

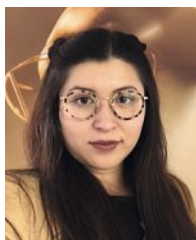
Non-Oxidative Coupling of Methane: Interplay of Catalyst Interface and Gas Phase Mechanisms

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Abstract: Non-oxidative coupling of methane (NOCM) is a sought-after reaction that has been studied for decades. Harsh reaction conditions ($T > 800\text{ }^{\circ}\text{C}$) in the face of limited catalyst stability lead to rapid catalyst deactivation and strong coking, preventing application thus far. Recent reports have shown the significance of an interplay of catalyst nature and reaction conditions, whereas metal carbides have prevailed to play a crucial role which involves incorporation of carbidic carbon in C_2H_x and aromatic products. This perspective gives an overview of proposed mechanistic pathways and considerations about experiment conditions in order to foster a rational catalyst design platform for NOCM.

Keywords: Carbon diffusion · Mars-van Krevelen mechanism · Metal carbides · Methane coupling



Seraphine B.X.Y. Zhang received her Bachelor's and Master's degree in Chemistry from ETH Zurich. She carried out her Master thesis in the laboratory of Prof. Dean Toste at UC Berkeley in 2018 working on asymmetric catalysis. In January 2019, she joined the group of Prof. Christophe Copéret as doctoral candidate focusing on development of alternative catalysts and gaining mechanistic insights in the field of methane coupling.



Christophe Copéret (CCH) obtained a PhD in 1996 with E.-i. Negishi (Purdue University) and was a postdoctoral fellow with K. B. Sharpless (Scripps Research Institute). CCH joined CNRS in 1998, became Research director in 2008 and moved to ETH Zurich in 2010, as Chair of Surface and Interfacial Chemistry. His research interest lies at the interface between molecular, surface and material chemistries. The objective of his laboratory

is to bring a molecular-level understanding of complex inorganic systems such as heterogeneous catalysts, hence the development of surface organometallic chemistry methodology as well as spectroscopic techniques such as solid-state NMR.

1. Introduction

The selective conversion of methane to its coupling products remains one of the holy grails in chemistry, with numerous studies, catalyst screenings and, as yet, no industrial application. Vast global natural gas reserves are at hand and excess natural gas is flared – a major greenhouse contribution and a multi-billion dollar waste. Direct methane valorization could play a key role in the supply of chemicals and fuels in the future, hence the development of novel processes is highly desirable and research in this field has gained renewed interest in the past years.^[1] Methane

valorization processes mainly focus on the following target products: ethylene, methanol, formaldehyde, methyl halogenides and aromatics.^[2] Despite over 30 years of research, the direct catalytic conversion of methane into fuels and useful chemicals remains one of the great challenges of the century.

The current industrial processes are summarized in Fig. 1, and the indirect conversion of methane to synthetic gas (syngas) and hydrocarbons or methanol are the most important industrial processes in use today based on natural gas. Syngas, a mixture of carbon monoxide and hydrogen, is first generated by steam reforming of methane over nickel catalysts. The syngas can then be valorized downstream with well-established Fischer-Tropsch processes in which cobalt and iron catalysts prevail, however, this two- to multistep upgrading of methane is energy- and cost-intensive.^[3] Syngas can further be converted to methanol using Cu-based catalysts.^[4] Methane can also be converted into hydrogen cyanide by reaction with ammonia, in absence of oxygen (BMA-process) or presence of oxygen (Andrussow-process). Both the BMA and the Andrussow process are industrially established technologies with Pt catalysts conducted essentially unchanged for decades.^[6]

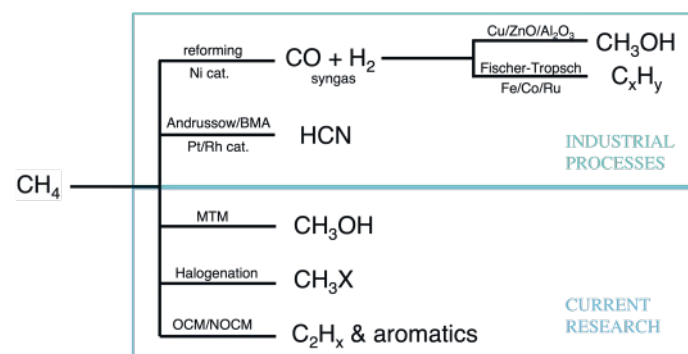


Fig. 1. Overview of the most important valorization processes for methane: Natural gas upgrading to methanol and hydrocarbons is performed via an indirect route. Current research is looking into direct transformation of methane to products.^[5]

