Catalytic Dry Reforming of Methane: Insights from Model Systems

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Catalytic dry reforming under industrially relevant conditions of high pressures and high temperatures poses severe challenges towards catalyst materials and process engineering. The demanding conditions under which the reaction is performed lead to a coupling of reactions occurring in the gas phase and reactions which are catalyzed by the material employed as catalyst. A profound analysis of the mechanisms occurring in gas phase and resulting products from gas phase reactions is key to understanding part of the challenges that any catalyst material, irrespective of its nature, will have to cope with. The deposition of coke on an active catalyst is as well one of the most limiting factors for catalyst lifetime and catalyst activity in dry reforming. Therefore, an understanding of the thermodynamics behind coke formation and an intricate description of the mechanisms driving the evolution of coke is a vital piece of the picture. Acid-base properties of the catalyst material and the role and nature of the active metal do also need to be considered. A large part of the review deals with mechanisms which are relevant for coke gasification and insights into materials properties, which are relevant to allow for reaction pathways along these lines. The review article focusses on research results which have been achieved using model systems – typically the analysis of model systems is a more rewarding exercise compared to fully formulated industrial catalyst systems, as here more elucidating structure-property relationships can be drawn. Additionally the article discusses dry methane reforming in the context of alternative syngas generation technologies and attempts to create an application perspective for the reader in the context of a sustainable approach towards carbon capture and storage.

Introduction

Carbon dioxide management in terms of carbon capture, utilization and storage (CCUS) has become an important topic in public discussion and is reflected in efforts in research and development both in academia and industry in the last two decades,[1] since CO₂ is one of the major greenhouse gases.[2] From an industrial point of view CO₂ is not only a waste product with a harmful environmental footprint, but also an interesting synthet,[3] if available at a point source. Therefore, its utilization and implementation in industrial scale as raw material into value chains offers certain potentials. Dry reforming is very often discussed in this context as a technology of choice regarding CCUS. However, two major crucial aspects must be considered for any CO₂ valorization technology, of course also for approaches in catalytic dry reforming, as discussed by Peters et al.[4] First CO₂ is a highly stable molecule and can be considered as the thermodynamic sink for many reactions involving organic substrates; this results in the fact that any process that intends to valorize CO₂ and to introduce reactivity will require enough energy input or reaction partners of a sufficiently high intrinsic energy level. This plays a major role in the design of any production process targeting carbon dioxide valorization and the choice of reaction partners. Another aspect that should be considered is the respective duration of the CO₂ fixation and the value and lifecycle of the products made in the respective reaction; all these parameters play an important role in the evaluation of any a CO₂ valorization technology relying on CCUS.

Of course, dry reforming is not the only conversion technology which utilizes carbon dioxide as synthet: a range of processes for the chemical valorization of CO₂ are already well established on an industrial level. Among several small-scale processes (e.g. Kolbe-Schmitt reaction[5]), two large-scale chemical processes that rely on CO₂ as feedstock are of importance, namely the methanol production from H₂ and CO₂ (Eq. 1)[6] and the production of urea from NH₃ and CO₂ (Eq. 2).[6]

\[3 \text{H}_2 + \text{CO}_2 \rightarrow \text{H}_2\text{COH} + \text{H}_2\text{O}\]  
\[2 \text{NH}_3 + \text{CO}_2 \rightarrow \text{CO} (\text{NH}_2)_2 + \text{H}_2\text{O}\]  

For methanol synthesis it can be argued that most of the technologies commercialized are process variants based on the conversion of syngas with a certain carbon dioxide content, typically around 2 to 6 vol% and adjusted hydrogen to carbon monoxide ratios; carbon dioxide plays an important role in the reaction mechanism over copper based catalysts and occurs in...
the rate determining step as key critical component. Methanol synthesis technologies for higher carbon dioxide partial pressures are under development and heavily sought after. The mentioned technologies and large-scale productions in place which utilize CO$_2$ as starting materials rely on reaction partners having a high reduction potential, such as hydrogen itself (Eq. 1) or ammonia (Eq. 2) and therefore are currently mainly dependent on hydrogen supply from fossil sources obtainable via reforming technologies.

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3 \text{H}_2 \quad \Delta H^\circ = 206.0 \text{kJ/mol} \quad (3)
\]

\[
\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^\circ = -41.2 \text{kJ/mol} \quad (4)
\]

As catalytic dry reforming is also part of the family of reforming technologies, we want to take a closer look at the current landscape which is industrially realized. The most economic routes to hydrogen rely up to now on natural gas as fossil feedstock with the consequence of an inherent carbon dioxide footprint. The same is true for synthesis gas or syngas that is in general an important chemical feedstock in the production of high-value chemicals and fuels. The term syngas in this article is used in a context that refers to H$_2$/CO mixtures of different ratios, which are accessible by the different syngas production technologies. The main state of the art large-scale production technologies for hydrogen and syngas today are catalytic and non-catalytic partial oxidation reactions (autothermal reforming ATR, combined reforming CR, partial oxidation POX and catalytic partial oxidation CPOX; Eq. 5), the steam reforming of methane (SMR; Eq. 3) with subsequent water-gas-shift stages (Eq. 4) and combinations thereof.

\[
\text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2 \quad \Delta H^\circ = -35.6 \text{kJ/mol} \quad (5)
\]

Dry reforming of methane (DRM; Eq. 6), a potential syngas production technology based on CO$_2$ and methane, has drawn a lot of attention, especially regarding raw material change, abundant gas supply, availability of bio-based gas and the demand of technologies with the potential of carbon dioxide import. The term “dry” in dry reforming is based on the...
substitution of water in steam reforming by CO₂ (Eq. 3 and 4). The idea of producing synthesis gas from CO₂ and CH₄ goes back to as early as 1888. Compared to SMR, DRM has several attractive aspects as the process has benefits regarding energy efficiency since no or a largely reduced steam content must be produced for the feedgas, therefore less energy be invested for the evaporation of water. Additionally, DRM holds the value proposition that a syngas can be prepared of low hydrogen to carbon monoxide ratios, an exercise which must be much harder to achieve starting from product gases obtained by SMR.

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H^\circ = 247.3 \text{kJ/mol} \]  

(6)

Therefore, a lot of research on dry reforming was and still is conducted not only because of the aspects of CO₂ utilization but also due to fact that access to CO rich syngas, that can be obtained from dry reforming, is facilitated. Easier access of CO rich syngas offers potential for certain downstream processes. However, the large-scale production of CO-rich syngas by DRM is still in its infancy and has not been realized until now on a broad front. The reasons for this state is that typically a strong deactivation tendency of the applied catalysts due to severe coke formation is observed, especially at the industrially relevant pressure corridor of 20 to 40 bars. This phenomenon has already been observed in 1928 by Fischer and Tropsch over Ni and Co catalysts. Numerous reviews on DRM have been written in recent years which mainly deal with different types of catalysts that are said to be less affected by coke formation.

