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Heterogeneous chemical reactions—A cornerstone in emission reduction of local pollutants and greenhouse gases

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Abstract

The current state and challenges of advanced experimental and modeling methods for a better understanding of heterogeneous chemical reactions are discussed using examples from developing and future technologies in the area of emission reduction of local pollutants and greenhouse gases. *In situ* and *operando* experimental techniques using laser and X-ray absorption spectroscopy, for instance, are able to resolve spatial and temporal concentration and temperature profiles in the near-wall gas phase, the interphase and inside the solid bulk. They have been exploited for a better understanding of the interaction of chemical reactions and transport processes. The experimental elucidation of chemical conversion on the microscopic scale leads to elementary step-like surface reaction mechanisms. The microkinetic description of gas-surface reactions is still challenging due to the complex influence of the modification of the solid material itself on the microscopic scale during the chemical reaction, which is caused by intrinsic materials' modifications due to adsorbed species and temperature variations. Furthermore, transient inlet and boundary conditions on the reactor scale have a strong impact on the material and reaction rate. In addition to thermochemical reactions, an additional complexity comes into play with electrochemical ones. This paper will discuss heterogeneous chemical reactions in the light of emerging technologies such as emission control of natural gas and hydrogen fueled engines, use of CO₂ in chemical (methanation, dry reforming) and steel industry (off-gas reforming), hydrogen production by pyrolysis of methane, small-scale ammonia synthesis and use, and recyclable carbon-free energy carriers. Hence, this article will also reveal a new playground and the potential of methods, know-how, and skills of the combustion community to significantly contribute to the solution of climate-change relevant challenges.

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Keywords: Heterogeneous chemistry; Reaction mechanisms, Emission control; Hydrogen; Carbon capture; Negative emissions

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1. Introduction

Heterogeneous chemical reactions are found in an uncountable number of natural and technological processes. The chemical species involved are present in at least two phases such gaseous, liquid, solid, and molten phases, with chemical reactions occurring in these phases as well as on their interphases. This paper lays particular focus on reaction kinetics of gas-solid interactions, which are present in many combustion-related applications such as catalytic combustion [1–5], combustion in porous media [6–10], pyrolysis [11–16], reforming processes [17–20], coking and soot formation [21–23], chemical vapor deposition [24,25], fuel synthesis [26–28], fuel and electrolysis cells [29–32], electrochemical synthesis [33–35], and emission control [36–41].

Heterogeneous reaction kinetics usually interfere with mass and heat transport processes over a broad range of time and length scales, which can be demonstrated using bundles of tubular fixed bed reactors as an example (Fig. 1). These reactors are widely used in chemical industry, especially for reactions with large heat release or supply. The mixture flows from top to bottom through a bundle of tubes where the conversion takes place (Fig. 1a). The tubes are bathed by a fluid (gaseous or liquid), which is guided around the tubes in a crossflow arrangement. This fluid serves as a

cooling or heating agent depending on the type of reaction (exothermic or endothermic). The tubes (Fig. 1b) are filled with catalytic particles. In each tube, the transport of momentum, energy, and chemical species occurs not only in flow direction, but also in radial direction (Fig. 1c). Channeling in the near-wall region affects the radial heat transfer; radiation plays a significant role at higher temperatures; local kinetics influence local transport phenomena, and vice versa; reaction rates are limited due to film diffusion. The catalyst material is often dispersed in porous structures like washcoats or pellets (Fig. 1d). Mass transport in the fluid phase and chemical reactions are superimposed by diffusion of the species to the catalytically active centers in the pores. The temperature distribution depends on the interaction of heat convection and conduction in the fluid, heat release due to chemical reactions, heat transport in the solid material, and thermal radiation. In this context, periodic open cellular structures (POCS) technically realized by 3D printing have been recently drawn a lot of attention in order to optimize heat transfer and heterogeneous reaction rates [42–45].

The chemical reaction itself takes place at active sites on the inner surface of the porous catalyst structure (Fig. 1e). Although this paper primarily discusses heterogeneous reaction kinetics, the interaction with the surrounding fluid flow is always

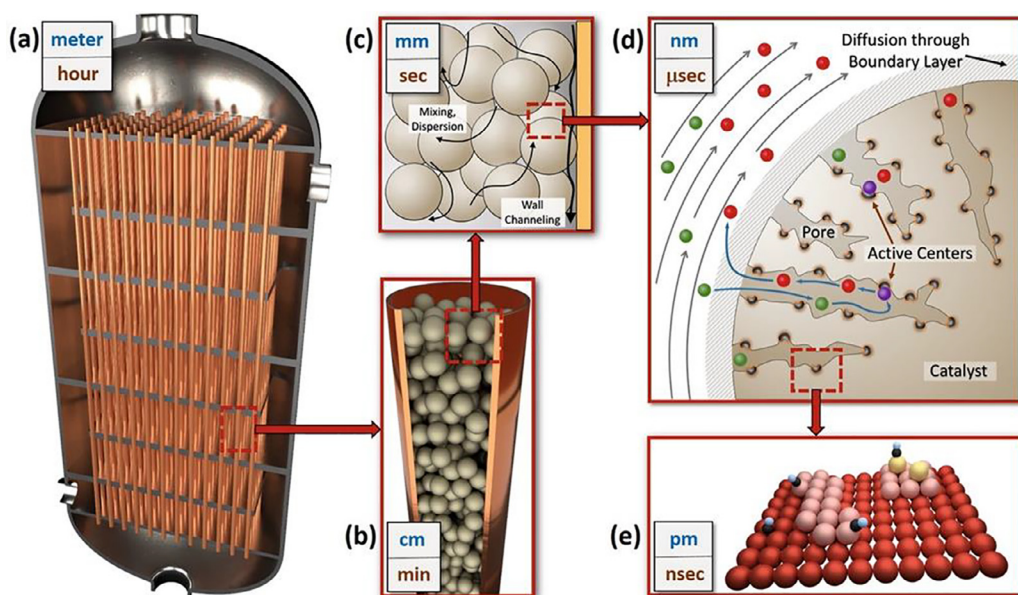


Fig. 1. Typical length (blue text) and time (brown text) scales in a catalytic bundled tubular packed bed reactor. Reprinted with permission from [46]. Copyright 2018 Springer Nature.

present as well since homogeneous reactions in the fluid may interfere with the heterogeneous chemistry.

In future, the processes described above will more often interfere with electrical processes due to electrification of the chemical industry and other sectors [47]. In case of endothermic processes such as catalytic steam and dry reforming using CO_2 as well as pyrolysis and deposition of solid carbon, the solid (catalytic) particles could serve as electron conductor and the bed could be heated resistively. Along these lines, electrochemical reactions as another class of heterogeneous reactions need to be mentioned. In fuel and electrolysis cells, electrochemical reactions interact with heat and mass transport (diffusion, flow through electrode channels) [29,48]. In high-temperature fuel cells such as solid-oxide cells fueled with non-only hydrogen fuels, thermochemical reactions will occur on metal electrodes in addition to the electrochemical conversion. Also, in co-electrolysis and even more in electrochemical synthesis of chemicals, the interaction of electro- and thermochemical heterogeneous reactions matter and need to be understood and modeled. Although this paper focuses on thermochemical reactions, the significance of a better understanding of simultaneous thermo- and electrochemical kinetics is expected to increase tremendously in future.

Despite a global consent on the demand for ubiquitous electrification, the conversion of electric energy into chemical energy carriers offers genuine opportunities, no matter whether the latter ones serve as temporary energy storage or as starting point for base chemical production. In particular, power-to-hydrogen [49] and power-to-methane [50] deserve to be mentioned in this context. Such power-to-gas (P2G) processes involve the production of sustainable H_2 followed by a methanation step in which CO and/or CO_2 react with H_2 to form synthetic natural gas. Here, both electrochemistry and thermochemistry interact again, now *via* system integration and heat recirculation.

Heterogeneous reactions in particular play a key role in current and future technologies for emission reduction of local pollutants and greenhouse gases. Without the claim of any completeness, the objective of this article is to present highly interesting advanced experimental methods for the investigation of heterogeneous chemical reactions. Furthermore, it will be discussed how these methods lead to a better understanding on the microscopic level. This information then results in models describing the kinetics of heterogeneous chemical reactions. The challenges of the microkinetic description of heterogeneous reactions, in particular gas-solid reactions, will be considered. At the microscopic scale, the associated modeling demands arise from the impact of *operando* bulk and surface modifications of the solid material itself, which is caused by adsorbed species or

temperature effects. In addition, transient inlet and boundary conditions on the reactor scale influence the reaction rate. Aside from methanation mentioned above, we will discuss emerging technologies such as emission control of natural gas and hydrogen fueled engines focusing on the exhaust-gas aftertreatment of CH_4 and NO_x , respectively, dry reforming for syngas production in chemical and steel industry, hydrogen production by pyrolysis of methane, and recyclable carbon-free energy carriers such as ammonia, borohydrides, and reactive metals, in particular iron (oxides).

Hence, this article will also reveal a new playground and the potential of methods, know-how, and skills of the combustion community to significantly contribute to the solution of climate-change relevant challenges. Embedded in a holistic approach comprising kinetic testing, modeling, theoretical considerations and characterization, the design of novel catalysts and reactors typically involves numerous experimental and computational methods that will be described in brief in the following Sections 2 and 3 while Sections 4 to 7 are structured along the technologies mentioned above.

2. Advanced experimental methods

Nowadays, there is a huge variety of experimental techniques and laboratory setups for the investigation of chemical kinetics of heterogeneous chemical reactions reaching from simple end-of-pipe (inlet/outlet streams) measurements of chemical conversion in tubes filled with solid material such as catalysts to temporally and spatially resolved observations of concentration profiles in the fluid and bulk phase of the chemical reactor. This section focusses on some of the recently evolving techniques that are especially suitable to study the kinetics of heterogeneous reaction systems in operation under transient conditions, i.e., the dynamics of the interaction of the surrounding fluid flow with the chemically active surface matters. However, for a comprehensive description of the standard tools, reference is given to textbooks and review articles [51–56].

2.1. Surface and bulk characterization

X-ray-based methods are invaluable techniques for profound *ex situ*, *in situ* and *operando* characterization of both surface and bulk of heterogeneous catalysts and can hereby provide insights on the micro, meso, and macro scale [57]. X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS), for instance, are powerful tools for monitoring the electronic state of catalyst samples (Fig. 2) and were recently used to capture the interface dynamics and noble-metal support interactions in single-atom Pt/CeO₂ [58] and Pd/CeO₂ [59] catalysts that are typically applied in the field of emission control. Transfer of such fundamental

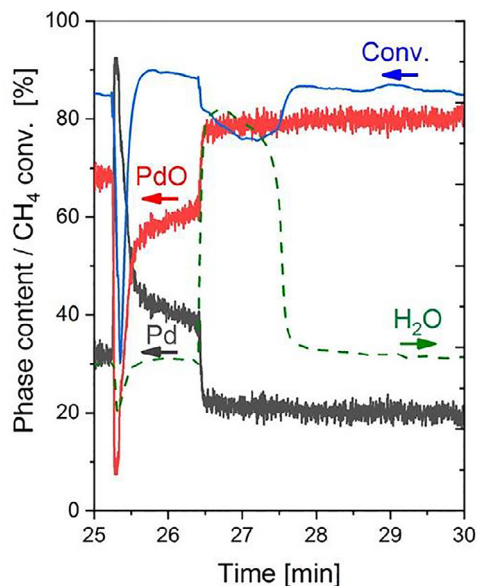


Fig. 2. Operando XAS allows to directly correlate the electronic state of a Pd/Al₂O₃ catalyst during methane oxidation with the dynamic operation conditions. Adapted with permission from [64]. Copyright 2021 American Chemical Society.

insights to real-world applications can contribute to optimal utilization of expensive and scarce noble metals, which is a key aspect in any commercial process that relies on heterogeneous catalysis, especially since the dynamic restructuring of supported metal nanoparticles can tremendously change the catalyst's behavior [60]. Equally important, the synergetic interplay in bimetallic materials like NiCoO catalysts for dry reforming of methane (DRM) or Ni-Fe-based CO₂ methanation catalysts can be understood and tuned when applying XAS in combination with X-ray diffraction (XRD) or X-ray emission spectroscopy (XES) [61,62]. Observing the dynamic structural changes of such bimetallic formulations during operation under realistic conditions does not only provide guidance in designing novel catalyst materials but also improves the mechanistic understanding that is crucial for microkinetic model development. Furthermore, recent advances in hard X-ray ptychographic computed tomography (PXCT, cf. Section 2.3) allowed three-dimensional insights into the coking of Ni/Al₂O₃ catalysts [63].