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Current research in methane valorization focuses on: (i) direct conversion of methane to methanol (MTM), (ii) methane halogenation, (iii) oxidative coupling of methane (OCM) and (iv) non-oxidative coupling of methane (NOCM) to ethylene and aromatics. The catalytic process for methane to methanol (MTM) is mainly inspired by methane monooxygenase from nature and attempts to mimic it using iron- or copper-exchanged zeolites with high pressure reaction conditions (>30 bar).^[7] There is a distinction to make between two processes in NOCM: the first seeks to yield primarily ethane and ethylene which are valuable feedstocks for further downstream processing and the second one aims at benzene formation (methane dehydroaromatization, MDA). At present, the primary source of ethylene is steam cracking where ethane and naphtha are treated at temperatures of 750 °C and above. This process is highly endothermic and has to be followed by complex separation of the products which renders it highly energy and carbon intensive with CO₂ emissions of 1–2 tons of CO₂ per ton of ethylene depending on the feedstock.^[8]

This review focuses on the exploration of heterogeneous catalysts in NOCM. Numerous catalytic systems have been prepared and tested in both oxidative and non-oxidative coupling of methane.^[2,6,9] In the following we chose to focus on mechanistic considerations that lead to gaining a deeper understanding for methane coupling processes, eventually allowing the development of a superior catalytic system.

1.1 Thermodynamic Limitations

Non-oxidative methane coupling is limited by severe thermodynamic restrictions which poses the requirement of high reaction temperatures to reach a workable methane conversion. When comparing thermodynamic limitations for NOCM and OCM, the non-oxidative conditions favor coke formation, while oxidative coupling strongly favors overoxidation to CO_x species over ethylene formation. NOCM, working in absence of oxygen, has gained momentum as it avoids overoxidation to CO_x species and thereby circumvents the major challenge associated with OCM.^[2]

Beside the thermodynamic constraints, it is critical to obtain high C₂ selectivity and to avoid coke formation in NOCM. Considering the thermodynamics for NOCM as shown in Fig. 2, it is evident that temperature is a major control handle for methane conversion and product selectivity. If 1100 °C is taken as a point of reference, the methane equilibrium conversion is 46% (Fig. 2a) when considering only C₂H_x product formation and can increase up to 67% (Fig. 2b) when the formation of aromatic products such as benzene and naphthalene is considered.

Overall, direct conversion to C₂ products is favored above 800 °C with ethylene as a major product. Notably, it is expected that, at this temperature, ethane readily dehydrogenates to ethylene and acetylene with increasing temperature as the product selectivity towards acetylene becomes preferred at about 1000 °C as seen in Fig. 2a.^[10] Acetylene can further oligomerize to form benzene and other aromatic products such as toluene, xylenes and naphthalene and the selectivity towards aromatics is favored at lower temperatures.^[11] In addition to thermodynamic considerations, NOCM faces the issue of rapid catalyst deactivation due to the formation of coke and polyaromatic hydrocarbons which cause catalyst fouling.^[12] Reported values of methane conversion in NOCM for the most part lie in the range of 1–20%,^[2] while the target for industrial application is set at a conversion of methane of at least 30% and selectivity for C₂ of around 80% resulting in a C₂ yield of ~25%.^[9a,13] Hence, the economic viability requirements for NOCM are not fulfilled at this point in time due to limited catalyst stability and high energy expenditure to sustain operating conditions for this endothermic process.

