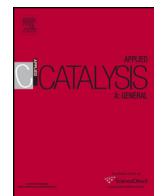




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On the coke deposition in dry reforming of methane at elevated pressures

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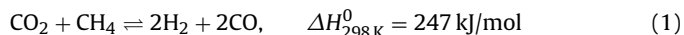
ABSTRACT

The reaction pathways leading to coke formation in dry reforming on Ni and Pt-based catalysts were investigated. Using isotope-labeled reactants (i.e., $\text{CH}_4 + {}^{13}\text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$) showed that initially ${}^{13}\text{CO}_2$ is converted faster than CH_4 and that this higher activity leads to a higher concentration of ${}^{13}\text{CO}$ compared with ${}^{12}\text{CO}$ in the product stream, suggesting little isotope scrambling among products at this stage. Gasification of carbon deposits was found to be an important pathway enhancing the catalyst stability. Analysis of the pathways leading to carbon deposits suggests that coke is formed predominantly via reverse Boudouard reaction on Ni, while both metals contribute to CH_4 dissociation. The pronounced reversibility of the C–H and C–O bond formation and cleavage was also shown by the presence of ${}^{13}\text{CH}_4$ formed from ${}^{13}\text{CO}_2$ and ${}^{12}\text{CO}$ formed from ${}^{12}\text{CH}_4$. Numeric calculations complementing the experimental results led to the proposal of a reaction pathway for the surface reactions, accounting for the differences between Ni and Pt.

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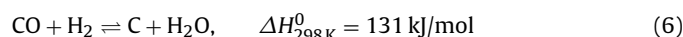
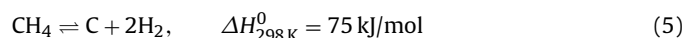
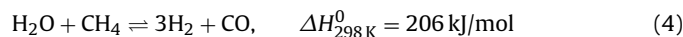
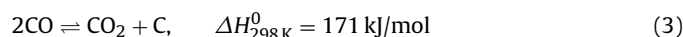
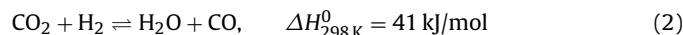
1. Introduction

Reforming is the key industrial technology to convert a large variety of carbon sources into either hydrogen or syngas, i.e., mixtures of H_2 and CO of varying stoichiometry. The latter can be transformed into products of value, like methanol or hydrocarbons as base platform chemicals for energy carriers or other chemical intermediates [1]. Synthesis gas production from CH_4 and CO_2 (dry reforming of methane, DRM) can be used to convert components in natural gas and CO_2 to a product with a H_2/CO ratio of 1 in a highly endothermic reaction (1). Other suitable sources for DRM of mixtures of CH_4 and CO_2 like biogas or emissions from landfill should also be mentioned in this context as potential feedstock.



DRM produces the synthesis gas with the lowest H_2/CO ratio among all reforming reactions and from the downstream side a handful of processes exist, which need a carbon monoxide-rich

input feed such as the iron-based Fischer–Tropsch process. DRM can also be utilized to reduce the H_2/CO ratio in the overall mix of steam reforming, methane partial oxidation and autothermal reforming [2]. The high concentration of carbon species in dry reforming and the absence of water shift the thermodynamic limit of carbon formation into the range of the standard process conditions of DRM, especially if the reaction is performed at elevated pressures [3]. Thus, carbon deposition is thermodynamically favored and, in consequence, catalysts tend to rapidly deactivate and accumulate carbonaceous deposits at a high rate. In addition to the target reaction, a significant number of (detrimental) side reactions involving reactants as well as products can occur.



The side reactions with the highest impact on the product composition are the reverse water gas shift reaction (RWGS, (2)) and

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the Boudouard reaction (3). Water formed in the RWGS can subsequently react with methane via steam reforming (4), producing a H₂-rich synthesis gas compared to the DRM. Cracking of methane (5), on the other hand, is an elementary step of DRM, leading to coke formation on the surface. Thus, methane cracking has to be considered as one of the key reactions in the formation of carbonaceous deposits and the deactivation of the catalyst by coking. The partial hydrogenation of CO (i.e., the reverse reaction of carbon gasification (6)) is another pathway that produces carbon deposits, especially at high concentrations of CO and H₂ [1,4].