2.2. Temporal-spatial analysis and resolution of the fluid phase

The inexpensive capillary sampling techniques became popular for measuring spatial profiles in flow reactors including porous and channel-like structures *in situ* [65–67]. In this technique, a small

amount of gases is sucked into a very thin capillary, which is moved through the reactor and hence provides species profiles and elucidates reaction sequences, even though their interpretation has to account for the impact of the capillary on the flow field [68] and transient processes cannot directly be studied.

Non-invasive laser-based techniques allow the *in situ* gas-phase species measurements over catalysts with high spatial and temporal resolution. The pioneering work by Mantzaras [3] introduced planar laser-induced fluorescence (PLIF), often combined with Raman spectroscopy, to the field of catalytically supported combustion studying the interaction of heterogeneous and homogeneous reactions in laminar and turbulent flow fields near walls as exemplary depicted in Fig. 3. They also frequently used their detailed experimental observations to evaluate elementary-step reaction mechanisms [69]. Recently, PLIF was also applied to resolve transient species profiles over emission control catalysts in slim channel flows [70].

OH-LIF imaging using a novel laser scanning technique combined with time-resolved diffuse backlight-illumination (DBI) was recently used to study the transition from single to group coal particle combustion [71,72], a technique that might be of interest for other high-temperature heterogeneous oxidation processes as well. Moreover, tunable diode laser absorption spectroscopy (TDLAS) recently allowed for temporally-resolved 2D reconstruction near surfaces, such as in test rigs, to study emission control by selective catalytic reduction (SCR) [73].

2.3. Monitoring in porous structures

Porous solid structures are widely used to conduct heterogeneous chemical reactions during the increase of surface-to-volume ratios such as in fixed bed reactors, washcoat layers or electrodes and membranes. Spatial resolution techniques meanwhile support the direct observation of the porous structure on the macro and microscale as shown in exemplary Fig. 4. For instance, PXCT can provide quantitative information on the structure, size distribution, and shape of pores with a 3D spatial resolution close to 50 nm [75].

Moreover, complex washcoat pores are often tomographically reconstructed from focused ion-beam scanning electron microscopy (FIB-SEM) measurements; the resolved structures are then the basis for numerical simulations of the interaction of chemical kinetics and diffusion in the porous catalysts [76].

Finally yet importantly, nuclear magnetic resonance (NMR) offers the possibility to monitor local transport phenomena of gas-phase reactions inside opaque structures *in situ* [77], even at high temperatures [78].

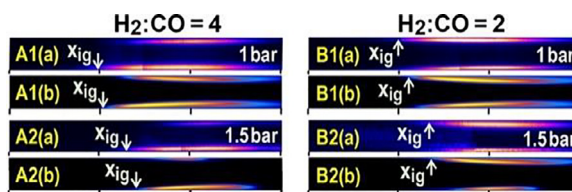


Fig. 3. PLIF-measured (a) and computed (b) OH distributions along a channel of 300 mm length during homogeneous ignition of $\text{H}_2/\text{CO}/\text{O}_2/\text{N}_2$ mixtures (flow from left to right; arrows marked x_{ig} denote homogeneous ignition positions). Adapted with permission from [74]. Copyright 2020 Elsevier/The Combustion Institute.

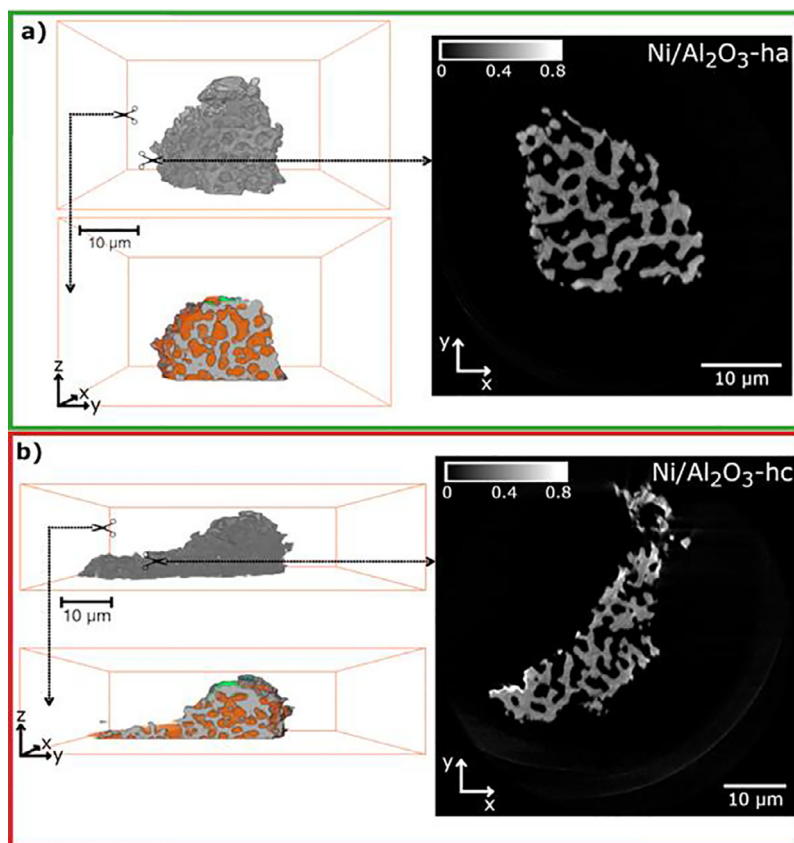


Fig. 4. PXCT of (a) an activated catalyst ($\text{Ni}/\text{Al}_2\text{O}_3\text{-ha}$) and (b) of an artificially coked catalyst ($\text{Ni}/\text{Al}_2\text{O}_3\text{-hc}$). Adapted with permission from [63]. Copyright 2021 Wiley-VCH.

3. Modeling and numerical simulation

Progress in combustion and energy sciences indispensably relies on mathematical models both for designing technical devices and processes as well as their optimization and control. In the last decades, the community moved from traditional empirical to mechanistic models that offer analysis and extrapolation capabilities. Full-blown multiscale reaction models that account for physical transport through 3D computational fluid dynamics (CFD) and integrate reaction mechanisms at the level of first-principles microkinetics have become standard tools promising higher reliability and interpretability

but also leading to steeply increasing computational costs. In addition, advanced multi-functional materials, which often show complex and dynamic chemical interactions between chemically and morphologically different active centers when operated under transient inlet and boundary conditions, call for new concepts of modeling heterogeneous kinetics. Hence, today we see two opposite trends in mathematical modeling: On the one hand more and more complex models are included into numerical simulations to describe the underlying physical and chemical elementary processes in greater detail, on the other hand data analysis and machine learning is applied to speed up simulations and development

processes, often leading to rather generic models at the cost of physical interpretation.

3.1. Modeling the heterogeneous reaction rate

The rate of a heterogeneous chemical reaction can be expressed by an arbitrary function of reactants' concentrations and temperature at the interface. In case of heterogeneously catalyzed gas-phase reactions, these *lumped* reaction rates can be derived from end-of-pipe measurements and are often based on catalyst mass, catalyst volume, reactor volume, or catalyst external surface area. The implementation of this microkinetic approach into reactor simulations is straightforward. However, it cannot account for the complex variety of phenomena, and extrapolation as well as model-based system optimization are very limited; the rate parameters must be evaluated experimentally for any variation in material and operating conditions.

The state-of-the-art modeling of gas-solid interactions, also extendable to include liquid and molten phases, is based on the mean-field approximation, in which the surface chemistry is treated by rate equations [79–82]. The state of the active surface is represented by mean values with respect to the spatial resolution of the surrounding flow field, i.e., the local (molar) surface reaction rate (Eq. 1) is calculated from the local temperature and concentrations of species in the adjacent fluid flow and of species adsorbed on the surface using an elementary-step like reaction mechanism.

$$\dot{s}_i = \sum_{k=1}^{K_s} v_{ik} k_{f_k} \prod_{j=1}^{N_g+N_s+N_b} c_j^{v_{jk}} \quad (1)$$

Deposition, storage, and ablation of material, growth and shrinking of the surface material, phase transition, and various adsorption sites can be considered within this concept as well. The rate expression (Eq. 2) can include functions accounting for energetic variations of the surface. This concept was first computationally realized in the CHEMKIN software package [80] and is today available in many multi-purpose kinetics and CFD codes [83–85]. The crucial issue of thermodynamic consistency of the microkinetics of surface reaction mechanisms has meanwhile also been addressed sufficiently [86,87].

Variation of the activity of the solid surface, for example due to aging-related dispersion reduction by sintering of active nanoparticles or due to the growth of active surface area by re-dispersion and by material deposition, can be modeled by local and temporal adaptation of the surface site density and/or active catalytic surface area describing the number of available adsorption sites [88].

$$k_{f_k} = A_k T^{\beta_k} \exp\left[\frac{-E_{a_k}}{RT}\right] \prod_{i=1}^{N_s} \exp\left[\frac{\varepsilon_{ik} \Theta_i}{RT}\right] \quad (2)$$

However, a wide variety of phenomena of heterogeneous reactions cannot adequately be handled by the mean-field approximation such as the interaction of diffusion and reaction of adsorbed species on the active surface, so-called spillover effects, i.e., adsorption of different species on (different) adsorption sites/active materials and their diffusion on the surfaces and/or support materials and interaction on other solid phases or their interfaces. Whenever those lateral interactions or lattice defects matter for the reaction rate, other modeling approaches such as kinetic Monte-Carlo simulations [89–92] are required.

Also, the inclusion of dynamic variations of the bulk material, for instance oxidation and reduction of a catalyst during operation, is rather challenging. Therefore, the future methodological development of dynamic microkinetic models should allow for prediction of the reaction kinetics taking into account the spatial and transient modifications of the catalyst/reactive solid itself, i.e., the varying electronic, structural and morphological material states need to be introduced into the rate equation. Variation of surface coverages and surface site densities alone are not sufficient because these material modifications may alter the reaction pathways. Therefore, the mechanistic aspects of the model depend on structural changes of the catalyst, e.g. re-dispersion and morphological changes of the catalyst particles during oxide phase formation, poisoning, deactivation or other related factors, and need to take into account such parameters as oxidative potential of surrounding gas flow and surface coverages of co-adsorbed species. The simple approach would be to interpolate between different mean-field models for differently sized particles and oxidation states, e.g., as recently tried for methane oxidation over Pd/PdO catalysts [93–95]. However, completely new concepts may be needed to account for the complexity of the dynamics of the materials under *operando* conditions. Such *dynamic* models should enable sufficiently fast *on-the-fly* recalculation of the thermodynamic and kinetic parameters of the reactions. In this respect, the use of the simpler empirical and semi-empirical methods for parameter estimation may even have advantages over DFT-based models especially for complex industry-relevant systems, at least for now.