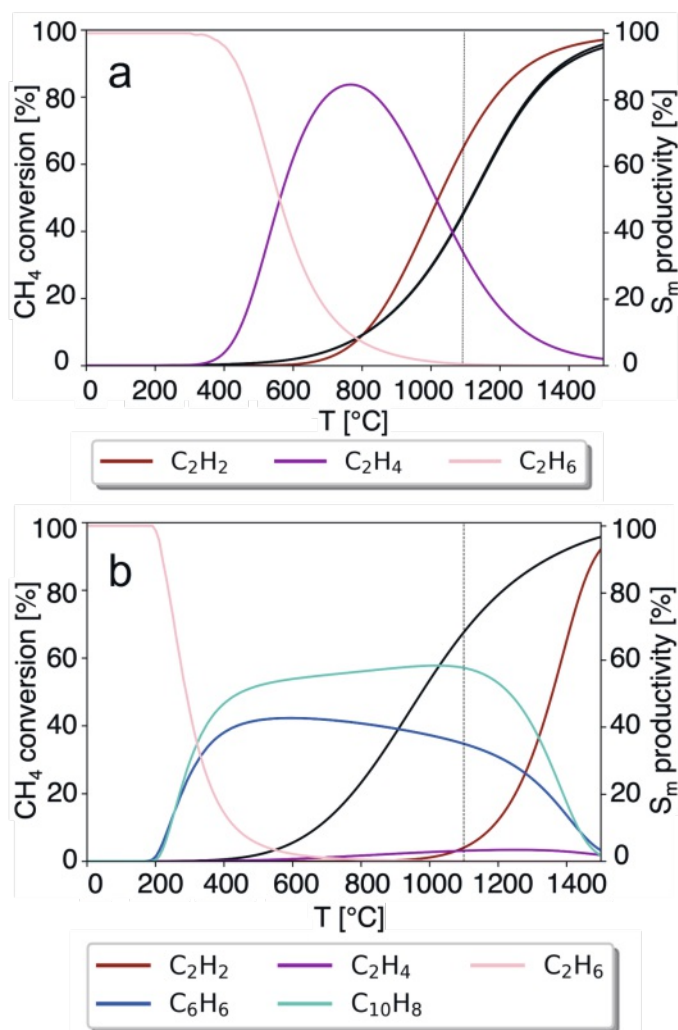


Fig. 2. Thermodynamics of methane conversion and molar product selectivity (S_m) for acetylene (C₂H₂), ethylene (C₂H₄), ethane (C₂H₆) (a), benzene (C₆H₆) and naphthalene (C₁₀H₈) (b) as function of temperature. The formation of coke and H₂ is omitted in above shown graphs. Calculated with HSC 6.

1.2 State-of-the-Art

Mo/ZSM-5 systems were first introduced in 1993 by Wang *et al.* and remain the gold standard until today for MDA.^[14] The reported performances show methane conversions of ~10% and selectivities up to 80% towards benzene.^[15] Apart from Mo, various other transition metals such as W, Re, Fe as well as Zn and Ga in zeolitic hosts were investigated for NOCM. Regarding structure, it has been recognized early on that metal carbides can be generated *in situ* under operating conditions which involve elevated temperatures (800–1100 °C) and as such they have been proposed to be the active component in numerous catalytic systems.^[16] The limiting factor for the use of zeolites is their applicable temperature range as many structures collapse above 800 °C.^[17] Despite extensive investigations, there is a lack of experimental evidence regarding the mechanism of the carbon coupling step and the structure of the active site. For MoO_x/ZSM-5 a characteristic induction period along with particle agglomeration is observed which is rationalized by a transformation of the molybdenum oxide to a molybdenum oxycarbide or carbide species which is presumed to resemble the active site in methane coupling.^[18] The selectivity for C₂ can be steered by increasing the space velocity which magnifies the ethylene to ethane ratio implying that ethylene is an initial reaction product and aromatics are secondary products.^[19] Xiao and Varma have shown in 2018 that a Pt-Bi alloy supported on a ZSM-5

zeolite is highly stable and selective for C_2 products. The addition of bismuth to the catalyst suppressed coke formation and therefore the selectivity for ethane was boosted with numerical values of 6% for methane conversion and 85% selectivity for ethane at 700 °C.^[20] It has to be noted that a diluted methane feed (10% CH_4/N_2) was used. In 2014, Guo *et al.* published an $Fe@SiO_2$ system with notable results: under operating temperature of 1090 °C a methane conversion of 48% with a high selectivity towards hydrocarbons of 99% with 48% selectivity for ethylene was reported.^[21] The activity is tentatively attributed to methane-induced reduction and redispersion of iron oxides, leading to the formation of ‘iron carbide’ single sites.^[21,22] While this report gained tremendous attention due to its outstanding performance, attempts to reproduce the catalyst synthesis and performance have remained challenging.^[23]

