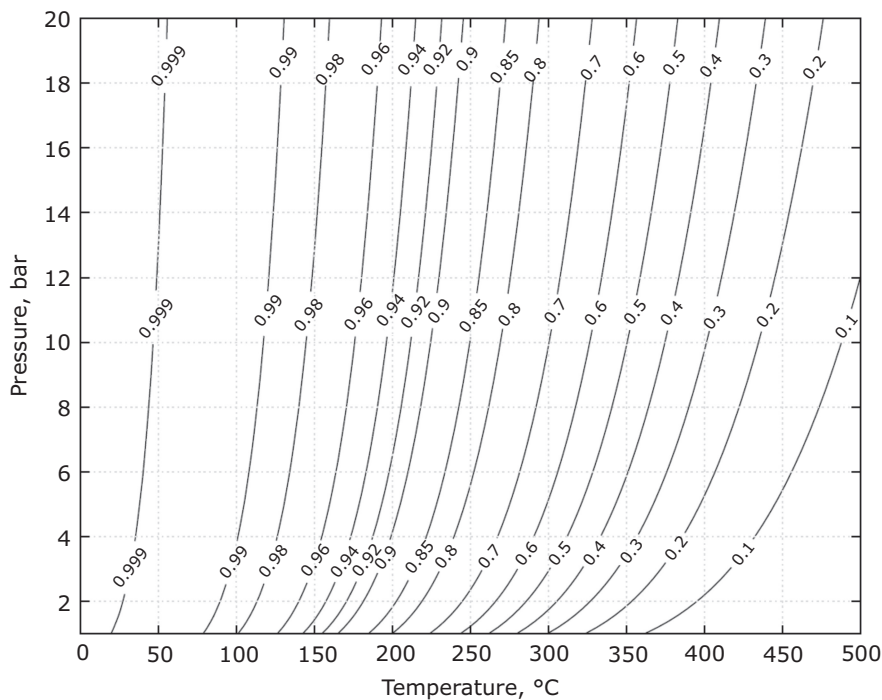
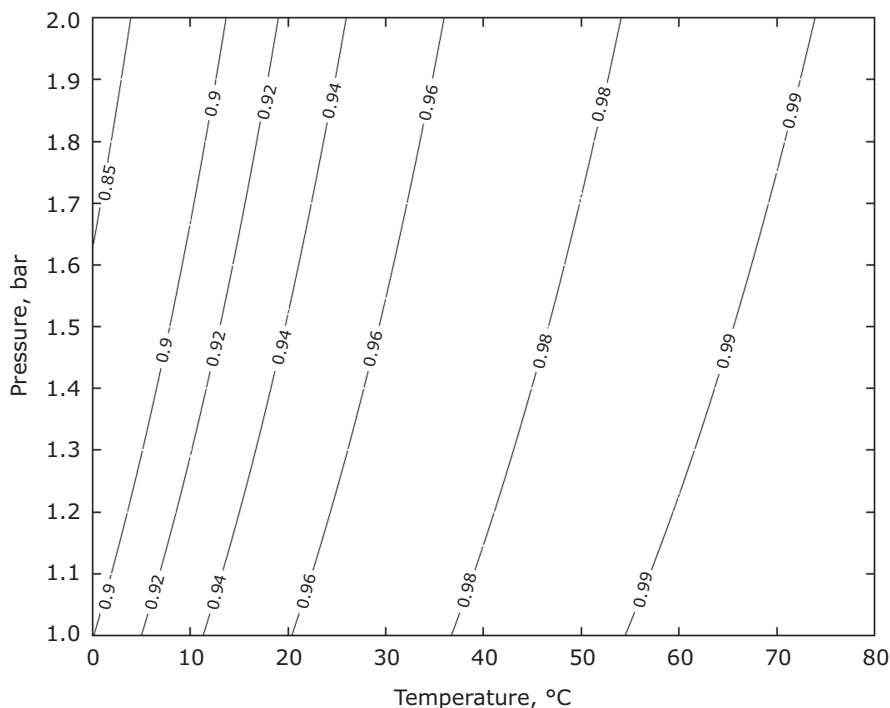Fig. 12. Equilibrium conversion of the hydrogenation reaction

Fig. 13. Equilibrium conversion of the dehydration reaction

separation needs to be implemented as its own process unit.

Due to numerous feedbacks and interferences between reactor performance, separation efficiency and the overall process due to operating conditions, heat integration and the influence of trace components, none of these designs can be done separately. Specialised solutions need to be identified and combined in an optimal manner to ensure high efficiency and sustainability of the overall process. Accordingly, this task requires special expertise not only in the basic principles of all individual process units – including especially reaction and separation steps but also in the technical implementation on

industrial scale. Only a few companies specialised in engineering, procurement and construction (EPC) of world scale petrochemical plants such as Linde Engineering, Germany, have the appropriate knowledge and experience to develop and provide a reliable and sustainable technical solution.

Conclusions

The C123 project aims to develop new technology for the upgrading of stranded natural gas or biogas to the easy-to-transport C3 commodities propanal and propanol, which can thereafter be transformed to propylene for the growing polypropylene market. The technology development aims to improve upon OCM technology by encouraging the production of carbon monoxide in addition to ethylene in the OCoM process and to develop a heterogeneous hydroformylation catalyst that provides comparable activity and selectivity to the well-known homogenous process.

There are many challenges ahead for this idea as the OCoM and hydroformylation processes are very different in nature and need to be united in as efficient an overall process as possible. Specific issues that impact the direction of OCoM and heterogeneous hydroformylation catalyst development and the overall process include the following:

- Should OCoM catalyst development emphasise ethylene production and accept a stoichiometric deficiency of carbon monoxide, or should a 1:1 mixture of ethylene and carbon monoxide be targeted? Does this ultimately depend on the methane feedstock and the location and size of the C123 process?
- What is the best process design to merge the disparate pressure and temperature regimes for OCoM and hydroformylation?
- How do the byproducts from each of the two process steps affect the other? Can extensive purification steps and large recycle streams be avoided?

Fortunately, the C123 project has an experienced consortium team that is tackling these issues in a unified catalyst and process development strategy, to bring this potentially disruptive technology to TRL5. C123 will also evaluate the process market viability and the end user requirements for the different final product opportunities that can be derived from C3 commodities. The methane sources and the challenges presented by stranded gas such as infrastructure and transport will also be reviewed.

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