Data derived from density functional theory (DFT) are increasingly used as the basis for the development of detailed heterogeneous reaction mechanisms due to the availability of easy-to-use electronic structure codes. Although modern DFT functionals are reliable for adsorbate thermochemistry and kinetics within a given uncertainty range, the user needs to prioritize intermediates and transition states, which means the simulation results also reflect the user's expectation [96,97]. Nevertheless, DFT simulations today are a very powerful tool for a better understanding of gaseous

molecules with and on surfaces and are the basis of many multi-scale modeling studies [98]. Recently, the DFT-derived energetics by van den Bossche and Grönbeck [99] was used as basis for the establishment of a surface reaction mechanism of methane oxidation over PdO [95], a system that has been studied for many years in the area of catalytic combustion and emission control [100,101]. However, the kinetic model had to be extended in order to capture the instant water deactivation that is highly significant for emission control applications [94], which points to the dilemma of the *uncontrolled* use of DFT data for modeling technical catalysts: DFT simulations are conducted for model systems for a rather limited range of operating conditions. The technical catalyst, however, is much more complex, exhibiting a wide variety of facets, structures, sizes, chemical states (oxidation, coverages, blocking) and it is exposed to varying gas-phase concentrations and temperatures, which lead to *operando* modifications of the catalytic material itself. In the case of methane combustion over Pd, hysteresis behavior is observed due to Pd oxidation and reduction and during operation deactivation occurs due to blocking of active sites by hydroxyl groups and sulfur. Hence, DFT data provide very useful insight into structures of adsorbed species, principal reaction paths, and energy barriers. The direct transfer of the kinetic data into a microkinetic model describing a technical system has to be taken with care.

Therefore, approaches were developed, in which uncertainties of the DFT data are methodologically exploited for the development of surface reaction kinetics. Kreitz et al. [102], for instance, used a global uncertainty analysis (GUA) in combination with experimental data for developing microkinetics for CO₂ methanation over Ni catalysts. Here, a structure-sensitive model was developed that accounted for uncertainties in the DFT-derived model parameters.

Today, the concept of rate equations using elementary-step-like reactions and the mean-field approximation is the approach of choice for the numerical simulation of technical devices with complex heterogeneous kinetics because it can rather easily be integrated into complex CFD simulations and is based on the molecular chemical processes. Aside from conventional finite volume Navier-Stokes CFD simulations, Lattice Boltzmann simulations are also coupled with surface reaction kinetics [103,104].

Although the progress of advanced experimental and theoretical methods can help to further improve the quality of rate parameters, they also reveal the limitations of this concept, in particular when lateral interactions, transient modifications of the bulk material with internal gradients on the nanometer scale, and structure-sensitivity determine the chemical reaction rate. Eventually, a novel or at least significantly extended concept is

needed for the calculation of the heterogeneous reaction rate to better account for the molecular behavior and *operando* materials' modifications.

3.2. Generation of microkinetic mechanisms

Nonetheless, the development of a reliable surface reaction mechanism based on the mean-field approximation already is a challenging process following an iterative procedure (Fig. 5): First, a tentative reaction mechanism can be proposed based on experimental surface science studies, on analogies to gas-phase kinetics and organo-metallic compounds, and on theoretical studies such as DFT, Molecular Dynamics and kinetic Monte-Carlo simulations, linear scaling relations [105] as well as semi-empirical approaches such as the unity bond index-quadratic exponential potential (UBI-QEP) method [106]. UBI-QEP can be combined with variational transition state theory (VTST) and two-dimensional collision theory to derive self-consistent mechanisms [107].

Although basing the development of microkinetic mechanisms on DFT data has become very popular, the pre-assumptions, simplifications, uncertainties, and the computational efforts of DFT calculations should be taken into account. Obviously, DFT is a very powerful tool, however, the question remains whether the DFT results are really more useful than those obtained by using the UBI-QEP approximation to get an initial guess for a mean-field model. The numerical effort for UBI-QEP is nearly zero, whereas the set-up of an initial parameter set for a surface reaction mechanism still requires days or weeks when using DFT. Thus, for fine-tuning the parameters to a non-perfect real-world system this empiric approach may be the faster choice, in particular if the catalyst itself exhibits severe modifications during operation.

Since this mechanism should include all possible paths for the formation of the chemical species under consideration in order to be "elementary-like" and thus applicable over a wide range of conditions, the quality of the mechanism also reflects the chemical knowledge and intuition of its constructor and obviously contains bias and uncertainties. The tentative mechanism and its associated data need to be evaluated by numerous experimentally derived data, which are compared with theoretical predictions based on the mechanism. Obviously, the basis for reliable models are reliable experimental data. The recommended guideline for the experimentalists is to collect as much information as possible with as few non-microkinetic effects as possible. Thus, simple reactor configurations such as a stagnation flow over homogeneous zero-dimensional surfaces, isothermal packed beds and simple channel flows for washcoated systems are often the reactors of choice. Whenever possible, spatially resolved data are preferred over end-of-pipe data. The tremendous progress concerning ex-

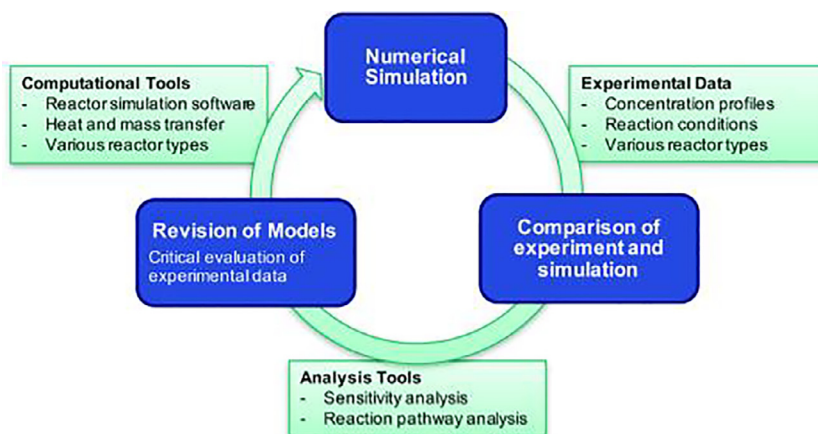


Fig. 5. Iterative process for developing detailed reaction mechanisms. Reprinted with permission from [108]. Copyright 2018 Royal Society of Chemistry.

perimental techniques to derive microkinetic data and to understand the impact of mass and heat transport on kinetics has already been discussed in section 2 and is described in many articles such as [3,65,109–112].

Consequently, for the simulations of the laboratory reactors, appropriate models for all significant mass and heat transport processes are required in order to evaluate the intrinsic kinetics and not to introduce bias due to the use of inappropriate models for the numerical simulation of the lab reactor behavior. Some crucial points are effects of the flow field, in particular with respect to turbulence, internal and external mass transfer limitations, and hot spots in exothermic reactions. In subsequent revision steps, the mechanism is iteratively refined and compared to the experimental data again. Ideally, the experimental data for the given chemical system should be numerous (varying operating conditions, different types of lab reactors, results from different researchers) so as to span a sufficiently large range of different conditions in order to reach a reliable result. An important aspect of the revision process is ensuring thermodynamic consistency. Key steps in improving the microkinetic scheme are the analyses of the reaction flow, the sensitivity of kinetic parameters [113], and the degree of rate control [114] leading to the uncertainties in the kinetic scheme, for which refined experiments and theoretical simulations are needed. This approach for the generation of microkinetic mechanisms based on detailed experimental and numerical information on the given chemical system has been used very successfully for homogeneous reaction mechanisms in the combustion community for decades and has meanwhile also become state-of-the-art for heterogeneous reactive systems.

As example methanation over Ni-based catalysts is given again, a chemical system being es-

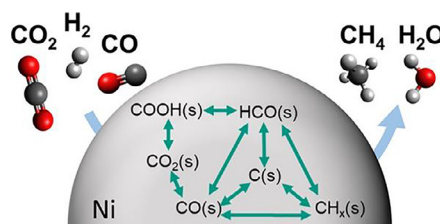


Fig. 6. Sketch of the major reaction paths in CO_2 and CO methanation over Ni-based catalysts. Reprinted with permission from [115]. Copyright 2021 American Chemical Society.

sential for power-to-gas processes with electrolysis-sourced hydrogen. Analyzing 20 different experiments from several groups, conducted in different reactors, using powder and coated monoliths as catalysts, under varying conditions, a microkinetic scheme of 49 reactions among 19 species could be established for the description of CO_2 as well as CO methanation [115], whose major reaction paths are shown in schematic Fig. 6.

An alternative approach for generating a reaction mechanism that requires less expertise and intuition and can hopefully reduce the problem of incompleteness and bias is the automatic generation of reaction mechanisms by computer-proposed and computer-evaluated elementary reactions [116,117]. The automatic reaction mechanism generator (RMG) by the Green group [118], originally developed for gas-phase pyrolysis, has meanwhile been extended to include reactions on surfaces as well [119]. A large set of elementary surface reactions with associated thermodynamic properties for the adsorbates and parametrized rate coefficients is automatically proposed by the software (RMG-CAT) that then selects the ones

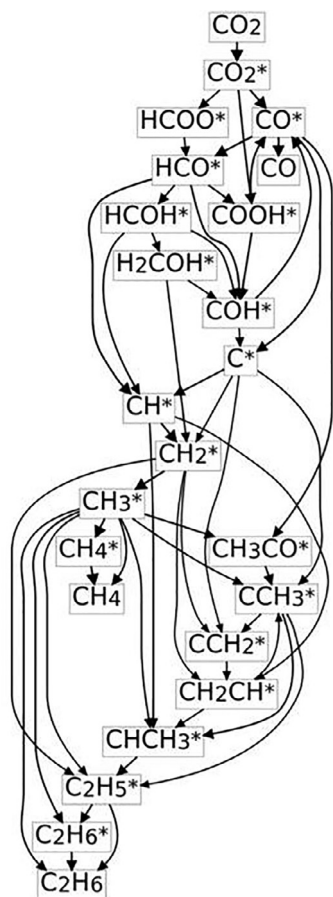


Fig. 7. Constrained RMG-generated mechanism (5000 RMG runs, 35 species/150 reactions) for CO_2 methanation over Ni-based catalysts. Adapted with permission from [120]. Copyright 2021 American Chemical Society.

with those species that have a sufficiently high formation rate. The method was successfully applied for dry reforming of methane over Ni by Goldsmith and West [119], finding the same set of elementary reactions as in a previously compiled microkinetic mechanism [87]. The automatic generation of reaction mechanisms needs to account for structural uncertainties due to missing reactions and intermediates as well as parametric uncertainties due to assumptions made in the derivation of kinetic data, for instance when choosing the exchange-correlation functional of DFT simulations. These considerations become part of the mechanism generation procedure and therefore lead to time-consuming analyses of all possible reactions and intermediates.

When generating a mechanism for CO_2 methanation using RMG (Fig. 7), Kreitz et al. [120] quantified the impact of parametric uncertainty on automatic mechanism generation for CO_2 methana-

tion on Ni(111) and found that the degree of rate control approach can be misleading if the parametric uncertainty is not considered.