With our review we want to give an overview on insights and findings that we consider relevant for DRM on an industrial scale and allow insights into our collaborative research conducted on the challenging aspects of the DRM-reaction like coke formation mechanisms under DRM conditions. We discuss in this paper learnings and alternative approaches for the design of catalyst materials obtained for model systems to overcome some of the inherent challenges of the reaction in order to build a basis for the large-scale application of dry reforming in industry.

As mentioned before, dry reforming of methane has only recently reached a commercial scale, up to now steam reforming (SMR), partial oxidation (POX) and autothermal reforming (ATR) are the dominating syngas production technologies. POX and SMR can be combined to use the individual heat characteristics of both reactions. The combined process is called autothermal reforming (ATR) if performed in a single reactor. In all these processes, except DRM, a hydrogen richer syngas (H₂/CO > 2) can be obtained and especially the combined technologies (ATR) can be used to obtain a broad range of syngas ratios (Figure 1). In all reforming processes the (reverse) water gas shift (RWGS) plays an important role and affects the obtained syngas ratio (Eq. 4).

Steam reforming of methane is a well-established technology and favored for syngas demands of high H₂/CO ratios (Eq. 3). The produced syngas has an H₂/CO ratio of approximately 4 which can be further increased by WGS stages to obtain a pure hydrogen feedstock (99.95%). The endothermic process runs at 800–950 °C and 15–40 bar over Ni-based catalysts. The steam-to-carbon ratio of the feed is held at around 2.5–3 to ensure coke free operation conditions on the catalyst. Since the invention of steam reforming of natural gas (Eq. 3) or higher hydrocarbons (Eq. 7) in 1912 extensive studies of catalyst materials have shown that Ni is the pareto optimum of performance and price compared to noble metal catalysts in SMR. Noble metal catalysts feature higher coking and sintering resistance due to thermodynamic reasons in equilibrium but are no economically attractive alternative in such a large-scale process like SMR.

\[ \text{C}_m\text{H}_n + m\text{H}_2\text{O} \rightarrow m\text{CO} + (m + n/2)\text{H}_2 \]  

(7)

Via partial oxidation (POX) of methane a syngas ratio typically of 2 is obtained (Eq. 8a) which is most suitable for most downstream processes, such as the direct methanol synthesis or Fischer-Tropsch synthesis. The slightly exothermic process is operated without catalysts at 1150–1500 °C and 25–80 bar and requires high purity oxygen as feed and therefore an oxygen plant in the form of an air separation unit. Currently three POX processes are run on more than 320 plants worldwide, the Texaco process, the Shell process and the Lurgi process. By applying a catalyst (Rh, Ru, Pt or Ni) in the CPOX process it could be shown that a reduction of the process temperature to 900–1000 °C is feasible. Further lowering of the process temperatures to 500–600 °C at < 5 bar seems to be possible. However, CPOX approaches can still be considered as a technology under development.

\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H^\circ = -35.6 \text{kJ} \cdot \text{mol}^{-1} \]  

(8a)

\[ \text{C}_m\text{H}_n + m/2\text{O}_2 \rightarrow m\text{CO} + (n/2)\text{H}_2 \]  

(8b)

Complete substitution of the oxidants O₂ (in POX) and H₂O (in SMR) by CO₂ in DRM (Eq. 6) directly produces a carbon rich syngas of H₂/CO ≤ 2.
However, the challenges of this reaction, besides being slightly more endothermic than SMR, are as already mentioned the severe coke formation tendency due to the carbon rich feed and the industrially relevant harsh reaction conditions temperatures over 800 °C to allow for sufficient conversion and pressures of 10–40 bars to obtain a product gas at sufficiently high pressure to avoid or minimize additional compression steps for downstream users.

Schwab et al. discussed in 2015 the aspects of dry reforming for syngas production on a large scale. They concluded that state of the art dry reforming technologies for syngas production lacks new impulses and the current state of the art of catalysts used for SMR shows insufficient performance under industrially relevant DRM conditions due to deactivation mainly by coking at pressures above 20 bars.[40,41]

Up to now two processes closely related to DRM reached commercialization, the CALCOR[42,43] and SPARG[44] process. The CALCOR process was designed to achieve a syngas composition with maximum CO content at smaller-scales of production. This process converts methane over Ni-based catalysts and circumvents the coke formation by applying pressures close to atmospheric pressure and therefore allows the use of high CO partial pressures.[45,46] Thereby a CO rich syngas with a lower limit of H2/CO ratios of 0.43 is obtained.[47] Further CO2 recycle and H2, H2O and CH4 separation stages allow a purification of the stream to obtain CO with purities of 99.2%. To integrate this process in a chemical value chain with typical downstream processes further compression steps are necessary since most downstream technologies work with higher pressures. On the other hand, compression of syngas with H2/CO ratios below 2 is technically not an easy task.

The sulfur passivated reforming process (SPARG) combines the characteristics of dry and steam reforming. Thereby a broad spectrum of H2/CO ratios is accessible. Coke formation is prevented by sulfur poisoning (0.7 coverage with sulfur) of the Ni-based catalysts, which leads to a reduced reaction rate of carbon formation. The sulfur poisoning, however, reduces the overall activity of the catalyst and can become a problem for many downstream processes if not properly being taken care of.[39]

The CALCOR or SPARG processes were both developed to prevent coke formation under dryer reforming conditions. Unfortunately, these processes are only feasible in certain downstream process scenarios and therefore lack bread in applicability. In order to overcome these shortcomings and to develop a more broadly applicable process a better understanding of the coke formation mechanisms and measures regarding catalyst developments that can cope with the challenge are necessary.

**Downstream processes for DRM requiring syngas of a low hydrogen to carbon monoxide ratio**

From an industrial point of view, it is always worthwhile to look down the value chain and analyze which downstream processes will benefit from the product produced; in the case of DRM a syngas with high carbon monoxide content. By far the most prominent and by volume the largest capacities in reforming are devoted towards the production of hydrogen – steam methane reforming is the dominating technology used today due to superior economy and process efficiency. Today the main hydrogen consumers on a global scale are ammonia production plants, refineries and chemical plants.

The most important downstream processes relying on syngas of a ratio of 2 are the methanol synthesis, processes relying on Fischer-Tropsch technology for the production of alkanes.[48] These processes require a H2/CO ratio of 2, which can be obtained by POX or ATR technology, as well as combined reforming as SMR with carbon dioxide import. Several downstream technologies, however, require CO rich syngas that could be provided with an efficient solution for DRM in place (Figure 2). It is sometimes debated whether the reverse water gas shift reaction (Eq. 4) can be an interesting alternative in production of carbon monoxide rich syngas. Provided the hydrogen used in the reverse water gas shift reaction is obtained from fossil sources (as for example from SMR of natural gas), the efficiency of the reverse water gas shift reaction can be debated. For certain technical reasons and from an energetic footprint any reverse water gas shift process relying on hydrogen based on natural gas will be inferior to DRM for obvious reasons.

