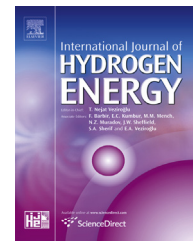




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Experimental study of methane dry reforming in an electrically heated reactor

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ABSTRACT

Dry reforming of methane (DRM) is an interesting process as it allows for CO₂ utilization and production of CO-rich syngas compared to methane steam reforming (SMR). Due to the endothermic reaction, reformer concepts suitable for high heat fluxes have to be developed. In this work, we therefore experimentally investigate a novel electrically heated reformer. Heating elements consisting of a FeCrAl alloy are coated with a LaNi_{0.95}Ru_{0.05}O₃ catalyst at different washcoat thicknesses. The effects of different operating parameters on the performance of the DRM reaction and the reverse water gas shift (RWGS) reaction are evaluated. A combined operation of dry and steam reforming is also investigated. The results show a maximal CH₄ conversion of 29.4% using one heating element at 900 °C. The H₂/CO ratio in the gas can be varied between 0.4 and 12.3 by combining steam and dry reforming. However, CH₄ conversion decreased when steam is added.

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Introduction

Carbon dioxide (CO₂) is the main contributor to the global greenhouse effect. It is therefore of great importance to reduce anthropogenic CO₂ emissions in order to counteract global warming [1]. In the context of the Energiewende, the German electricity market experiences a structural change by replacing fossil fuels with renewable energies such as wind, biomass, solar or hydropower. The inherent variability, especially of wind and solar energy, leads to a fluctuating power supply. To save temporal excess energy large scale storage system are needed. Against this background, the

interest in power-to-gas technologies has increased as it offers the possibility to for large scale energy storage in the form of substitute natural gas [2,3]. Another idea recently discussed is the use of excess power for processes in the chemical industry [4]. Synthesis gas, a mixture of H₂ and CO, is suitable for this approach as it is the basis for the production of a wide range of chemicals. It can also be used to produce synthetic fuels, pure hydrogen or carbon monoxide and is therefore a versatile intermediate. Furthermore, the production of syngas can be realized using CO₂ as a carbon source in the process. Research in the field of CO₂ recycling for the production of valuable feedstock for the chemical industry has drastically increased in recent years [5].

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Nomenclature**Abbreviations**

ATR	autothermal reforming
DRM	dry reforming of methane
GHSV	gas hourly space velocity in 1/h
POX	partial oxidation of methane
RWGS	reverse water gas shift reaction
SMR	steam methane reforming

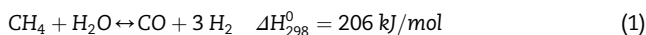
Symbols

c_p	heat capacity, J/kg/K
$c_{i,s}$	concentration of component i at the surface, mol/m ³
$D_{eff,i}$	effective diffusion coefficient of component i , m ² /s
δ_{wc}	thickness of washcoat layer, m
$\Delta H_{r,j}^{298}$	heat of reaction for reaction j , J/mol
k_j	rate constant for reaction j , mol/g _{cat} /s
$K_{ads,i}$	adsorption equilibrium constant of component i , 1/bar
\dot{m}	mass flow rate, kg/s
\dot{n}_i	molar flow rate of component i , mol/s
n	reaction order, –
η	efficiency, –
$r_{eff,j}$	effective reaction rate of reaction j , mol/s
p	pressure, bar
p_i	partial pressure of component i , bar
P_{el}	electrical power, W
Ψ	Weisz modulus, –
T	temperature, K
X_i	conversion of component i , –
y_i	molar fraction of component i , –

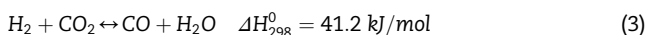
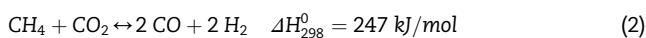
Subscripts

<i>feed</i>	conditions at reactor inlet
<i>out</i>	conditions at reactor outlet

Conventionally, syngas is produced by methane steam reforming (SMR) following the equation.

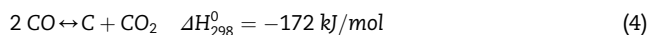


The product is a hydrogen-rich syngas with a H₂/CO production ratio of around 3. Partial oxidation (POX) and autothermal reforming (ATR) of methane are alternative routes to syngas, which allow for the production of a gas with a lower H₂/CO ratio. Dry reforming of methane (DRM) is an interesting process [2] to produce a CO-rich reformat. Here, CO₂ instead of steam is used to reduce CH₄ for the production of syngas with an equimolar ratio of hydrogen and carbon monoxide.

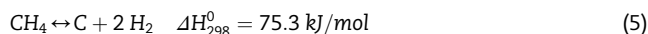


The simultaneous occurrence of the reverse water gas shift reaction (RWGS), which is the reaction of CO₂ with H₂ shown in (3), additionally favors the CO production at high temperatures leading to H₂/CO ratios lower than 1. Especially the dry reforming reaction is extremely endothermic, leading to

severe temperature gradients at high conversions as observed in fixed bed reactors [6]. Therefore, high heat fluxes are required in the reactor for dry reforming of methane (DRM). The reaction temperature is a crucial parameter in dry reforming, as carbon formation due to CO disproportionation known as Boudouard reaction (4) is critical at temperatures under 700 °C [7].



Methane cracking (5) is another carbon forming side reaction, which occurs at high temperatures. In this reaction CH₄ decomposes into solid carbon and H₂.



Since lower CO₂/CH₄ ratios in the feed gas favor the methane decomposition, Nikoo and Amin [8] suggest to feed CO₂ in excess to prevent carbon formation during dry reforming. Sun et al. [9] recommend based on their thermodynamic analysis conditions for dry reforming of CO₂/CH₄ ratios of a least 1.5 and temperatures above 800 °C.

The challenge of a reactor concept for the dry reforming of methane is therefore to provide an effective heat transfer to the catalyst in order to avoid cold spots. Furthermore, the stability of the catalyst, especially in view of deactivation due to coke formation, has been a significant issue to be addressed. A fast response of the reaction system would increase the practicability to use electrical excess power for the heat supply as it can be adapted to a fluctuating availability of renewable energies.

A large number of different reactor concepts for highly endothermic reactions exist in literature. Often they are applied to reforming of methane and other hydrocarbon feedstocks. On industrial scale, steam reforming is mainly carried out in fixed bed tubular reactors using catalyst pellets. The tubes are externally heated by gas burners. Since the heat has to be transferred through the reformer tubes and fixed bed, heat flux and reaction temperature are limited. In total only 50–60% of the heat is transferred to the process through the tubes [10]. For the use in small scale applications (e.g. for decentralized power generation systems) more efficient reactors are needed as miniaturization leads to proportionately higher heat losses [11]. Examples are compact systems with integrated heat exchangers which are coupling endothermic and exothermic reactions. Kolios et al. [12] and Gritsch [13] investigated the coupling of methane combustion with steam reforming in reactors and developed a heat integrated reformer, which consisted of multiple channels formed by folded-sheets. In these channels alternately operated reforming and combustion reactions in co-current flow leading to a methane conversion of 98–99% for the reforming side. A similar reactor concept has been developed by Tonkovich and coworkers, consisting of a steam reformer with micro-channels [14,15]. A modular reactor for the coupling of SMR with the combustion of methane has been developed by CompactGTL [16] and is designed for the conversion of associated gas on remote oil fields. Multiple plates with channels for the combustion and the reforming reaction are assembled alternating to form a reactor. The concept focusses on exchangeability of the catalyst and fast adaption to various

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