3.3. Digitalization and machine learning

As discussed above, the development of reliable reaction mechanisms for a particular chemical reaction system of interest may include the analyses of a very large number of experimental and modeling studies, which are difficult to assess as a whole and the entire iterative development process sometimes becomes a tedious endeavor. The use of various reactors for the measurements of conversion, selectivity, yields, concentration and temperature profiles, coverages, and state of the solid materials to determine reaction rates call for a variety of reactor models and computer codes to numerically simulate those reactors using the microkinetic scheme under development. Furthermore, several different computer codes based on alternate algorithms and physical as well as chemical assumptions may exist for the conduction of the numerical simulations. This variety bares many uncertainties on the quality and applicability of experimental data, physical and chemical models, and numerical algorithms and computer codes. The complexity of the development process calls for an automated workflow that archives, structures and links experimental data, models, and computer codes. Databases containing all relevant experimental and modeling information for one given chemical or physical system can be used to faster evaluate both models and experiments by automatized comparisons. However, the database also needs to contain all meta data of the experimental setup such as inlet and boundary conditions, geometrical measures, materials and properties (e.g., porosity of a fixed bed) of the reactor, and information on the active surface (catalyst material, structure, size and support), in short, all information and parameters that are needed to numerically simulate the behavior of the reactor, i.e., the inputs for the flow solvers. Such an approach would eliminate parts of the friction of collecting, passing on, and validating the huge amount of scientific and engineering data that emerge, which often prevents people from truly benefiting from the existence of those data and unfortunately leads to the development of models that are based on a limited number of experimental information, sometimes only from the researcher's group itself. There is basically no real benefit of those *lumped* models, here chemical kinetic schemes for heterogeneous reactions, for the community because the narrow database for evaluation prevents extrapolation.

The combustion community can serve as role model for providing efficient workflows when it comes to homogeneous kinetics in particular. Several tools have been developed over the years such as PrIme (Process Informatics Model) [121], RE-SPECTH (short for reaction kinetics, spectroscopy,

thermochemistry) [122], CloudFlame and others [123–125]. The Faravelli group presented a generalized framework for models/experiments comparison and applied it to n-heptane combustion kinetic mechanisms [126]. Later, the same group described the design of an integrated framework to automatically take advantage of large amounts of scientific data extracted from the literature to support research, and in particular scientific model development was recognized as requirement emerging from the combustion kinetics domain [127]. They also presented a toolbox for optimization of chemical kinetic mechanisms by handling experimental targets from different sources [128].

Recently, a project has been developed to establish a computer algorithm and platform for an efficient management of research data in the field of heterogeneous reaction kinetics. The computational platform CaRMeN (Catalytic Reaction Mechanism Network) has been initially developed to automatically and easily test kinetic models against a large experimental database in a plug-and-play fashion [108,115,129] such as in the methanation case mentioned before [115]. Since the computer implementation is very flexible, the platform is meanwhile used for a wide variety of problems related to heterogeneous, homogeneous, and electro-chemical reactions, in which an automated workflow for combining experimental, modeling and simulation information is of use.

Neural networks have also been used to predict rates of heterogeneous reactions, for instance in the area of emission control [130]. Existing physical and chemical models are often used to generate baseline data and the network is then trained by data from lab-scale measurements and/or the technical application. For this, both detailed reaction kinetic schemes [131,132] and DFT data can be used to train the network [133]. Recently developed tools for better catalyst screening using *artificial intelligence* (AI) [134,135] may be extended to also developing reaction mechanisms in future.

4. Emission control of modern natural gas and hydrogen combustion engines

For decades the desire for clean air made emission control a vibrant area of heterogeneous catalysis research and evoked numerous scientific and technical advancements that are of tremendous significance also in adjacent fields. Nowadays, the need for abating local and global pollutants is continuously increasing and beyond toxic or noxious species such as nitrogen oxides (NO_x) or carbon monoxide (CO) that evolve during combustion processes, increasing focus is laid on the reduction of greenhouse gas emissions such as carbon dioxide (CO₂), methane (CH₄) or nitrous oxide (N₂O). With no claim to completeness, the follow-

ing subsections elucidate how heterogeneous catalysis paves the way to clean modern combustion processes and presents future challenges.

4.1. Natural gas engines

Since methane as the main component of natural gas has the highest H-C-ratio of all hydrocarbons, engines running on natural gas exhibit advantageous CO₂ emissions and can achieve a greenhouse gas advantage of up to 35% compared to conventional diesel engines [136] if operated under highly fuel-efficient lean conditions. An essentially closed carbon cycle and therefore net-zero carbon emissions can be theoretically achieved by replacing fossil natural gas by methane originating from renewable power-to-gas processes and from biogas. Despite an overall clean combustion, increasingly stricter emission standards necessitate a modern exhaust gas after-treatment system. Typically, such systems comprise an oxidation catalyst for removal of species such as formaldehyde and methane, and a unit for selective catalytic reduction (SCR) of NO_x using ammonia as reducing agent, possibly supplemented by an ammonia slip catalyst (ASC) [137].

While the conversion of noxious and potentially carcinogenic formaldehyde that can form during combustion in the engine [138] requires only moderate temperatures of about 250 °C over Pt-based catalysts [139,140], the pronounced transport limitation of catalytic HCHO oxidation as revealed by PLIF particularly at low concentrations rises the need for optimized catalytic converters accounting for the combined effects of chemical kinetics, diffusive mass transfer, and flow field [141]. Furthermore, the catalytic conversion of the strong greenhouse gas methane, which evolves due to incomplete combustion, poses a major challenge. Despite decades of research in academia and industry, methane total oxidation over the catalytically most active palladium remains challenging. In particular, hydroxyl groups originating from the inevitable exhaust gas component water and from the catalytic methane oxidation itself can adsorb on the support material and the noble metal particles and can even react with PdO to form Pd(OH)₂, hereby causing a declining catalytic activity due to a loss of active surface sites [142,143]. Furthermore, the combination of *in situ* DRIFTS (diffuse reflectance infrared Fourier-transform spectroscopy) measurements with *operando* XAS under pulsed oxygen and water flow conditions recently allowed Velin et al. [144] to uncover hampered PdO redox dynamics due to OH groups, which is considered crucial since during methane oxidation according to the Marsvan-Krevelen reaction mechanism [145] lattice oxygen plays a key role. Similarly, sulfur species that originate from the natural gas itself or from lubricants used in the engine form sulfites and sulfates with both noble metal and support mate-

rial and hereby heavily deactivate palladium-based methane oxidation catalysts [146,147]. With an increasing share of biogas that contains comparably high sulfur and phosphorous levels, both acting as strong catalyst poison, longevity of heterogeneous catalysts becomes even more relevant. Beyond the addition of platinum as dopant [148,149] and support material variations [147,150,151], process control is also a premier factor governing high methane conversion rates. Temporary rich conditions can facilitate the decomposition of sulfur compounds stored on the support material and the noble metal, which particularly recovers the active surface sites and hereby restores the catalytic activity [146,147,152–154]. In the context of real-world applications, reductive pulsing is also a feasible strategy for overcoming water inhibition, since in addition to sulfur compounds also adsorbed hydroxyl groups are removed from the catalyst surface on a regular basis and at the same time the short rich phases maintain a highly active state of palladium [64,155]. After first demonstration at an 1.4 l 4-cylinder TSI engine running on compressed natural gas (CNG) [156], the concept of long-term lean operation with short fuel-rich phases has meanwhile been successfully expanded to other gas engines, e.g. for marine applications [157].

Especially in the light of the upcoming EURO VII standards, also species that remained unregulated so far as well as secondary emissions that emerge in the after-treatment system during dynamic operation become a major concern. Dependent on the oxygen concentration during rich regeneration of sulfur-poisoned oxidation catalysts, for instance, Auvinen et al. [158] observed formation of toxic NH_3 and evolution of N_2O , which compared to CO_2 has a more than 300 times higher greenhouse potential. Deng et al. [159] reported N_2O evolution when investigating the chemical interaction of NH_3 and NO_x with CH_4 and C_2H_4 at moderate temperatures and various pressures by both, kinetic modeling and experiments. Furthermore, several recent studies point to formation of highly toxic HCN over state-of-the-art SCR catalysts as a reaction product of formaldehyde and ammonia [160–162].

Since the catalytic converters are today often close-coupled to the combustion engine, the higher temperatures and pressures – in case of a pre-turbine positioning – can lead to homogeneous gas-phase reactions in the tailpipe and in the catalyst section [163]. Recent studies showed that the (combustion) reaction mechanisms often but not at all conditions can predict the homogeneous conversion of the exhaust gases in this highly diluted, low-temperature regime [164]. The understanding of these processes strongly benefits from establishing homogeneous reaction kinetics at a wide range of conditions [165–170]. In addition, homogeneous reactions of the exhaust may also play a role in exhaust-gas recycling [171].

Summarizing, future strategies for minimizing the many different pollutants to near-zero levels must involve a highly optimized overall system that combines precise engine control and combustion with an advanced after-treatment system that is capable of coping with the dynamic conditions typical for transient engine operation.

4.2. Hydrogen combustion engines

Although the continuous optimization of modern combustion engines minimized engine-out pollutant levels and also substantially reduced CO_2 emissions due to high fuel efficiency, renunciation of carbon-containing fuels is considered to pave the way towards net-zero greenhouse gas emissions. In this context, hydrogen as a fuel for internal combustion engines (ICEs) has already been subject to numerous reviews [172–177] and enjoys growing popularity for long-haul route and heavy-duty applications that cannot be realized with battery electric vehicles (BEVs). Moreover, in contrast to fuel cell powered vehicles (FCVs), H_2 -ICEs do not rely on scarce and expensive materials and exhibit a comparably high technology-readiness level since their similarity to conventional engines allows retrofitting [178]. Apart from almost negligible CO , CO_2 and HC concentrations originating from combustion of lube oil in the combustion chamber [179,180], nitrogen oxides (NO_x) represent the only relevant pollutants emitted by H_2 -ICEs. Engine- and combustion-related measures such as exhaust-gas recirculation [181,182], optimized ignition timing [183] and in particular an adjustment of the fuel-to-air equivalence ratio allows for efficient NO_x control [173]. Choosing an air-to-fuel-ratio of $\lambda > 2$, for instance, can suppress NO_x formation to almost zero [176,184].

However, during dynamic operation as typical for mobile applications, engine-related measures alone are not sufficient for NO_x reduction, necessitating a modern exhaust gas after-treatment unit. Considering heavy-duty as the primary field of application for hydrogen combustion engines, NH_3 -SCR over catalysts based on vanadium-tungsten-titania (VWTi), iron- or copper-zeolites is the most relevant technology among the well-established de- NO_x concepts, whereas NO_x storage and reduction (NSR) catalysts may be favored for light-duty applications [185].