Downstream processes of large volume that currently rely on CO rich syngas are Oxo-processes (hydroformylation of olefins Eq. 10) and the production of acetic acid (Eq. 9). Processes which have untapped potential in coupling to DRM, due to the upside of carbon dioxide recycling and do require low hydrogen to carbon monoxide ratios are the direct synthesis of dimethyl ether (DME) and the direct conversion of such a syngas to olefins e.g. in the Fischer-Tropsch to Olefins reaction (FTTO).

\[
\begin{align*}
2\text{CO} + 2\text{H}_2 &\rightarrow \text{H}_2\text{C}\text{COOH} &\Delta H^\circ &= -435.0\text{kJ/mol} \tag{9} \\
\text{R—CH} &= \text{CH}_2 + \text{CO} + \text{H}_2 &\rightarrow \text{R—CH} &= \text{CH}_2 — \text{CHO} \tag{10}
\end{align*}
\]

Currently DME can be produced on an industrial scale by methanol dehydration at 250–400 °C and 20 bar and so derives from a syngas ratio of 2. The currently commercially available technology uses a two-step process,[49] combining a methanol synthesis and a dehydration stage (Eq. 11). The co-production of water requires an additional separation stage after the dehydration reactor.

\[
\begin{align*}
2\text{CO} + 4\text{H}_2 &\rightarrow 2\text{H}_2\text{COH} &\rightarrow \text{H}_2\text{COCH}_3 + \text{H}_2\text{O} \tag{11}
\end{align*}
\]

A more efficient pathway towards DME relies on the direct synthesis of and can be performed with a syngas of ratio 1, a syngas obtainable via dry reforming[50,51] (Eq. 12). The benefit of this reaction is the overall higher energy efficiency, overall higher conversions per pass compared to methanol synthesis, the avoidance of a separate dehydration step (a separate dehydration would have to be carried out in a separate reactor).
A very unique feature of a direct DME process with the DRM step, is the potential of CO\(_2\) recycling and net consumption. 

\[ 1.5 \text{CO}_2 + 1.5 \text{CH}_4 \rightarrow 3 \text{CO} + 3 \text{H}_2 \rightarrow \text{H}_2\text{COCH}_3 + \text{CO}_2 \]  

**(Dry reforming of methane: basic considerations)**

**Thermodynamic equilibrium of DRM**

Optimizing a process always goes hand in hand with an in-depth understanding of the process characteristics. In this regard, the thermodynamic aspects of DRM are important to understand the origin of coke formation and the prerequisites for the implementation of a commercial DRM process. As mentioned before, CO\(_2\) and CH\(_4\) are highly stable molecules and especially CO\(_2\) can be regarded as “thermodynamic sink”. Therefore, valorization of CO\(_2\) is always an endothermic reaction and high activation energies are necessary for the downstream chemistry.

Thermodynamic equilibrium analysis of the DRM reaction was performed from different groups under various reaction conditions and with different models applied. Roussière\(^{[52]}\) calculated thermodynamic equilibria for different pressures, temperatures and feed compositions with the help of DETCHEMEQUIL\(^{[53]}\) based on the Gibbs free enthalpy minimization. His investigations showed that, even if not present in the beginning, steam/water is always observed under thermodynamic conditions due to RWGS. This poses the question of how co-feeding of water influences the thermodynamic equilibrium in DRM. However, Roussière's thermodynamic equilibria analysis shows that small amounts of steam in the initial feed have only a minor influence on the obtained final syngas ratio – although counterintuitive: DRM at completely “dry” conditions will as a product gas always contain water in the product gas. This is thereby a way of removing coke deposits by gasification, without changing the syngas ratio.

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  

Roussière concluded that higher temperatures are beneficial for syngas production by DRM, as expected for an endothermic reaction and a temperature range above 800 °C is necessary to achieve degrees of conversion of methane and carbon dioxide that render the process economic. The lowest syngas ratio can be obtained with feed ratios CH\(_4\)/CO\(_2\) close to 1, where the addition of small amounts of water (steam) to the feed has also a negligible influence.

Regarding coking tendency, a thermodynamic equilibrium analysis has been published by Aramouni et al. who additionally considered carbon and the respective particle size of the active metal of the catalyst applied in their model. In this study it was shown that the particle size seems to have a significant influence on the carbon deposition and an ideal particle size for avoidance of coke was found to be 5 nm, which is in agreement with previous results from Bengaard et al.\(^{[54]}\) and Kim et al.\(^{[55]}\) who described the thermodynamic stability limit for carbon deposits on the catalyst to be 80 atoms. This finding is further supported by experimental results from Goula et al.\(^{[56,57]}\)
Chein et al.\cite{27} focused in their thermodynamic equilibria modelling more on high pressure conditions due to their industrial relevance and considered additionally the effect of inert gas $N_2$. They concluded that increasing pressure has a negative effect on $\text{CH}_4$ and $\text{CO}_2$ conversion and favors carbon and water formation, while $N_2$ co-feeding can be used to alter the hydrogen to carbon monoxide ratio of the product gas. Özkara-Aydinoğlu\cite{28} carried out thermodynamic equilibria analysis for different pressures at temperatures of 200–1400°C (Figure 3) and concluded that the pressure related negative effect on $\text{CH}_4$ and $\text{CO}_2$ conversion can be compensated by increased reaction temperature and becomes negligible at temperatures above 1200°C.

**Figure 3.** Conversion of methane (a) and $\text{CO}_2$ (b) and final $\text{H}_2$/CO (c) ratio calculated for the temperature range 200–1400°C at 1, 10 and 20 bar. From Özkara-Aydinoğlu.\cite{28} Reproduced with permission from Ref. [59] Copyright 2010 Elsevier.