Another class of catalysts for NOCM, that have gained recent interest, involves supported systems with highly dispersed metal sites, in particular Pt systems were thoroughly investigated. Wang and Miller reported that $Pt@CeO_2$ exhibited a conversion of 14% with 75% selectivity for C_2 at 975 °C, notably in a highly diluted stream of methane (1% CH_4/He).^[24] Further relevant single site catalysts reported in the context of NOCM are tantalum and tungsten hydrides supported on silica and alumina respectively. Under very mild conditions of 475 °C exceptional ethane selectivity of 99% could be shown, albeit at low methane conversion of 0.2% due to the thermodynamic limitations.^[25]

2. The Key to Product Selectivity

Considering the inert nature of CH_4 , the high temperatures serve in favoring coupling products whereas the catalyst surface mediates the C–H activation and serves as a handle to control selectivity. Simultaneously, due to the elevated temperatures the relevance of homogeneous gas phase reactions cannot be neglected and proposed mechanisms frequently include radical pathways.^[26]

A general scheme for a methane coupling reactor is shown in Fig. 3. It is essential to emphasize the interplay of surface and homogeneous gas phase contributions. A plethora of mechanistic pathways is possible. Most considerations entail homo- or heterolytic C–H activation on the catalyst surface which can either be a single activation to form a methyl moiety or multiple C–H activations which can lead to methyldiene, methyldiyne or overactivation resulting in carbonaceous deposit. Meanwhile, the adsorbed hydrogen species (H_{ads}) are assumed to be able to diffuse over the surface in a fast manner.^[27]

The key question to address here is where the C–C coupling takes place as it could proceed (i) via coupling of $CH_{x,ads}$ which can then desorb as C_2H_{2x} ($x = 1, 2, 3$) or higher hydrocarbons which subsequently are able to participate in gas phase processes or (ii) via coupling of methyl radicals of which the concentration is presumed to be governed by catalyst nature and temperature. Several studies have shown that increasing residence time in the reactor hot zones led to a rise of selectivity for aromatic products, thus strongly suggesting that some amount of C_2H_x products will further couple and oligomerize to form benzene, naphthalene and polyaromatic hydrocarbons (PAH).^[28]

The mechanistic aspects of NOCM are a matter of debate. While there is no general consensus regarding the mechanism, current literature and prominent pathways are summarized in Fig. 4. Dissociative adsorption of methane on metal surfaces occurs already at low temperatures (100–500 °C) and can be followed by further dehydrogenation of methyl adsorbates to CH_x species and subsequent coupling to the corresponding C_2 species (Fig. 4(i)) as the most simple mechanistic proposal.^[27,29]

Due to the high temperatures gas phase reactions often involve radical pathways which have been proposed for methane coupling mechanisms mainly involving methyl radicals as initiator for formation of C_2 products (Fig. 4(ii)). Herein, the methyl