The ammonia needed for NH_3 -SCR is usually provided by thermolysis and hydrolysis of a urea-water solution (UWS, AdBlue, DEF) that is sprayed into the tailpipe. Spray-wall interactions can lead to liquid and molten films and solid deposits of urea and by-products that decompose at rather high temperatures. Even though the preparation of ammonia from urea water sprays still represents a challenge in aftertreatment engineering, as complex interactions of multiphase physics and heterogeneous chemical reactions have to be

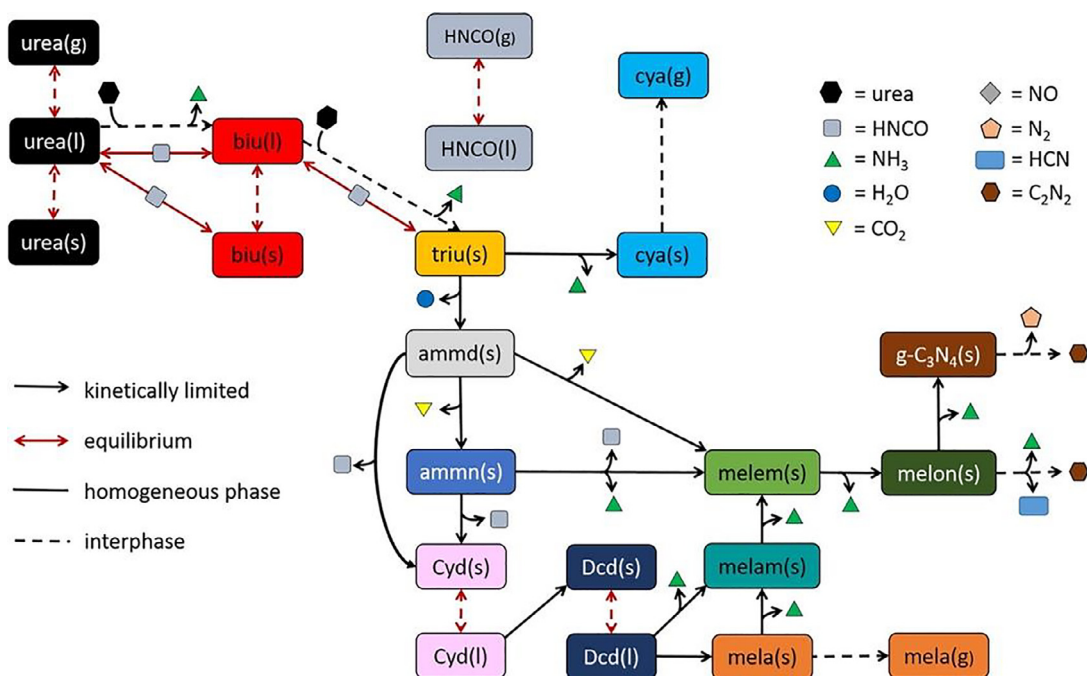


Fig. 8. Reaction mechanism of urea decomposition and byproduct formation. Reprinted with permission from [188]. Copyright 2021 Elsevier.

handled, very reliable and efficient aftertreatment systems have meanwhile been designed. A recent article reviews the ongoing development of SCR systems with focus on the efficient evaporation and decomposition of the injected spray for a homogeneous ammonia distribution in front of the SCR catalyst, focusing on critical aspects such as spray evaporation and impingement, liquid film, and deposit formation [186]. Concerning the critical urea by-product formation, a novel reaction mechanism was recently proposed that emphasizes the role of a thermodynamic equilibrium of the reactants in liquid and solid phases, and explained the observed phenomenon of liquefaction and resolidification of biuret by formation of an eutectic mixture with urea [187]. The reaction scheme was recently extended to also describe the high-temperature by-product formation (ammelide, ammeline, cyanamide, and melamine) from urea decomposition (Fig. 8) [188]. However, the formation of solid particles on the nanometer scale through crystallization of urea in the vaporizing urea-water droplets, the interaction of UWS and its decomposition (e.g., *via* isocyanic acid) and by-products with the SCR catalysts, and the impact of the high steam concentration on evaporation and hydrolysis still remain unresolved issues. The latter one is of special significance for hydrogen fueled combustion engines exhibiting high engine-out water emissions of typically up to 15 – 20% [189].

While hydrogen as a fuel is essentially free of catalyst poisons like sulfur and hydrocarbons that can bias the SCR activity, the higher water concentrations can accelerate hydrothermal catalyst aging. As revealed by *in situ* XRD, pair distribution function analysis, and TEM-EDXS (transmission electron microscopy – energy dispersive X-ray spectroscopy), high steam concentrations can dealuminate the aluminosilicate-framework of zeolites, which ultimately causes a collapse of the catalyst's structure, or can change the particle size and morphology of active metal species [190]. This degeneration affects not only the catalytic activity but also deteriorates the selectivity and i.e. benefits N_2O formation [191]. Moreover, especially in the presence of water vapor, tungsten and vanadium are highly volatile species whose release from SCR catalysts already starts at 500 °C [192]. In addition to avoiding a continuous loss of material and concomitant activity decline, the toxicity of vanadium also complicates the usage of VWTi-catalysts.

Direct usage of hydrogen as reducing agent during so-called H_2 -SCR offers a more elegant solution, since it makes an additional tank for aqueous urea-solution redundant and avoids the UWS-related issues discussed above. Commonly, platinum shows the highest activity for H_2 -SCR and allows sufficient NO_x removal already below 100 °C, whereas the more selective palladium produces less undesired byproducts [193]. Despite a series of en-

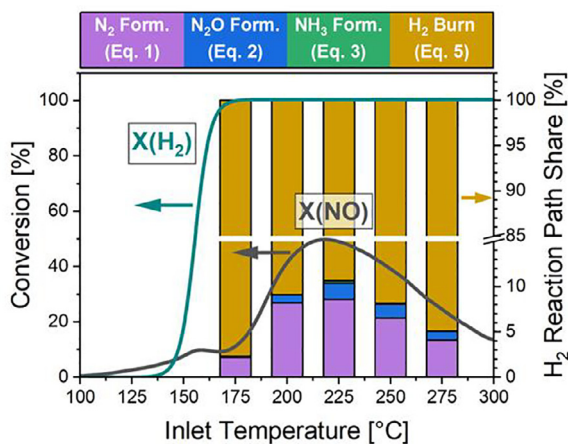


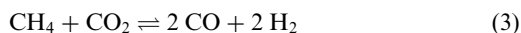
Fig. 9. Typical NO conversion and H₂ reaction path shares during H₂-SCR. Adapted with permission from [195]. Copyright 2021 American Chemical Society.

encouraging studies that were comprehensively summarized in a review by Hu and Yang [194], the impact of high water concentrations on both the immanent catalytic activity and the longevity of the catalyst remains unclear and the temperature window, in which H₂-SCR can be applied, needs to be extended. In the latter context, heterogeneously catalyzed H₂ combustion in the oxygen-rich exhaust atmosphere strongly competes with the selective NO_x reduction reaction (Fig. 9) [195]. Another challenge is the suppression of the formation of the strong greenhouse gas N₂O over the catalyst. Hence, future research needs to address these issues in order to allow for widespread application of H₂-SCR.

5. Use of CO₂ for syngas production

5.1. Catalytic dry reforming

Methane is a versatile feedstock molecule for a large variety of value-added chemicals, however, even when applying a heterogeneous catalyst, its activation requires comparably harsh conditions [196]. Steam methane reforming (SMR) and the subsequent water-gas-shift (WGS) reaction as the premier process for syngas production, for instance, account for the majority of the global annual hydrogen production, but also cause massive CO₂ emissions. In the course of reducing greenhouse gas emissions in the chemical industry, dry reforming of methane (DRM, Eq. 3) is considered an auspicious approach for direct gas phase conversion of CO₂ to produce syngas [197], which could ultimately enable a decarbonization of petrochemical value chains at a scale of multi-Gt CO₂ per year [198].



DRM is carried out catalytically at temperatures above 800 °C at 10–40 bar, can be adjusted to be very CO-rich and is therefore an important feedstock for various chemical products, such as formic acid, acetic acid, polycarbonates, phosgene, dimethyl ether, and oxo products [20]. Considering the industrial demand for low-cost materials, base metals such as Ni and Co are commonly chosen as heterogeneous catalysts for DRM, either as single-metal catalysts [20] or as bimetallic Ni-Co catalysts [199–201]. DRM is today offered on a commercial scale [202] after overcoming sintering and severe coking issues [203, 204]. An essential part of the development of the DRM technology was the understanding of the reaction mechanism and coking behavior. A main point of discussion were the reaction pathways and the intermediates towards the formation of CO. Following the approach of analyzing all available experimental and theoretical information as discussed above, elementary-based reaction networks were proposed for catalysts based on Ni [87] and Co [205], which include both direct oxidation of surface carbon by oxygen and by hydroxyl species and the formation of carboxyl COOH* as proposed by theoretical studies [206] as shown in Fig. 10. These separate mechanisms may also be used as basis for the development of detailed surface kinetic models for bimetallic Ni-Co catalysts; however, the complex interaction of both components impedes a simple combination of the Ni and Co mechanisms.

5.2. Dry reforming in steel industry

There are non-catalytic dry reforming processes, where the kinetics can be represented by homogeneous elementary-step reaction mechanisms. One

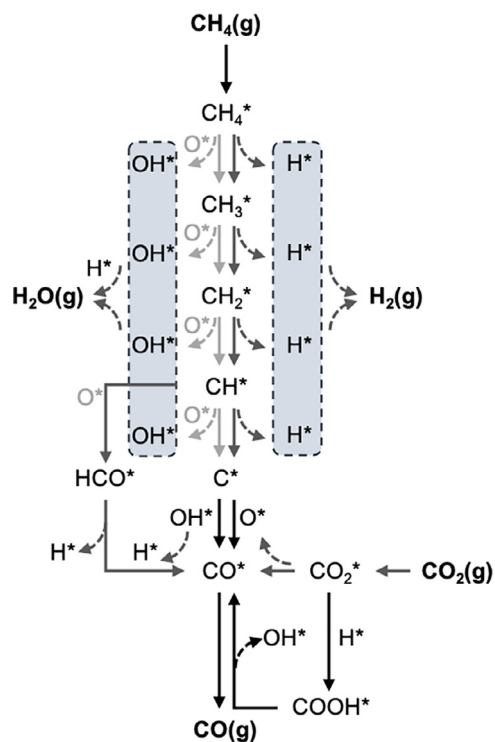


Fig. 10. Reaction pathways for dry reforming of CH_4 over Ni and Co surfaces. Figure based on [87, 205].

of these processes is the application of piston engines as reactors for the conversion of CO_2 via dry reforming of methane, where a part of the fuel is consumed by oxygen to produce the required heat to drive the endothermic dry reforming reactions leading to the production of syngas [207–209].

In steel plants (Fig. 11), the coke oven gas (COG) contains significant amounts of H_2 and CH_4 , while the blast furnace gas (BFG) contains much CO and CO_2 . In a recently proposed technology [210], these two gas streams are mixed and reformed according to Eq. 3 in the regenerative heat exchanger (cowper), which is periodically (ca. 30 min) cooled (on blast) and heated (combustion; off blast) and exhibits strong spatial and temporal temperature variations (1400 – 800 °C). The produced syngas (H_2 , CO) stream is fed to a blast furnace to support the reduction of the iron ore. In the proof-of-concept study [210], a maximal reduction of 78% CO_2 of the COG/BFG stream could be achieved, which can result in up to 12% reduction of CO_2 emissions of the steel plant.

Both homogeneous dry reforming processes could be kinetically simulated by successfully employing the PolyMech mechanism that was originally developed by Maas and co-workers and which consists of 558 reactions among 83 species [211]. The reaction network includes the oxida-

tion of methane as well as the pyrolytic pathway of methane conversion, reactions towards unsaturated and some aromatic hydrocarbons. The latter can serve as precursors of coke formation, which is an inherent problem in dry reforming processes, which, therefore, is considered as a heterogeneous reactive system here.

5.3. Coke formation

Coke formation is not only a major challenge for the technical realization of dry reforming but for many technical processes treating carbon-containing molecules. The underlying mechanisms of the formation of carbonaceous deposits are complex and not fully understood yet. Coke formation and deposition can be the result of several catalytic reactions such as the CH_4 cracking and the Boudouard reaction, leading to different coking behavior when different catalysts are used [212,213]. The nature of the metal itself plays a decisive role in the mechanism of coke formation, however, characteristic properties such as the particle size and the respective metal-support interactions have a strong impact on the equilibration of coke formation and gasification processes that result in the accumulation of coke. Additionally, a source of carbon formation exists that is often not valued enough in the catalysis community but very well known in the combustion community: the gas phase chemistry occurring under rich conditions in parallel with the heterogeneous reactions on the active metal. At high temperature, hydrocarbons such as C_2H_4 , C_2H_2 , and C_6H_6 are formed from methane via stepwise dehydrogenation and coupling reactions [214–216]. These gas phase reactions have to be coupled with adsorption, surface reactions, and even desorption (e.g., H_2) describing the heterogeneous conversion on the surface. A simple approach for coupling gas-phase kinetics and growth of carbonaceous overlayers is presented in Fig. 12 [215,217]. These hydrocarbons are also the precursors for soot formation, which lead to generic coke precursors, such as polyaromatic hydrocarbons (PAHs) via hydrogen abstraction and carbon addition [23,218,219]; also soot particles adsorb on the catalytic surfaces. The development of detailed reaction mechanisms for coking due to the interactions between gas phase and active surfaces is still a formidable task.