**Catalyst materials for dry reforming**

From an industrial point of view catalyst performance is an important aspect, but catalyst cost cannot be neglected. As in other reforming technologies base metals are the preferred metals of choice in the industrial realization of DRM on a large scale. Work on catalysts containing platinum metals as active component has nevertheless its place, as the learnings from this work on platinum metals in DRM delivers insights that contribute to the overall understanding and the advancement of science. From the previous section on thermodynamic equilibrium analyses it becomes clear that DRM under conditions of high to complete conversion of methane and carbon dioxide requires temperatures of at least 800°C. These conditions pose several challenges for a catalyst material since most catalysts are prone to deactivation upon sintering and coking\cite{29,30,31} Also, irreversible reactions of the active metal with the support are plausible under these high temperature conditions. The activity of catalysts for dry reforming depends on a range of factors as the active metal (species, reducibility, particle size), the support (kind of support, surface area, acidity, basicity, oxygen storage capacity) and interaction of both\cite{32,33} Several reviews\cite{34,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59} summarized the developments in the field of catalyst materials for dry reforming of methane and focused on the properties and catalytic behavior of different catalyst systems. While different active metals have been considered, most of the discussed systems can be either assigned to noble metals\cite{59} (Rh, Ru, Pt, Ir, and Pd) or base metals (Ni, Co). As mentioned above: while noble metals show good performance and stability in high temperature applications, they are considered uneconomical for large-scale applications.\cite{51,53,54,55} Investigations from Ashcroft et al.\cite{59} showed little to no coke formation can be observed over $\text{Al}_2\text{O}_3$ supported Pd, Rh, Ru and Ir catalysts at high conversion compared to quickly deactivating Ni-based catalysts which display similar initial activity. While Ashcroft et al.\cite{59} reported the highest specific rates for Rh and Ir other authors published different orders of activity.\cite{59,60} Mortensen et al.\cite{60} pointed out in their review that the respective order of activity may be significantly influenced by details of the catalyst preparation and resulting features like the dispersion, metal-support interactions and the reaction conditions. They compared experimental results from Ferreira-Aparicio et al.\cite{61} and Rostrup Nielsen and Bak Hansen\cite{60} with DFT derived orders of activity for SMR from Jones et al.\cite{62} The kinetics of SMR and DRM are discussed as similar, as has been shown by Wei and Iglesia\cite{63} and therefore the activity should as well correlate with the adsorption energies of O and C. Based on this assumption the two dimensional volcano plot by Jones et al.\cite{62} (Figure 4) shows that catalysts based on Ru and Rh are based on theoretical calculations the candidates of highest intrinsic activity for DRM. In terms of base metals, Ni and Co have proven to be the candidate metals of highest intrinsic activity. The higher adsorption energy of oxygen containing species on Co as active metal indicates that it can most likely be poisoned by oxygen, or even go through oxidation to oxidic phases, which agrees well with experimental studies on Co catalysts.\cite{64,65}
Ni is far less expensive than the noble metals Ru and Rh therefore the pareto optimum considering economic aspects and achievable activity levels. This is reflected in literature where Ni-based catalysts are the most widely studied catalysts coupled by the fact that Nickel has been the workhorse in SMR and ATR. A comprehensive overview of current findings in research on Ni-based catalysts is given by Jang et al. in their recent review, where especially properties of catalysts and their influence on the activity in DRM are discussed. Co as active metal on different supports has been comprehensively reviewed by Ruckenstein and Wang; Cobalt is discussed to display lower intrinsic activity. Weak metal-support-interactions are discussed as potential reason for that behavior. On the other hand, Co based catalysts are reported to display increased coke stability. The activity of Ni and Co-based catalysts can be further increased by the addition of noble metal dopants. Several researchers also investigated bimetallic Ni–Co catalysts to merge the high activity of Ni with the coke stability of Co-based catalysts, still results give no clear indications whether synergies can be achieved.

Strong metal support interaction (SMSI) can play an important role to achieve highly dispersed active metal sites. On the other hand, SMSI is discussed to lead to lower reducibility of the active metal of a supported catalyst and thereby reduce either the initial activity of the material or to lead to deactivation triggered by the formation of solid solutions.

In the case of DRM, Ruckenstein and Wang could prove both of these effects have relevance for Co supported on different oxides. Co supported on SrO and BaO showed only little activity, which was attributed to a strong sintering of SrO and BaO particles accompanied by encapsulation of the Co sites. Catalysts supported on SiO	extsubscript{2}, Al	extsubscript{2}O	extsubscript{3} and CaO showed good initial activity but were prone to deactivation under reaction conditions. According to the investigations of the author team MgO was the only support allowing for high activity and stability of the active metal over times of 50 h. Furthermore, Ruckenstein and Wang observed lower reducibility of the Co species on Al	extsubscript{2}O	extsubscript{3} and MgO, with Co(O)/MgO mixed oxide phases forming on MgO being very hard to reduce. The low reducibility in the case of Co(O)/MgO arises from the identical crystal structures of CoO and MgO (NaCl-type). From the observations of the authors this property is also beneficial in hindering the sintering of metallic Co-species. Guo et al. observed similar results for Ni supported on Al	extsubscript{2}O	extsubscript{3}–Al	extsubscript{2}O	extsubscript{3}–MgO and MgAl	extsubscript{2}O	extsubscript{4} under DRM conditions. While Ni/Al	extsubscript{2}O	extsubscript{3} deactivated rapidly, Ni/ MgAl	extsubscript{2}O	extsubscript{4} showed no deactivation and stable catalytic performance over 200 h. It was concluded that the strong interactions between Ni(O) and MgAl	extsubscript{2}O	extsubscript{4} prevent sintering and prevented the formation of a catalytically inactive NiAl	extsubscript{2}O	extsubscript{4} spinel.

**Kinetics of dry reforming**

Several kinetic models are discussed at present in literature as appropriate to describe the mechanism of the catalyzed DRM reaction. For the reforming over Ni-based catalysts mainly models with different modifications are discussed and have been compared and summarized by Mark et al. and Kathiraser et al. Besides simple power law models, which cannot sufficiently describe the various elementary steps of the reaction mechanism over a wide parameter range, especially the Eley-Rideal (ER) type of models and Langmuir-Hinshelwood-Hougen-Watson (LHHW) models are applied. An associated assumption made in a number of publications is that the rate-determining-step (RDS) involves the reaction of adsorbed species with other reactants from the gas phase.

A number of authors developed approaches for the kinetic description of the dry reforming reaction (DRM) where CH	extsubscript{4} and CO	extsubscript{2} are both first adsorbed on the catalyst surface prior to reaction; two possible mechanisms are currently being discussed as most relevant with regards to representative description of data obtained by various catalyst systems. Akpan et al. assumed that the methane dissociative adsorption is the RDS. The following reaction mechanism was postulated (•: unoccupied active site and O\textsubscript{ad}: lattice oxygen of support), which was validated by experimental studies over Ni/CeO	extsubscript{2}–ZrO	extsubscript{2}.

\[
\begin{align*}
\text{CH}_4 + 2\,* & \rightarrow \text{CH}_2(\,*\,) + \text{H}^\,* \\
\text{CH}_2(\,*\,) + \,* & \rightarrow \text{CH}_4(\,*\,) + \text{H}^\,* \\
\text{CH}_3(\,*\,) + \,* & \rightarrow \text{CH}_2(\,*\,) + \text{H}^\,* \\
\text{CH}(\,*\,) + \,* & \rightarrow \text{C}(\,*\,) + \text{H}^\,* \\
\text{C}(\,*\,) + \text{O}_2 & \rightarrow \text{CO}_2 + \text{O}_\text{ad} + \,* \\
\text{CO}_2 + \text{O}_\text{ad} & \rightarrow \text{CO} + \text{O}_2 + \,*
\end{align*}
\]
4 H⁺ → 2 H₂ + 4*
H₂ + Oₓ → Oₓ+ + H₂O

Becerra et al. postulated a similar model but assumed direct reaction of gaseous CO₂ with adsorbed methyl species.