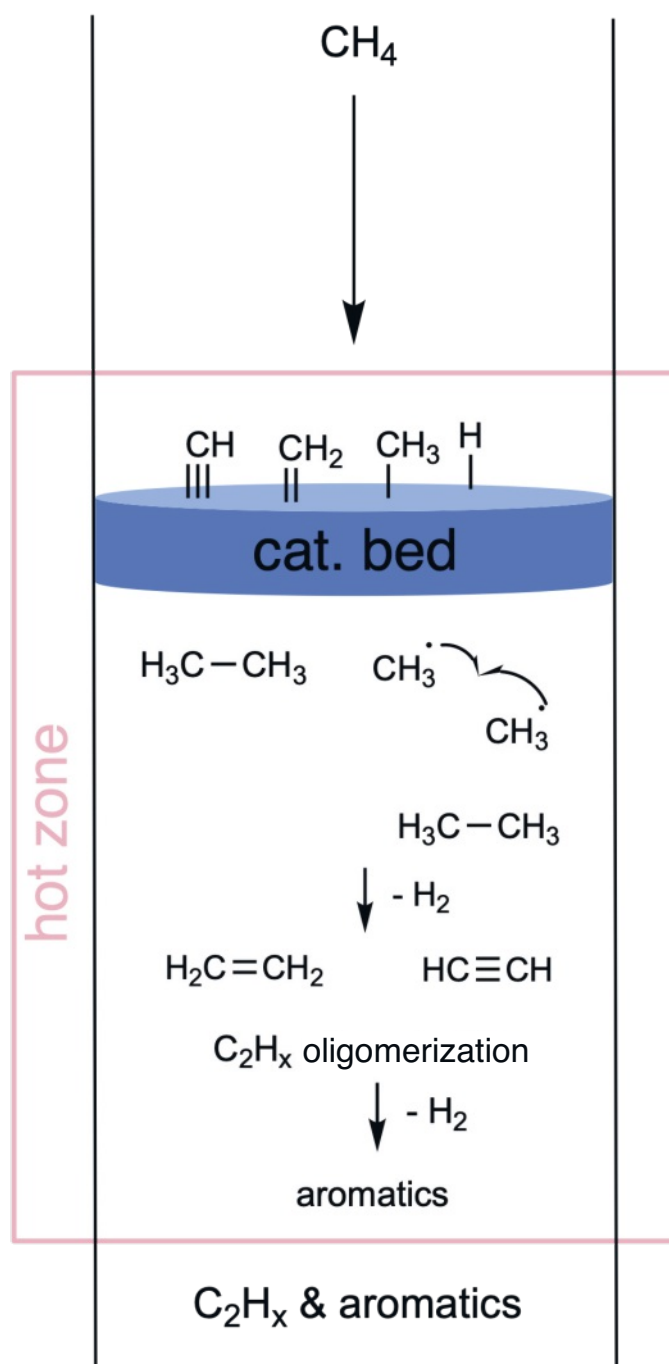
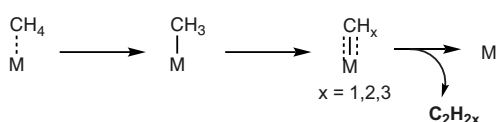
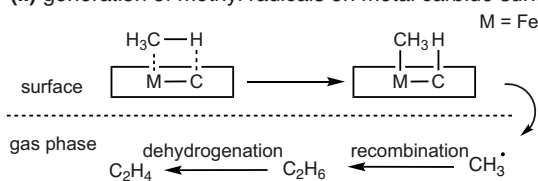


Fig. 3. General drawing of a methane coupling reactor setup showing different possibilities for surface and gas phase coupling contributions.

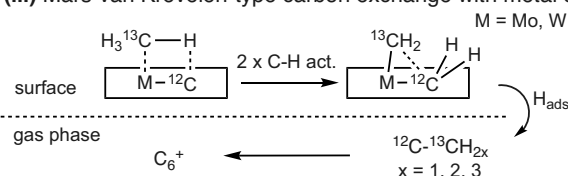
radical formation is rationalized by homolytic bond splitting of the methyl moiety on the catalyst surface as has been proposed for Fe/SiO_2 catalysts. The C–H bond cleavage is promoted by a metal carbide catalyst surface at elevated temperature, followed by gas phase recombination to hydrocarbon products.^[3,21,30] Numerous reports assign the *in situ* formed metal carbide site as the active site. A recent study by Zhang *et al.* was able to confirm the crucial role of the carbidic carbon for Mo_2C and WC (Fig. 4(iii)).^[31] By applying labelling strategies with $^{13}CH_4$ as reactant gas, it could be revealed that the metal carbide partakes in product formation and is able to exchange carbidic carbon, thus suggesting a Mars-Van Krevelen-type mechanism^[32] with carbon of the metal carbide matrix involved in product formation (instead of oxygen in metal oxides). To further support this hypothesis, an enrichment of ^{13}C was found in the spent metal carbides which was probed by ss-NMR with signals for Mo_2C at 274 ppm and