Industrial DRM is operated at elevated pressures and temperatures. At these conditions, homogeneous gas phase reactions could significantly contribute to coke formation in the entrance region of the catalytic bed. In a potential hot zone upstream, methane can be converted to C_2H_2 and C_3 - C_4 olefins, which can lead to coking on the catalytic surface and even clogging in the bed's entrance region [204]. Also, in the case of reforming the COG/BFG of a steel plant, significant coke formation was observed on the cowper's wall materials

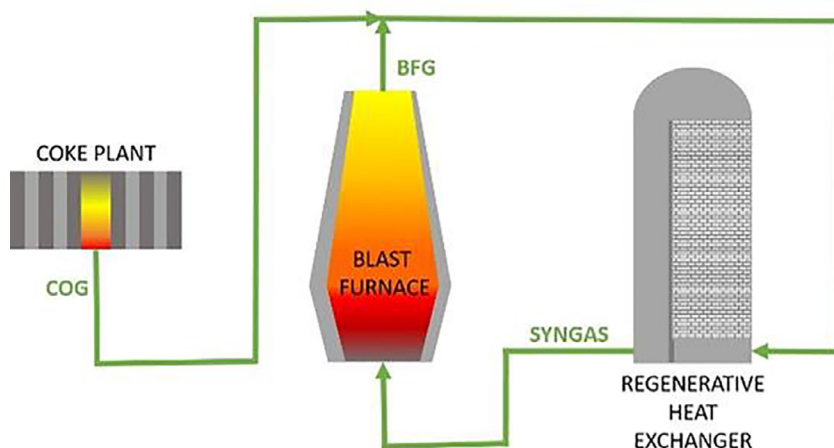


Fig. 11. Concept for reducing CO₂ emissions from flue gases of steel industry by dry reforming of methane and re-use in the process. Reprinted with permission from [210]. Copyright 2021 Wiley-VCH.

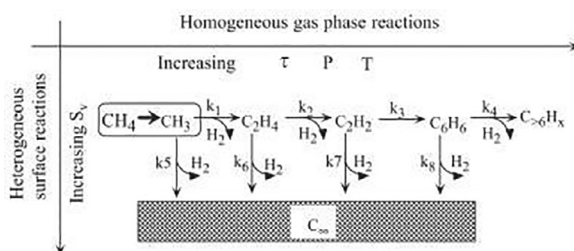


Fig. 12. A multi-step deposition model considering the hydrogen inhibition. Reprinted with permission from [215]. Copyright 2007 Elsevier.

in a certain temperature range, which could be numerically predicted by the reaction mechanisms *via* the presence of coke precursors [210].

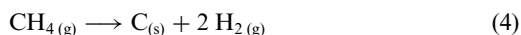
6. Methane pyrolysis and coupling

6.1. Methane pyrolysis for hydrogen production

Beyond its use for chemical synthesis of value-added chemicals, natural gas with methane as main component can serve as feedstock for hydrogen production. In this context, solid carbon is the desired product and pyrolysis is considered an auspicious approach for the reduction of GHG emissions in the chemical industry [220]. While the pyrolytic conversion of fossil natural gas into elemental carbon and gaseous hydrogen terminates the carbon cycle, the sustainable conversion of biomass that binds atmospheric CO₂ into biogas, which can subsequently undergo pyrolysis, ultimately offers the chance of bio-chemical CO₂ removal from earth's atmosphere. Hence, pyrolysis of C-containing molecules can account for a gas to solid process that causes negative emissions. Beyond simple sequestration and storage, the utiliza-

tion of accruing carbon can make methane pyrolysis not only an ecologically appealing, but also an economically competitive technology [221].

Similar to the processes discussed previously, methane decomposition under pyrolytic conditions is more difficult than for any other hydrocarbon. According to fundamental considerations based on a detailed chemical kinetic mechanism developed in the Curran group [216], three reasons account for methane's behavior during pyrolysis: i) A net zero effect of H-atom abstraction by $\cdot\text{CH}_3$ radicals due to the reaction $\text{CH}_4 + \cdot\text{CH}_3 \rightleftharpoons \cdot\text{CH}_3 + \text{CH}_4$, ii) a quasi-equilibrium state in which $\cdot\text{H}$ atoms are produced and consumed in the reaction $\text{CH}_4 \rightleftharpoons \cdot\text{CH}_3 + \cdot\text{H}$ and iii) the high bond dissociation energy for C-H bonds. With approximately 75 kJ/mol, methane pyrolysis according to Eq. 4 is an endothermic process in which heat is the main energy vector governing high conversion.



As assessed by Schneider et al. [222], thermal decomposition, plasma decomposition or catalytic decomposition in optimized reactors can decrease the process energy demand. During the latter one,

the catalyst choice tremendously influences the type of carbon produced during pyrolysis. Nickel, for instance, favors the formation of filamentous carbon at 500 – 700 °C [223], iron-based catalysts operated at 700 – 800 °C allow producing carbon nanotubes [224] and graphitic carbon can be produced below 1050 °C over a wide range of metals like Co, Ni, Fe, Pd, Pt, Cr, Ru, Mo, and W if the reaction conditions are chosen appropriately [225]. After separation from the catalyst, especially well-defined materials are suitable for direct further usage. Although catalytic decomposition over metal catalysts enables high conversion rates at moderate temperatures below 1000 °C, typically coking and a concomitant fast activity drop impede long-term operation or at least requires regeneration periods.

Liquid bubble column reactors using molten salts or metals such as alkali-halides [226,227] or tin [228,229], respectively, could facilitate the separation of solid carbon and are therefore considered as a technical multi-phase solution for industrial-scale methane pyrolysis. Notably, the molten media surrounding the small gaseous bubbles ensure an efficient heat transfer. After CH₄ cracking in the bubbles, the density difference between liquid medium and solid carbon allows for carbon removal while H₂ is continuously leaving the column as a gas. In addition to efficient liquid-solid separation, high stability of the molten media themselves and the development of corrosion-resistant materials that endure possibly aggressive molten media at high temperatures are prerequisites for long-term operation in real-world applications. In addition, plasma applications can provide the high temperatures necessary for cleaving methane's stable C-H bonds [230].

Coking is highly desired if granular carbon is utilized in a moving fixed bed reactor as recently demonstrated in a thermal decomposition process developed by a research consortium around BASF SE, which was supported by the German Federal Ministry of Education and Research [13]. Herein, carbon particles do not only ensure efficient heat transfer, but also act as nucleus for carbon that deposits during chemical vapor deposition (CVD). As the carbon particle bed is continuously moving, instantaneous reactor clogging can be avoided. Methane pyrolysis and deposition in a moving bed involves several major chemical processes such as homogeneous gas-phase reactions, adsorption of light molecules and aromatic and polyaromatic compounds on the carbon particles and reactor walls, molecular growth and soot formation in the gas-phase, deposition of soot particles on and between the carbon pellets and on reactor walls, and the desorption of molecules from the carbon structures (mainly H₂), as illustrated in Fig. 13.

The growth and movement of the particles leads to spatial and temporal variation of external and internal porosity impacting the flow through the bed, external and internal diffusion, and the heat

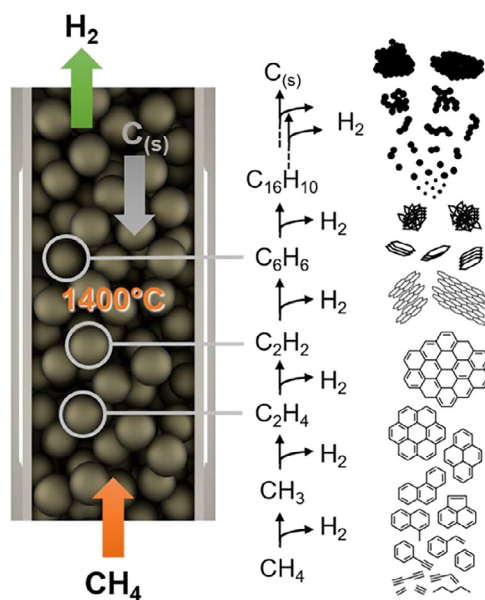


Fig. 13. Sketch of the interaction of chemical processes of methane pyrolysis in a moving bed reactor filled with carbon particles.

balances. Chemical models for gas-phase kinetics [231], formation of soot particles [232] and for the deposition of carbon precursors [215] that were established in the combustion community have recently been applied to better understand this complex reactor [233].

Along with kinetic simulations, profound on-line and off-line analysis of both gas phase compounds and liquid products evolving during hydrocarbon pyrolysis by methods like Fourier-transform infrared (FTIR) spectroscopy, gas chromatography (GC) and mass spectrometry (MS) [234–237] provided recondite snapshots of the extremely complex reaction mechanism network of pyrolytic hydrocarbon decomposition. It is generally accepted that carbon formation proceeds *via* a multi-step mechanism involving methane activation with subsequent formation of ethane, ethylene, acetylene and further reaction of these C₂ hydrocarbons to form C₆ aromatics and polycyclic hydrocarbons that nucleate to form primary solid particles, whose coagulation and agglomeration ultimately results in soot generation [214,235,237]. This step-wise growth of molecules, particles and ultimately bulk carbon was recently subject to a comprehensive study utilizing Raman spectroscopy [238] and is schematically illustrated in Fig. 14. Moreover, it is well-known that the type of carbon particles used as catalyst has an impact on the deposited carbon [239] and on the catalytic activity [240,241], i.e. disordered forms of carbon were demonstrated as catalytically more ac-

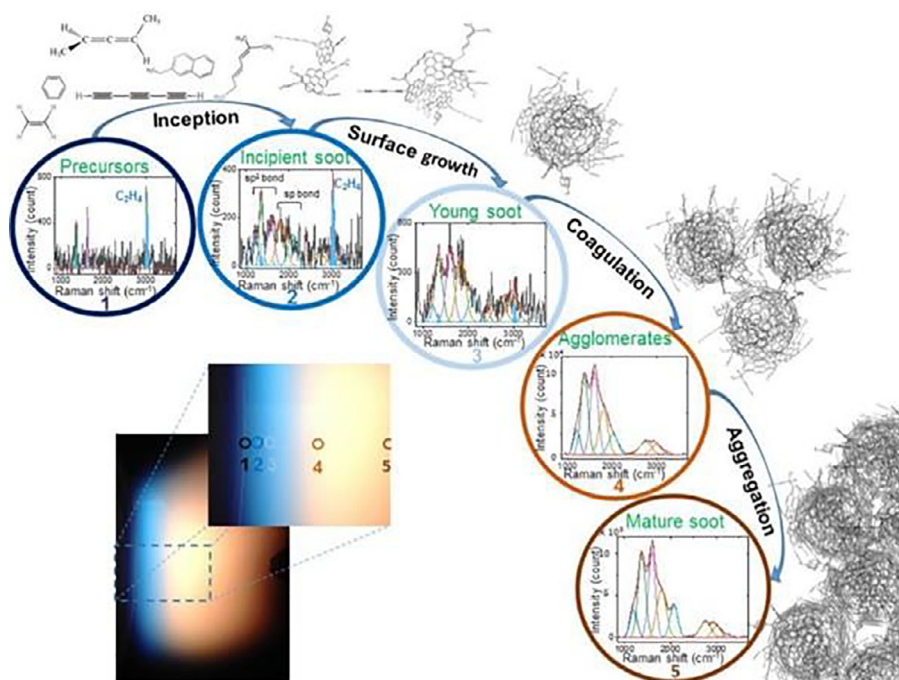


Fig. 14. Schematic illustration of the carbon particle formation starting from small molecules and resulting in aggregated soot particles as exemplarily observed by Raman spectroscopy in an ethylene/oxygen flame. Reprinted with permission from [238]. Copyright 2021 Elsevier/The Combustion Institute.

tive than ordered structures like graphite powders [240].