CH₄* + CO₂ → CO + x/2 H₂ + *

Erdohiyi et al. reported a similar approach to the kinetic description of the mechanism for DRM over Rh/Al₂O₃, while Richard et al. described the same reaction with a simplified Langmuir-Hinshelwood mechanism, where both gaseous species are adsorbed on the surface.

More widely applied are so called Langmuir-Hinshelwood-Hougen-Watson kinetic models derived reaction mechanisms. A kinetic model built on such an approach has first been presented by Xu and Froment for the case of steam reforming of methane and has further been improved by Zhang and Verykios. Zhu et al. derived a reaction mechanism based on experimental results and conclusions made by Wei and Iglesia that involve the step-wise activation of adsorbed CH₄ and adsorbed CO₂ and oxidation of CH₄ (0 ≤ x ≤ 4) species by surface oxygen resulting from CO₂ decomposition. The formation of surface OH species and formate-type species as intermediates is considered within the mechanism.

CH₄* → CH₄* CH₄ adsorption
CH₄* + x* → CH₄* + x H* CH₄ dissociation
CO₂* + x* → CO₂* CO₂ adsorption
CO₂* + * → CO* + O* CO₂ dissociation
CO₂* + H* → COOH* + * H-assisted CO₂ dissociation
COOH* + * → CO* + OH* (3)
CH₄* + OH* → CH₃OH* + *
Oxidation of adsorbed CH₄ via OH groups
CH₃OH* + (x + 1)* → CO* + (x + 1) H*
CH₃* + O* → CH₃O* Oxidation of adsorbed CH₃
CH₃O* + x* → CO* + (x + 1) H*
H* + H* → H₂* + *

There is currently no general agreement in literature on the RDS of the DRM reaction; a summary of the state of discussion is given by Kathiraser et al. The generally most widely accepted RDS is the activation of CH₄ by hydrogen abstraction, as proposed by Zhang and Verykios, Wang and Au and Wei and Iglesia. While all the mentioned models are developed for Ni-based catalysts, it appears that they are also suitable for describing the DRM reaction kinetics over supported noble metal catalysts (Rh, Pt, Ir).

Schulz et al. compared the respective reactions pathways (Figure 5) via isotope labeled reactants in the dry methane reforming over Ni- and Pt-based catalysts. A very important finding of Schulz et al. refers to the fact that a pronounced reversibility of C–H and C–O bond formation is found. The experiments show that the initial rates for carbon dioxide conversion are higher than for methane conversion over Nickel – a fact that is attributed to the energetically more difficult methane activation through C–H activation over Nickel. For Platinum the situation is different: here the rates of conversion for methane and carbon dioxide are almost equal. Coke formation on both Platinum and Nickel occur via methane dissociation and decarbonation, yet for Nickel the Boudouard reaction is a predominant coke formation pathway (Eq. 14). Also, the observed rates of coke formation on Nickel were much higher compared to Platinum – the lower coking rates of the latter are attributed to higher gasification rates via methanation. Schulz also reports a differing mode of activation for carbon dioxide for the two metals: while over Nickel carbon dioxide is activated via dissociative adsorption, this activation mode does not occur over Platinum. For Nickel based catalysts this mode of carbon dioxide activation is also seen as the reason for the more pronounced coking tendency.

Understanding Coke formation and growth behavior of carbonaceous deposits under DRM conditions

Thermodynamics of coke formation

Understanding coke formation and growth behavior as main deactivation pathway for catalysts applied in DRM is a major
The challenge to be understood and solved. Coke can be formed by a variety of reactions including catalytic and non-catalytic pathways. Besides the generation of coke precursors and coke by non-catalytic gas-phase reactions, which will be discussed separately, three main pathways must be considered as relevant for coke formation under DRM conditions. The Boudouard reaction as carbon source based on CO disproportion (Eq. 14) is generally more favorable at lower temperatures.

\[
2 \text{CO} \rightarrow \text{CO}_2 + C \quad \Delta H_{298} = -171 \text{ kJ mol}^{-1}
\] (14)

The reduction of CO by H\(_2\) to carbon and water is favorable at low temperatures but of low relevance due to its always larger Gibbs energy, except for gas mixtures containing high H\(_2\) partial pressures.\(^{[112]}\)

\[
\text{CO} + \text{H}_2 \rightarrow \text{H}_2\text{O} + C \quad \Delta H_{298} = 131 \text{ kJ mol}^{-1}
\] (15)

Coke formation as a result of methane decomposition (methane cracking via radical pathways and subsequently methane decarbonation) on the other hand is thermodynamically favored at high temperatures.

\[
\text{CH}_4 \rightarrow 2 \text{H}_2 + C \quad \Delta H_{298} = 75 \text{ kJ mol}^{-1}
\] (16)

The consequences of these different coke forming reactions can properly be illustrated by means of CHO ternary diagrams.\(^{[109,110,111]}\) Kee et al.\(^{[111]}\) for example calculated the respective equilibria for a pressure of 25 bar and various temperatures (Figure 6). The authors defined arbitrary the coke deposition boundary by an equilibrium content of graphitic carbon of 1 ppm. Coke formation is apparently thermodynamically favored at completely “dry” reforming conditions and coke formation is predicted from thermodynamic considerations. Under dry reforming conditions Giehr et al.\(^{[112]}\) predicted that graphite formation should be the thermodynamically preferred modification of carbon deposits. Nevertheless, other carbon forms like fullerenes, amorphous and filamentous carbon are commonly reported in experimental studies,\(^{[46,63,85,113,114,115]}\) although their formation should be thermodynamically less favored. Effective carbon removal via a range of reactions

![Figure 6. C/H/O ternary diagram including limit lines for carbon deposit formation as a function of gas phase composition and temperature. Adapted from Kee et al.\(^{[111]}\).](image-url)
(gasification of carbon with water (reverse reaction of 15) or hydrogen (reverse reaction of 16), and the reverse Boudouard reaction (14)) are discussed below and from a thermodynamic point of view are effective modes of carbon removal in the temperature range were coke formation occurs; one has to take into account that most reactions allowing carbon removal are exergonic in nature\cite{112} (see Figure 7).