(i) dissociative chemisorption of CH₄ on metal surfaces [27,29]

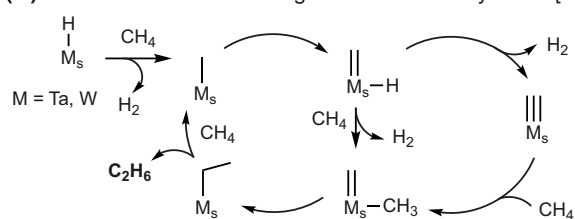
(ii) generation of methyl radicals on metal carbide surface [3,21,30]



(iii) Mars-van Krevelen-type carbon exchange with metal carbides [31]



(iv) methane activation on single sites of metal hydrides [33]



(v) bifunctional catalysis on Mo/HZSM-5 [34]

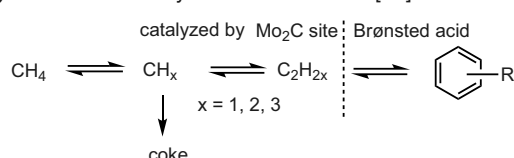


Fig. 4. A collection of postulated mechanistic pathways for methane activation and coupling in non-oxidative methane coupling.^[3,21,27,29–31,33,34]

for WC at 307 ppm. The lifetime of the catalyst in terms of selectivity in this study was found to depend on the carbon diffusion coefficient of the corresponding metal carbide at 1100 °C, showcasing the metal carbide as a dynamic active site. It is likely that alkylidene species are involved as intermediates as they have been previously proposed to be stable at high temperatures on metal, Mo₂C and WC surfaces.^[35]

Considering the detailed activation process on the surface, there are many plausible assumptions and Fig. 4(iv) shows the proposed mechanism for stepwise C–H bond activation of methane on single sites of metal hydrides to form a carbene or carbyne species which activates a second methane molecule through σ -bond metathesis, yielding a methyl-methylidene complex, followed by migratory insertion to form an ethyl species which is displaced by methane and therefore releasing ethane.^[33]

While it is very difficult to elucidate mechanistic pathways and identify reaction intermediates at elevated temperatures (>700 °C), several reports have shown that carbidic carbon is pivotal for C–C coupling.^[31,36] Bhan and co-workers have proposed that Mo₂C is the primary relevant species to determine

reaction kinetics.^[37] Vollmer *et al.* have used a ¹³C labelling strategy to show for MDA on Mo/ZSM-5 that the resulting benzene contained at least one carbon originating from Mo₂C.^[36a] This is aligned with the postulated bifunctional catalysis for Mo/HZSM-5 systems in MDA (Fig. 4(v)). It was proposed that methane is activated on the molybdenum carbide sites and partially dehydrogenated to CH_x species or fully dehydrogenated to coke. The coupling of CH_x species is then followed by oligomerization of ethylene or acetylene to higher hydrocarbons and aromatics such as benzene facilitated by Brønsted acid sites of the zeolite framework.^[34]

A common feature that can be found in the postulated reaction mechanisms are metal carbide/carbyne species and the carbon diffusion dynamics of the corresponding metal carbides. The carbon exchange dynamics of metal carbides should be studied in more detail in order to predict catalytic activity experimentally and computationally. A novel descriptor to gain a deeper understanding of the methane coupling activity could be carbon diffusion coefficients of the respective transition metal carbides formed *in situ*. Recent reports of Mars-van Krevelen type behavior involving the carbidic carbon in carbon homologation processes in the field of dry reforming of methane, CO₂ methanation and Fischer-Tropsch synthesis indicate a more ubiquitous character for this mechanism, not limited to methane coupling.^[36b,40]