Despite these insights on a molecular level, especially the interplay between homo- and heterogeneous processes remains poorly understood and requires further profound research efforts. In particular, intensive use of non-intrusive and non-invasive modern *in situ* and *operando* characterization techniques promise novel fundamental insights, which can be gained during process operation without biasing the process itself. Analogous to the approach chosen by Le et al. [238] for investigating soot formation in a low pressure premixed ethylene/oxygen flame, for instance, online Raman spectroscopy can provide clear proof of species involved in primary particle formation, i.e. unsaturated carbon chains during chemical condensation. Johansson et al. [242] extracted particles from an atmospheric-pressure laminar premixed ethylene/oxygen flame and analyzed them in a vacuum ultraviolet aerosol mass spectrometer (VUV-AMS). In the light of additional theoretical considerations, the authors suggest soot inception and growth *via* a complex mechanism involving resonance-stabilized hydrocarbon-radical chain reactions. More detailed computational investigations on the prevailing electronic structure and the associated reactivity of PAHs in combustion environments as recently published by No-

bili et al. [243] will finally provide the fundamental knowledge required for understanding the transition of polycyclic aromatic hydrocarbons in the gas phase into carbonaceous solid particles. Taking the subsequent heterogeneous chemistry into account, i.e. dissociative methane adsorption followed by stepwise decomposition to elemental carbon and hydrogen, ultimately allows for developing models that are able to describe and predict the overall process of methane pyrolysis. Such fundamental understanding is considered a prerequisite for designing real-world pyrolytic processes for hydrogen production from natural gas in industrial scale.

6.2. Methane coupling

Regardless of its fossil or renewable origin, methane as the simplest of all hydrocarbons can serve as building block for value-added chemicals such as olefins or aromatics, and, in general, is a climate-friendlier feedstock than oil. As reported in a comprehensive review by Schwach et al. [244], direct methane conversion routes *via* coupling reactions can take place under both oxidative and non-oxidative conditions and would allow higher energy efficiency compared to carbon atom utilization *via* reforming and subsequent upgrading, e.g. during Fischer-Tropsch processes. There is a vast literature on methane coupling, both for ox-

idative and non-oxidative paths [245–247]. For the latter one, single-atom catalysis has been discussed as promising route lately. Since the present paper is a combustion-related contribution, our focus here will be laid on oxidative high-temperature coupling.

With their pioneering study in 1982, Keller and Bhasin [248] proposed oxidative coupling of methane (OCM) for C_2 formation and initiated four decades of intensive research in the field of OCM. Countless mainly metal oxide-based catalyst formulations have been evaluated predominantly in fixed bed reactor configuration, among which $Mn-Na_2WO_4/SiO_2$ is one of the most promising materials [249]. In this context, Karakaya et al. [250] recently developed a detailed gas-surface reaction mechanism for oxidative coupling of methane over a $Mn-Na_2WO_4/SiO_2$ catalyst for non-isothermal conditions. However, efficient OCM was also observed over noble metal-based catalysts [251,252]. Despite its enormous academic and industrial appeal, to date OCM remains non-commercialized, mainly due to drawbacks in finding suitable catalyst materials exhibiting high selectivity, yield and longevity [253]. In particular, total and partial oxidation reactions compete with the OCM reaction.

In order to avoid overoxidation, Schmidt and co-workers [251,252] operated Pt-coated monoliths at extremely short contact times of approximately 5 ms and observed primarily acetylene at overall C_2 selectivities of up to 20% at high space velocities, low fuel-to-oxygen ratios, and low N_2 dilution. Based on pronounced temperature gradients along the monolith structure, i.e. 200 °C at the catalyst inlet and 1500 °C at the catalyst outlet [252], the authors presumed a complex reaction network involving homo- and heterogeneous contributions. In this respect, it is assumed that methyl radicals (CH_3) play a key role in the coupling mechanism and indeed, by combining spatially resolved species profile measurements and detailed kinetic simulations, Schwarz et al. [254] presented direct proof of methyl combination to form ethane followed by dehydrogenation towards ethylene in the context of fuel-rich methane oxidation. Very recently, the combined use of detailed chemical reaction schemes for both the homogeneous and heterogeneous reactions allowed the numerical simulation of the high-temperature methane coupling [255].

Similarly, online vacuum ultraviolet soft photoionization molecular-beam mass spectrometry (VUV-SPI-MBMS) revealed methyl radicals as key species during coupling reactions under oxygen-free conditions for producing olefins, aromatics, and hydrogen [256]. In order to overcome catalyst coking, which represents the major deactivation pathway during catalytic non-oxidative coupling, Guo et al. [256] suggested an $Fe@SiO_2$ catalyst with lattice-confined single iron sites embedded within a silica matrix. Herein, the isolated ac-

tive sites hindered undesired surface reactions between the methyl radicals and hereby suppressed carbon formation. Operating this $Fe@SiO_2$ catalyst in a hydrogen-permeable tubular membrane reactor allowed Sakbodin et al. [257] precise process control and promoted activity and product selectivity, particularly by exploiting the hydrogen content in the reactor as key control parameter. As discussed above, influencing product selectivities by adjusting the H_2 feed stream content is of equal importance in the context of methane pyrolysis.

7. Carbon-free energy carriers

A worldwide replacement of conventional fossil fuels by biofuels and hydrogen would result in a substantial reduction of greenhouse gas emissions evolving from the world's energy system and could trigger further far-reaching changes. Embedded in a global strategy that comprises social, political, economic, and technological aspects at the same time, such transformations can ultimately result in a circular economy [258]. Within the context circular economy in the chemical industry, processes that can dynamically store and release chemical energy are of utmost interest. The following subsections will shed light on some of the most promising energy carriers that are subject to current research projects, which aim at using resources for the longest time possible and ultimately at closing the loop in industrial processes.

7.1. Ammonia as hydrogen energy carrier

In addition to pure hydrogen for chemical energy storage, carbon-neutral hydrogen-containing compounds are considered, among which ammonia is of particular interest. Due to a global annual NH_3 production of almost 180 million tons by the Haber–Bosch process, the already existing reliable infrastructure eases ammonia handling, distribution and long-time storage. Additionally, NH_3 liquefaction for volume-efficient storage consumes substantially less energy than H_2 liquefaction [259].

In future, the ammonia production by the Haber–Bosch process may use renewable power for hydrogen production by electrolysis and other electrification measures of chemical plants to be more climate-friendly. From a reaction mechanism point of view, the threefold Nobel prize awarded process is an excellent example for which tremendous efforts it may take to understand the heterogeneous kinetics of catalytic reactions in detail. In light of the extraordinary importance of ammonia, research on improved catalyst formulations has been ongoing ever since the commercialization of the synthesis. As an alternative to centralized Haber–Bosch, small-scale distributed ammonia synthesis processes have been investigated, which depend on effective catalysts that can be

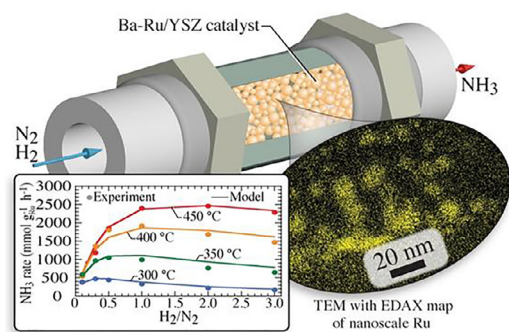


Fig. 15. Illustration of a packed-bed ammonia-synthesis reactor. The TEM blow-up shows dispersed nanophase Ru on the YSZ support. The inset graph shows measured and model-predicted NH_3 synthesis rates as functions of inlet stoichiometry and temperature; courtesy of R.J. Kee, adapted from [260].

operated under modest elevated pressure. For instance, barium-promoted ruthenium catalysts on yttria-stabilized zirconia has been tested recently in a packed-bed reactor (Fig. 15) [260].

The synthesis rate at 400 °C and 10 bar was reported to be higher than the most active oxide-supported Ru catalysts according to the literature and becomes inhibited by H_2 adsorption below 350 °C. The same group recently studied a Ru catalyst on the ternary $(\text{BaO})_x(\text{CaO})_y(\text{Al}_2\text{O}_3)_z$ support using a physics-based machine learning model to correlate the NH_3 production rates with physico-chemical properties of the BCA supports; they also provided a microkinetic reaction mechanism that is schematically shown in Fig. 16 [261].

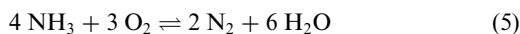
Avoiding very high pressures reduces high capital cost and electrochemical promotion potentially enables carbon-free ammonia leading to a lot of interest in electrochemical ammonia synthesis [262]. Polarized protonic-ceramic electrochemical cells, with either steam electrolysis or methane reforming on the anode, a proton-conducting ceramic membrane, and ammonia synthesis on the cathode have been studied by Stoukides and co-workers [263]. Protons play a significant role in catalytic ammonia synthesis in general. Due to the unfavorable thermodynamic equilibrium as temperature increases, low-temperature (e.g., $T < 450$ °C) catalysts are needed. However, even with the best catalysts, synthesis is greatly reduced by kinetic limitations below about 500 °C. Practical protonic-ceramic electrochemical cells usually operate between 500 °C and 700 °C. Electrochemical cells do produce ammonia, but at low rates, which calls for novel catalysts and supports for direct electrochemical ammonia synthesis.

Aside from the chemical use, ammonia can be converted into mechanical and electrical work by combustion processes in engines, turbines and fuel

cells or used as source for hydrogen by homogeneous, heterogeneous, and electrochemically driven pyrolysis.

In addition to its relatively high energy density, ammonia exhibits rather narrow explosion limits and its decomposition is relatively easy, making NH_3 a compound that can be directly used as a fuel for combustion engines. Despite drawbacks such as the comparably low flammability of NH_3 and particularly the high NO_x emissions evolving during the combustion process [264], recent studies such as an experimental investigation by Lhuillier et al. [265] on the ammonia combustion behavior in a spark-ignition engine by means of laminar and turbulent expanding flames are encouraging with respect to optimizing real-world combustion systems. In addition to the de NO_x technologies mentioned in section 4, a recent study by Ariemma et al. [266] suggests that the addition of water to the reactant mixture can reduce NO_x evolution during mild ammonia combustion, which is a promising engine-related strategy for suppressing NO_x emissions especially under fuel-lean conditions. In the context of a micro gas turbine, also Okafor et al. [267] aimed at overcoming the major challenge of NO_x formation. In a laboratory high pressure combustion chamber equipped with an FTIR gas analyzer, the authors identified factors governing high NO_x emissions and tuned the fuel injection angle, the combustor inlet temperature, the equivalence ratio, and the ambient pressure for minimizing engine-out NO_x emissions while maintaining high combustion efficiency. Further progress in optimizing the NH_3 combustion process can be expected with ongoing development of characterization techniques that provide insights into combustion flames. For instance, Pugh et al. [268] utilized time-resolved OH^* , NH_2^* and NH^* chemiluminescence for investigating NH_3 -air and NH_3 - H_2 -air flames and their results ultimately allow to tune the primary flame configuration for minimizing emissions.