High pressure and temperatures above 550 °C (both of relevance for the industrial process) favor methane cracking, while lower temperatures may lead to pronounced coke formation from Boudouard reaction. Both reactions have been investigated for their respective influence on coke formation at standard and reaction conditions by Giehr et al.\cite{112} It was concluded that coke formation has its origin from the main contribution from methane cracking under the experimental conditions investigated by Giehr.

\textbf{Coke formation mechanisms – molecular precursors to coke formation}

As discussed in the previous section; as diverse catalyst candidate materials are applied by various groups in dry reforming of methane it can be expected that the governing coke formation mechanisms may be differing in nature. Sometimes even conflicting findings may arise due to differing kinetics in coking and decoking pathways that are catalyzed by the respective materials. Varying reactor geometries, test conditions and programs applied will also add to altered findings in the performance results, but have to be taken into account when comparing results head to head. The catalysts mainly worked on in literature can roughly be divided in two groups; the noble metals (like Pt) and refractory metals, especially Ni. As already mentioned above from an economic perspective base metals are of major interest for industrial applications of DRM, studies comprising platinum metals are of scientific high interest. As a second important aspect, non-catalytic reactions that proceed in the gas phase play an important role and are an often overlooked source for coke precursor formation, more specifically higher hydrocarbons, leading to subsequent pronounced solid coke formation on the catalyst. At the industrially relevant high pressures and temperatures non-catalytic gas phase reactions become of major importance in terms of coke precursor formation and have been investigated by Kahle et al.\cite{116} for the case of DRM experimentally and via modelling approaches. The team investigated coke formation over Pt-catalysts under DRM conditions (temperatures above 850 °C and pressures above 20 bar). Under these experimental conditions coke formation is observed to start at the entrance of the catalyst bed and upstream of the catalytic zone and not in the catalyst zone itself and downstream of the catalyst section. This distinct coking behavior can be related to non-catalytic homogeneous reactions in the gas phase which lead to the formation of highly potent coke precursors.\cite{117} For these gas phase reactions, a reaction pathway was originally proposed by Becker and Hüttinger,\cite{118,119} who described a methane dehydrogenation pathway followed by coupling reactions of formed radicals to higher hydrocarbons (Figure 8).

The formation of light hydrocarbons by radical recombination reactions, with resulting products such as acetylene (C$_2$H$_2$) and small olefins may be source to the formation of even heavier coke precursor species. Combination reactions of acetylene, and alternatively addition and dehydrogenation steps of small olefins like ethylene and propylene, may give rise to increasing concentration of aromatics (C$_6$H$_6$) and polycyclic aromatic hydrocarbons (PAHs)\cite{120,121} which are also highly potent coke precursors. The consequences of these findings are fundamental in nature: not only is C1 related coke build-up highly relevant, but even if present in much lower concentration in the feed, coke precursors like acetylene, small olefins and aromatics are present and any catalyst material will be subject to the consequences of their presence. The deposition of carbon through these coke precursors occurs also according to Cava et al., via condensation of the small hydrocarbons under formation of larger entities and assemblies in the gas phase.\cite{122} Kahle et al. discuss three different gas-phase reaction mechanisms as prevalent in their publication. Mechanism 1 is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.png}
\caption{Overview of coke forming reactions (orange: Boudouard reaction, catalytic CH$_4$ cracking and homogeneous CH$_4$ cracking) and removing reactions (blue: methanization, gasification and reverse Boudouard reaction) under DRM conditions.}
\end{figure}
based on a reaction scheme developed for isoctane combustion (4238 reactions), which originally stems from Lawrence Livermore National Laboratory.\cite{114} Coupling this reaction scheme to the toluene scheme by Dagaut et al.\cite{115} leads to a mechanism consisting of 8927 elementary reactions and was experimentally validated by the oxidation of toluene, the ignition of benzene-oxygen-argon mixtures, and the combustion of benzene in flames. Mechanism 2 derives from the Golovitchev group\cite{116} and consists of 690 elementary reactions and mechanism 3 is based on results from the Dean group\cite{117,118} who included the reaction pathways for aromatics and some polyaromatic hydrocarbons.\cite{119} For all three mechanisms Kahle et al.\cite{120} performed simulations for an empty reactor tube and could show that the formation of saturated and unsaturated hydrocarbons (C$_2$H$_6$, C$_3$H$_8$, C$_4$H$_{10}$, C$_5$H$_{12}$) can be explained via all three mechanisms (Figure 8). Norringa et al.\cite{121} obtained comparable results that also confirm the findings for the evaluation of the chemical kinetics of ethylene pyrolysis at 900°C. Kahle et al. further investigated the effect of feed variation, specifically variation of H$_2$ and H$_2$O partial pressure in the inlet gas. Hydrogen addition to the initial feed has a large effect on the inhibition of coke formation due to an inhibiting effect on methane pyrolysis and hydrocarbon formation (Figure 9).\cite{122,123,124,125} Water addition has a smaller but still pronounced effect on the inhibition of the non-catalytic pyrolysis pathways of methane compared to hydrogen but is still an effective inhibitor for coke formation if used in the appropriate partial pressure regime.

Coke formation in presence of a catalyst is reported to be strongly dependent on the nature of the catalyst, support material, active metal and the particle size of the active metal\cite{126,127} since different reaction pathways are possible over differing catalyst materials respective intermediates formed on the catalytic species will also differ.\cite{128} Mainly the coke formation over base metals like Ni and noble metals like Pt have been investigated.\cite{129,130,131} Coke formation over noble metals and refractory metals differs in terms of the primary coke source and absolute extent of coke formation. Schulz reports that coke formation is catalyzed on the base metal mainly via dissociation of CO$_2$ and the Boudouard reaction, while CH$_4$ dissociation is the main coke source over Pt, most probably stemming from the fact that Platinum has a higher potency for C–H activation.\cite{132} The significantly different extent of coke formation of Pt and Ni results also from higher gasification rate of carbon species; with Pt displaying a mechanism in which coke is gasified via methane formation, it appears that Ni is capable of catalyzing the reverse Boudouard reaction as discussed by Schulz et al.\cite{133}

**Growth patterns of nano-sized coke deposits on catalyst materials**

The size of supported nanoparticles of a respective active metal does not only have a major influence on the activity of a catalyst material in reforming reactions in general and espe-
cially in DRM, but also plays a major role in coke formation and coke growth mechanisms.\cite{140,141,142} Titus et al. proposed a coke growth mechanism for DRM based on TEM investigations and observations of the growth modes of coke on the catalyst candidate system NiO–MgO-ZrO\textsubscript{2}.\cite{141} According to their results coke deposition and growth on supported Nickel catalysts proceeds via a two-step process (Figure 10). In the first step a growth of multi-walled carbon nanotubes (MWCNT) with the nanoparticles of the active metal Nickel at the tip of the MWCNT can be observed. This growth mode of carbon is dislocating the Ni-nanoparticles from the support material. In the following step in the so-called “filling-in phase”, larger amounts of amorphous and graphitic layered carbon are deposited around the Ni-particles and the MWCNTs. It can be speculated that the increased surface area provided by the MWCNT leads to the formation of this less dense coke phase in the voids. It could also be shown that more active catalysts with increased Ni loading tend to show an increased final amount and overall rate of coke formation, this clearly illustrates that coke formation is a catalyzed phenomenon for this type of catalyst under observation. The mechanism described by Titus et al. captures well singular spotlight observations of other groups and can describe a range of coke patterns observed for a range of reports in literature.