One aspect to govern methane conversion and hydrocarbon product selectivity is the nature of the catalyst (*vide supra*), however, another very important factor is the reaction conditions used, *i.e.* reactor material, operating temperatures, gas hourly space velocities and gas compositions. Adjusting these factors tailored to the desired product can make it or break it. Postma *et al.* demonstrated the significance of the axial temperature profile with an Fe/SiO₂ catalyst as methane conversion was increased by a factor of 8 (to 8%) by increasing the residence time of the gas feed in the hot zone of the reactor while shifting selectivities for hydrocarbon products from C₂ species to aromatics and decreasing coke deposit.^[38] Table 1 shows a selection of NOCM catalysts with different reaction conditions leading to different product selectivities. In general, a range of temperatures is screened in order to increase methane conversion which is often coupled with a loss of product selectivity, *e.g.* for the PtBi/ZSM-5 catalyst.^[20] The first entries of the table compare Fe/SiO₂ catalysts where methane conversion varies from 8 to 48% as many parameters were changed such as catalyst weight, gas hourly space velocity (GHSV) and gas feed compositions. Only if all parameters are constant and the reactor setup is known, can catalysts be compared objectively. Varying the concentration of methane in a dilution stream with an inert gas can strongly influence the amount of coking. Notably, dilution in N₂ appears to be beneficial by minimizing coking, possibly through formation of metal nitrides.^[41]

3. Conclusions

Methane coupling catalysts have tremendous potential, however, the limited knowledge regarding the mechanism encumbers further development. This review emphasizes that surface and bulk processes need to be studied in more detail in addition to gas phase processes, as only the combination of both can give a full picture of the methane coupling mechanism. Our recent work has revealed the role and dynamic behavior of metal carbides which involves incorporation of carbidic carbon in C₂H_x products reminiscent of a Mars-Van Krevelen type mechanism involving carbon instead of oxygen.^[31]

This perspective gives an overview of proposed mechanistic pathways and considerations about experiment conditions in order to foster a rational catalyst design platform for NOCM. At the same time, it is crucial to take into account reaction parameters in

Table 1. Summary of selected well-performing catalysts in the field of NOCM, showing catalyst loading, temperature, gas hourly space velocity (GHSV), gas feed, methane conversion and hydrocarbon (C₂) as well as aromatics (C₆⁺) selectivities. The carbon balances are closed with selectivity towards coke.

Reference	Catalyst (lg)	T [°C]	GHSV [mL gcat ⁻¹ h ⁻¹]	Gas feed	CH ₄ conversion [%]	C ₂ selectivity [%]	C ₆ ⁺ selectivity [%]
Postma <i>et al.</i> ^[38]	Fe/SiO ₂ (0.26)	1000	3'640	90% CH ₄ /N ₂	7.7	50	38
Guo <i>et al.</i> ^[21]	Fe/SiO ₂ (0.75)	1000	10'000	90% CH ₄ /N ₂	31	50	50
Guo <i>et al.</i> ^[21]	Fe/SiO ₂ (0.75)	1090	21'400	90% CH ₄ /N ₂	48	48	52
Sakbodin <i>et al.</i> ^[39]	Fe/SiO ₂ (0.38)	1000	3'200	90% CH ₄ /Ar	12	65	35
Sakbodin <i>et al.</i> ^[39]	Fe/SiO ₂ (0.38)	1050	3'200	90% CH ₄ /Ar	20	65	33
Su <i>et al.</i> ^[16a]	Mo/ZSM-5 (0.2)	800	1'500	90% CH ₄ /N ₂	18	2	75
Zhang <i>et al.</i> ^[31]	Mo ₂ C (0.1)	1100	24'000	10% CH ₄ /Ar	23	21	–
Zhang <i>et al.</i> ^[31]	WC (0.1)	1100	24'000	10% CH ₄ /Ar	10	32	–
Xie <i>et al.</i> ^[24]	Pt/CeO ₂ (0.2)	975	6'000	1% CH ₄ /He	14.4	75	22
Xiao, Varma ^[20]	PtBi/ZSM-5 (0.5)	650	12'000	10% CH ₄ /N ₂	4	85	5
Xiao, Varma ^[20]	PtBi/ZSM-5 (0.5)	700	12'000	10% CH ₄ /N ₂	5	65	–

order to tune the selectivity towards the desired products. Only the linking of catalyst nature and design of the experiment will lead to sufficient product yields and drive the implementation of methane coupling on industrial scale.

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