While ammonia would degrade polymer electrolyte membrane fuel cells (PEMFC) [269], solid oxide fuel cells (SOFC) exhibit substantially higher robustness and can serve as suitable technology [270,271] for direct utilization of ammonia as a fuel while circumventing the adverse drawbacks of combustion engines. SOFCs allow for direct operation with ammonia and oxygen and emit only nitrogen and water as exhaust gases according to Eq. 5:



Of equal interest is the usage of ammonia as a hydrogen carrier within a modern energy infrastructure [259,272,273]. Upon decomposition according to Eq. 6, which represents the reverse Haber-Bosch process, ammonia acts as source for

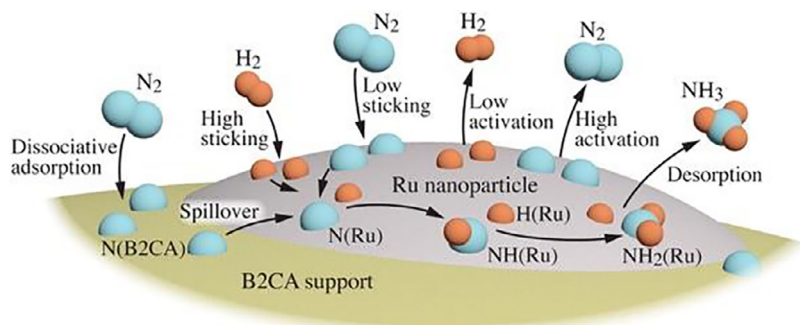


Fig. 16. Illustration of a microkinetic model for NH_3 synthesis over $\text{Ru}/(\text{BaO})_x(\text{CaO})_y(\text{Al}_2\text{O}_3)_2$ catalysts. Reprinted with permission from [261]. Copyright 2021 Elsevier.

high-purity hydrogen (along with elemental nitrogen).



In heterogeneously catalyzed ammonia pyrolysis, the need for applying an efficient catalyst is consensus, also to avoid ammonia residues in the evolving hydrogen, which could harm downstream applications. In their review article, Schüth et al. [273] clearly conclude that ruthenium (Ru) is once more the most active catalyst. While the majority of studies investigates only single catalyst formulations and strongly differing experimental conditions impede a profound comparison, Ganley et al. [274] examined a series of materials systematically and suggest a catalytic activity in the order $\text{Ru} > \text{Ni} > \text{Rh} > \text{Co} > \text{Ir} > \text{Fe} \gg \text{Pt} > \text{Cr} > \text{Pd} > \text{Cu} \gg \text{Te, Se, Pb}$. Furthermore, mechanistic considerations reveal differences over the metals, i.e., the nitrogen desorption as rate limiting step on Fe, Co and Ni, whereas over Rh, Ir, Pd, Pt, and Cu the N–H bond scission limits ammonia decomposition. Since ammonia synthesis and decomposition is governed by the equilibrium, solid-oxide support materials discussed above for ammonia synthesis also have a great potential for ammonia decomposition. Additionally, they can be used in proton-conducting high-temperature cells, in which electrochemistry can support decomposition into pure hydrogen and nitrogen streams.

7.2. Metal borohydrides as hydrogen energy carrier

Metal borohydrides have received significant attention over the past two decades as carbon-free chemical hydrogen storage materials, because the chemically bound hydrogen can be released *via* hydrolysis under relatively mild conditions. The first focus of research efforts has been on sodium borohydride (NaBH_4). However, the limited solubility of the hydrolysis byproduct sodium metaborate

(NaBO_2) entails the risk for byproduct accumulation within the hydrogen release reactor and eventual system clogging [275,276]. Another potential hydrogen energy carrier among the borohydride is potassium borohydride (KBH_4), a colorless solid that is soluble in water. Due to its higher molar mass (54 g/mol) compared to sodium borohydride (38 g/mol) and therefore lower theoretical gravimetric hydrogen storage capacities, KBH_4 has not gained so much attraction in the past, as more attention was paid to the hydrolysis reaction [277–280], although the hydrolysis product potassium metaborate (KBO_2) is much less susceptible to crystallization than NaBO_2 [281]. The promising energy storage and regeneration cycle (Fig. 17) includes several heterogeneous reactions [282], which have not yet been resolved in detail. Aside from the catalytic dehydrogenation using Co-based catalysts and the hydrogenation using Mg, catalyst stability and reduction of the byproduct MgO represents major challenges.

7.3. Reactive metals as energy carrier

Reactive metals such as Al, Na, Mg Zn, and Fe have recently attracted keen attention as carbon-free chemical energy carriers of electrical energy in a circular economy [283,284]. These metals can be used for seasonal energy storage, i.e., they can store energy in large capacities without significant loss over months and years. These energy carriers are to be seen in a demand scenario that is currently covered by large power plants and are as complementary to batteries as short-term energy storage. Since metals can be oxidized and reduced at different locations and time, they are promising recyclable fuels as exemplarily shown for iron in Fig. 18.

Energy storage by reduction of iron oxides can take place directly electrochemically or, especially in regions of low-cost renewable energy, thermochemically *via* hydrogen that was produced by electrolysis. Temporally and spatially flexible energy re-

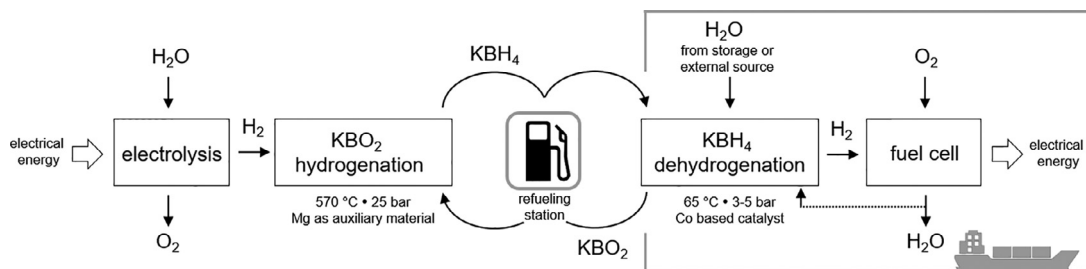


Fig. 17. KBH_4 -based energy storage cycle for marine applications.

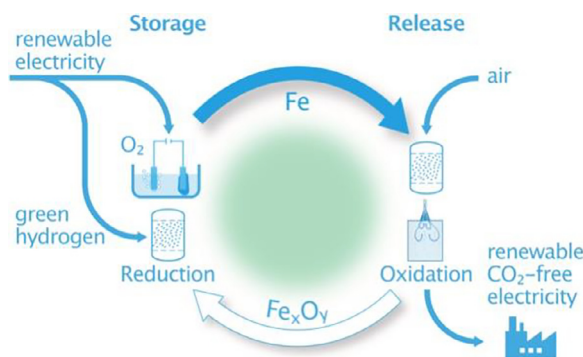


Fig. 18. Energy storage and use in a spatially and temporally separated reduction and oxidation cycle of iron (oxides). Reprinted with permission from [285]. Copyright 2022 Elsevier.

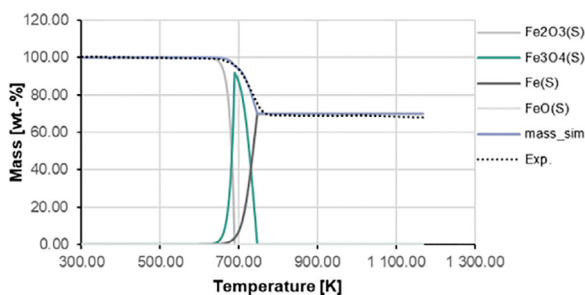


Fig. 19. Thermogravimetric analysis of Fe_2O_3 reduction with H_2 and simulation using a multi-step mechanism.

lease is realized by thermochemical oxidation of the iron on a large-scale in regions of high energy demand. The energy carrier is transported between these regions mainly by ships. The technical realization of this circular economy concept can be partially built on existing infrastructures, e.g., oxidation of iron in modified power plants for electrical power generation. Iron in powder form is of special interest among the reactive metals due to its very high volumetric energy density, non-toxicity, easy transportation, long-time storage and low hazard potential, small material losses in the cycle, and low water requirements, and finally yet importantly iron is rather inexpensive. Due to similar burning velocities and reaction temperatures as natural gas

and coal powder, retro-fitted power plants may be used for the oxidation stage [285].

Due to iron's complex oxidation states and the interaction with mass and heat transport processes, the description of the occurring heterogeneous reaction kinetics of iron's thermochemical oxidation and reduction is challenging. Thermogravimetric, differential thermal, and XRD analyses combined with modeling can be seen as first step towards a microkinetic understanding of the oxidation/reduction cycle (Fig. 19) [286]. *Operando* XAS studies as described above for a better understanding of catalytic emission control can similarly lead to better understanding and control of the iron oxidation states. Notably, the direct electrochemical

reduction of iron oxide offers the potential of the production of iron particles cured from impurities but is scientifically mostly unexplored.

Another highly attractive reactive metal is aluminum [287]. The reduction of aluminum oxide (bauxite) can use the existing electrolysis process with covering the high electricity demand by renewable sources in the future. The energy is then released by oxidation with steam to form hydrogen, which can be converted into electricity in turbines and fuel cells or used directly in the chemical industry for instance. These examples underscore the tremendous potential of using reactive metals for large-scale energy storage. Hence, a rapid development of this research area can be expected.

8. Conclusions and final remarks

Without any claim of completeness, this article highlights several methodological approaches suitable for gaining profound insights into heterogeneous reactions. By means of specific examples we aimed at demonstrating how these experimental and theoretical techniques, some well-established others just emerging, enable and promote advances in energy and combustion science and hereby contribute to more sustainable chemical processes. The importance of heterogeneous but also homogeneous chemistry in current and future technologies for the reduction of local pollutants and greenhouse gases as well as many other areas is obvious [125,288–291].

While each of the previously discussed technologies alone can already have a tremendous impact, the decisive vector for a successful transformation into a sustainable energy system will be the establishment and realization of a convincing overall strategy that adequately satisfies political, economic, and social needs at the same time. In this respect, the efficient combination and coupling of different technologies offers the chance to ensure a synergistic co-existence of different processes along the value-chain, particularly in the fields of energy and chemistry. As an example, we would like to mention coupling of solid oxide electrolyzer cells (SOEC) for producing hydrogen *via* high-temperature steam electrolysis with a downstream carbon dioxide methanation unit for producing synthetic natural gas [292–294].

In the context of maximizing resource utilization and minimizing local and global pollutant emissions, circularity will remain the most challenging aspect. The need for reducing greenhouse gas emissions initiated the development of new technologies and despite at times controversial debates it remains unclear whether one technology prevails or whether the future energy system will be much more diversified than nowadays. However, methane pyrolysis and electrolysis cells

for large-scale hydrogen production, ammonia or metal borohydrides as carbon-free energy carriers and hydrogen combustion engines as well as fuel cells for power generation are only few examples of a remarkable number of emerging technologies all along the value chain that axiomatically rely on hydrogen as a resource. Hence, the recent releases of national and international hydrogen strategies are not surprising: the United States of America [295,296], the European Union [297], Germany [298], and China [299] for instance. As outlined, the technological fields discussed also present a playground for research and development for the scientists and engineers of the combustion community. In this context, understanding, predicting, utilizing and improving the interactions of electro- and thermochemical homogeneous and heterogeneous reactions as well as mass and heat transport using the aforementioned techniques is of utmost importance.

In conclusion, the combustion community's skills and know-how along with the advanced methodological approach play a pivotal role in successfully tackling challenges in the context of climate change and sustainability. Gaining a comprehensive knowledge on the complex chemical reactions and multiphase phenomena during heterogeneous processes while covering all relevant length and time scales requires a holistic approach that equally relies on fundamental microkinetic modeling and process design on an industrially relevant scale. Under consideration of these aspects, the combustion community can be one of the key drivers in minimizing local and global pollutants and overcoming anthropogenic climate-change-related challenges. Ultimately, this commitment can not only promote emerging technologies but can also stimulate innovations within the chemical-technical industry.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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