Controlling coke formation: Insights from catalyst model systems

Addition of water to the feed

Steam reforming conditions favor much less catalyst coking than dry reforming conditions and therefore the addition of certain amounts of water can be considered as way to reduce coke deposits in DRM. As discussed above: for thermodynamic reasons small amounts of water, even for inlet gas compositions that are totally “dry”, will result in water being present in the outlet gas in any case, as predicted by thermodynamics. Kahle et al. investigated in detail the addition of water to the feed in DRM and showed that non-catalytic coke precursor formation can be reduced to a certain extent in comparison to completely “dry” conditions.\cite{140,146} This is in line with the fact that the formation of methyl-radicals can occur via two pathways and only the less energetically favored and therefore prominent pathway 2 is inflicted by water addition.

\[
\text{CH}_4 \leftrightarrow \text{CH}_3 + \text{H} \quad \text{Pathway 1}
\]

\[
\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 + \text{H}_2\text{O} \quad \text{Pathway 2}
\]

In presence of a catalyst, H\textsubscript{2}O addition to the feed clearly leads to an inhibition of coke precursor formation also via gasification of once formed carbon deposits.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}
\]

Gasification of coke via cyclic operation

Coke deposits can in principle be removed via the reverse Boudouard reaction in order to restore catalytic activity. This has been investigated for Ni catalysts supported on SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} by Takenaka et al.\cite{142} In their experiments methane decomposition was provoked on a Nickel based catalyst at 550 °C, which resulted in formation of carbon deposits. In a second step the coke deposits were gasified in a pure CO\textsubscript{2} atmosphere at 650 °C via the reverse Boudouard reaction. The obtained results showed that the initial catalyst activity could only be recovered for Al\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} supported catalysts; additionally, it was observed that no tremendous sintering of the Ni particles occurred. In case of Ni/SiO\textsubscript{2} it could be seen that the Ni nanoparticles were significantly enlarged through sintering through the regeneration cycle. Xu et al.\cite{143} followed similar ideas of carbon dioxide-based catalyst regeneration and investigated the regeneration of Ni/ZrO\textsubscript{2} after methane decomposition. Later Steib et al.\cite{144} could show that the regeneration can be applied after catalyst coking stemming from application of dry reforming conditions as well. In both cases no or only minor sintering of the Ni nanoparticles on the support material was observed which is attributed to the intrinsic metal support interaction between Ni and ZrO\textsubscript{2}. Steib et al. proposes a complete cyclic catalyst regeneration scheme (Figure 11) of activation-reforming-coking-regeneration-reforming-steps.\cite{145}

![Figure 10. Schematic representation of the stages of carbon growth on Ni particles on MgO on ZrO\textsubscript{2} (MWCNT: multi-walled carbon nanotubes).\cite{144} Adapted from Titus et al.\cite{141}](image-url)
The role of acidity and basicity of the catalyst material

The acidity/basicity of the catalyst may influence the catalyst activity and selectivity patterns. Acidity/basicity of a given catalyst system should therefore be extremely relevant for DRM, as most coke forming reactions can be understood as unselective reaction paths. (Highly) acidic support materials are usually anticipated as non-ideal catalyst or support materials for DRM due to the intrinsic enhancement of methane cracking by acid sites. Therefore, acidity usually is treated as a property that must be moderated to limit the latter undesired effect of coking. Basicity is in some papers treated as a desirable materials property, allowing for enhanced carbon dioxide adsorption and subsequently enhanced carbon dioxide activation. Reports that treat the topic of the influence of acidity and basicity in depth are rare, nevertheless the topic as such is of high relevance and will be discussed in the following. Ferreira-Aparicio et al. have investigated the role of acidity and basicity in DRM for catalysts with Ru supported on Al₂O₃ and SiO₂. The authors conclude from their study that surface hydroxyl groups and the capability of carbon dioxide dissociation or alternatively the capability of forming formate intermediates play a major role in the accumulation of coke forming species and the resilience of the resulting catalyst material. They propose a bifunctional mechanism triggered by surface hydroxyl groups. Das et al. concluded in their investigations of Ni supported on modified silica and alumina that a moderate acidity-basicity is best for a stable and active DRM catalyst.

The above-mentioned observations are contrasted by the findings of Titus et al. who investigated the basic and acidic site density of Ni/MgO-ZrO₂-based catalysts. Titus et al. showed that the basic and acidic site density is balanced and negligible in absolute concentration for materials treated prior to catalytic testing at temperatures relevant to the temperature corridor that DRM is usually performed at. In their results they showed that acid and base site density over MgO/ZrO₂ is also independent of the MgO content, beyond a certain threshold of MgO. From that finding it was concluded that despite previous reports the basic site density of different compositions in the model system NiO-MgO-ZrO₂ has only a minor or even negligible effect on the stability under DRM conditions and that rather a higher Ni dispersion, due to stronger interactions between MgO and NiO, is responsible for an improved stability towards coking.

Alternative approaches apart from oxide-based carrier materials should be mentioned in this context. Such materials that due to their inherent carbon dioxide adsorption properties have proven to show enhancement in low temperature carbon dioxide conversion have not been applied in dry reforming – but could give a perspective beyond oxides as support materials.
Controlling coke formation through stabilization of nickel nanoparticles on hexaaluminates: Understanding the reduction mechanism of the active metal Ni

Roussière et al. investigated Ni-hexaaluminates ANiAl_{12-y}O_{19.6} (A = Ba, Sr and La and y = 0.25, 0.5, 1) as catalyst candidate materials in DRM. These materials are of interest since hexaaluminates are known for their resilient nature: they maintain their specific surface areas even under drastic reaction conditions like high temperatures of 1300°C and hydrothermal load. In addition, hexaaluminates stabilize Ni nanoparticles and prevent their sintering. Metallic Ni nanoparticles form under reducing conditions from Ni-containing hexaaluminates, are considered as active phase in DRM. The deactivation of Ni- or Co-based catalysts is discussed to be mainly due to coking and not through sintering and loss of active surface area, but especially the latter effect is important to be considered, since ensembles of large Ni particles are reported to be more prone to coking. In depth investigations of different Ni hexaaluminates show that the activity and stability of the catalyst can be related to the size and texture of the Ni nanoparticles. While materials with large and/or unsupported Ni nanoparticles are highly active, they tend to deactivate rapidly since the coke selectivity is enhanced. Ni hexaaluminates show decreased activity and increased coking after calcination at higher temperatures beyond 1300°C, which is in good agreement with reduced stabilizing surface defects and therefore larger particles. The more stable catalyst materials generally are found for lower Ni content associated with a high Ni dispersity and a strong textural growth of Ni nanoparticles. Especially the textural growth is related to a strong interaction of the Ni nanoparticles with the support material. Roussière et al. developed a “coupled electron defect migration reduction mechanism” to describe the migration of Nickel in the oxidic hexaaluminate material and developed a rationale for the textural growth of Ni nanoparticles during the reduction on hexaaluminate materials (Figure 12).

The mechanism can be described in three steps.

- In a first step oxygen is removed from the mirror planes (MP) of the hexaaluminate. A hypothesis which is in line with the higher oxygen diffusion within the mirror plane and the therefore higher reducibility of the oxygen.
- In a second step Ni²⁺ cations in the spinel block (SB) migrate into the mirror plane to the surface defect sites (i.e. grain boundaries), where they are reduced to Ni⁰ on the outer surface of the grain.
- Ni⁰ nanoparticles are most probable to form at defect sites next to steps and edges of the material. These nucleation centers facilitate growth and the prevailing growth pattern of the Nickel particles are tetrahedral particles which can be shown in STEM images.

The form of the nanoparticles is reasoned to originate from the fact that the hexagonally dense packing of oxygen on the hexaaluminate surface induces the specific growth pattern of metallic Ni crystallizing in an fcc lattice. This growth pattern allows the formation of Ni–O bonds at the grain boundary.

**Decoking mechanisms via redox-catalysis on Co/y-Al₂O₃**

Although reported as specifically less active in DRM compared to Ni catalysts, Co-based catalysts show superior stability towards coke formation. This is discussed as being related to an additional decoking mechanism catalyzed by Co-containing species. Based on thermodynamic calculations and steady state reactor simulations Giehr et al. could show that while Ni is reduced over the whole length of the reactor, the oxidation state of cobalt in the model compound CoAl₂O₄ strongly depends on the axial position within the reactor and the respective spatial partial pressure regime. In the first part of the reactor cobalt is most likely to be oxidized by CO₂ or H₂O.

![Figure 12](https://www.chemcatchem.org)
and spinel structures are the predicted reaction products (Eq. 23).\cite{165}

\[ \text{Co} + \text{Al}_2\text{O}_3 + \text{CO}_2 \rightarrow \text{CoAl}_2\text{O}_4 + \text{CO} \]  

(23)

Besides a Langmuir Hinshelwood mechanism that can serve as a mechanistic approach for the reverse Boudouard reaction over reduced Co\textsuperscript{0}, the CoAl\textsubscript{2}O\textsubscript{4} as a mixed metal oxide can supply oxygen in a MvK-mechanism and oxidize carbon deposits to CO and CO\textsubscript{2} (Eq. 24). The reaction of MAI\textsubscript{2}O\textsubscript{4} with solid carbon (Figure 13) is discussed in the literature as being thermodynamically favored.\cite{112}

\[ \text{CoAl}_2\text{O}_4 + \text{C} \rightarrow \text{Co} + \text{Al}_2\text{O}_3 + \text{CO} \]  

(24)

Giehr describes that carbon deposit formation is observed in the first reactor half through methane cracking; a fact that can still be brought in good agreement with the enhanced coke stability. Giehr et al. suggest a catalytic cycle for carbon deposit removal,\cite{112} which explains the superior stability of Co based mixed metal oxides like Cobalt Spinel.\cite{112} Similar coke removal mechanisms have been proposed for different catalyst materials by Theofanidis et al.\cite{166,167} (Fe–Ni/MgAl\textsubscript{2}O\textsubscript{4}) and Kim et al.\cite{168} (Ni–Ce mixed oxide catalysts).

Conclusions

Coke formation is the main reason for deactivation in dry reforming of methane under industrially relevant conditions due to the necessary high temperatures (thermodynamic) and pressures (economical). Therefore, understanding coke formation is an important factor for the development of novel coke resilient catalysts systems with high activity and stability. The sources of coke under dry reforming conditions are twofold: firstly coke can be formed directly on the catalyst surface based on reactions like methane cracking and the Boudouard reaction and secondly coke formation on the catalyst surface can be driven by coke precursors derived from gas-phase coke precursors (acetylene, olefins and aromatics), which can also be deposited on the catalyst. The actual coke sources, in case of catalytic coke formation, depend on the reaction conditions and on the respective active metal since the reaction pathways vary for noble and base metals and the nature of the catalyst support. The growth of carbon on the catalyst surface is discussed to proceed via the formation of carbon nanotubes underneath the metal particles and consecutive filling of the voids in-between.

In recent years several strategies have been developed to come up with new concepts of multifunctional catalyst materials that can cope with coke formation: either by the prevention or system inherent removal of coke deposits under reaction conditions. The addition of water to the feed is the widest applicable strategy, which has, in case of small water amounts, only limited influence of the final desired syngas ratios. More catalyst specific ways to control coke formation have been derived for Ni-based model systems where especially strong metal support interactions are important, either to maintain small nanoparticles during reaction or after regeneration procedures or to stabilize small nanoparticles right from the beginning. A more specific way to reduce coke formation could be shown over Co-based catalysts, where a Mars-van Krevelen mechanism enables a de-cooking process. Overall theoretical and experimental model systems help to understand the challenge of coke formation under dry reforming conditions and demonstrate ways to maintain high activity over prolonged amount of time. Several approaches are discussed in literature, which all together gives a conclusive picture of the obstacles that are crucial and must be overcome in order to limit the coking on catalyst materials in the field of dry reforming.

Figure 13. Proposed reaction scheme of combined Langmuir Hinshelwood and Mars-van Krevelen pathway over Co species.\cite{112} Graphics adapted from [112].
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Keywords: dry reforming · carbon deposits · industrially catalysis · high throughput experimentation · multi-scale modelling

Getting in formation: Coke formation is the main reason for deactivation in dry reforming of methane under industrially relevant conditions due to the necessary high temperatures (thermodynamic) and pressures (economical). Therefore, understanding coke formation is an important factor for the development of novel coke resilient catalysts systems with high activity and stability.