Thermodynamically, the deposition of coke is favored at lower temperatures, requiring the use reaction conditions above 873 K to minimize catalyst deactivation [5]. The deposition of coke becomes more favorable at higher pressures (especially above 10 bar), which are however essential for the overall process economics, as it reduces the number of compression steps required for the downstream processes typically operating at pressure levels between 20 and 70 bar. Noble metals, such as Pt or Ru, show a lower tendency to coking compared to base metals [4,6–8], but the significantly lower cost of base metal catalysts such as Ni make them preferred active components for industrial catalysts.

Ni is particularly prone to build up carbon nanotubes (CNTs) under dry reforming conditions. These carbon deposits may limit the access to the active metal, may lead to reactor plugging, and in the worst case to destruction of reactor pipes. The rate of carbon formation has been associated with two key reactions, the recrystallization of carbon at the base metal surface and the dissociation of CH₄ at Lewis acid–base sites of the support [8]. With respect to the first, carbon nanotubes have been found to require a minimum size of the metal particles of above 2 nm to be formed under these conditions. Dissociation of CH₄ leading to coke formation can be minimized by reducing the concentration of Lewis acid sites on the support. It is obvious that at the high temperatures used for reforming, it is challenging to synthesize thermally stable catalysts and metal particles, which do not exceed the upper limit of 2 nm. Alternative conceptual approaches to enhance catalyst stability such as poisoning of the metal (SPARG process) and other means to reduce buildup of carbon at the catalyst have been vividly explored [9–13].

The high reaction temperatures, necessary for reaching sufficient conversion levels, require highly thermo-stable catalysts and we have previously reported new approaches to generate such catalysts based on Ni-containing hexaaluminates [14,15]. The structure of hexaaluminates consists of spinel blocks into which active metals, e.g., Ni, are inserted. Cation-containing (e.g. La³⁺, Ba²⁺, Sr²⁺) mirror planes between the spinel blocks further stabilize the structure. The layered structure of hexaaluminates provides a high thermal stability, making them attractive for high-temperature processes [16–21]. As La³⁺-stabilized Ni-hexaaluminate have been identified as being particularly promising, they are explored and compared to Pt-based catalysts with respect to the mechanism of carbon deposition, because the insight into this aspect of the reaction is important for further developments.

Thermodynamics guide to low pressures and high temperatures to favor DRM over carbon deposition. DRM has been mechanistically explored for many years [3,7,22,23], however, most studies addressing coke deposition have been carried out at atmospheric pressure [24–26]. Cui et al. [27] showed the temperature dependence of the DRM mechanism in a temperature range of 823–1123 K. The authors postulated that the surface reaction of adsorbed CH_x with surface oxygen (originating from CO₂) becomes rate determining above 923 K, with the decomposition of CH₄ to CH_x* and H* being a fast step in the reaction network.

This fact points to the possibility that carbon deposition may involve reactions at these temperatures, which are thermodynamically less favored than the reactions involved in typical coke build up. Detailed studies have been reported by the group of Iglésia

[28,29], using isotope labeling to probe the importance of such reaction steps. In contrast to Cui et al., the activation of the C–H bond in CH₄ was identified as the rate-determining step in CO₂ and H₂O reforming over Group VIII metals. In consequence, all other steps must have been faster under these conditions. Little is known about the impact of a higher overall pressure on CH₄ dissociation as well as the other reaction pathways. The ratio between the rates of reactions leading to the buildup and the removal of carbon species will determine the rate of coke formation on the catalyst surface.

The goal of this work is, therefore, to explore the pathways by which carbon deposition occurs at elevated pressure. A high-temperature stable Ni-hexaaluminate catalyst and a Pt/ZrO₂ catalyst are compared. To study the pathway of coke deposition, ¹³CO₂ was used to trace the origin of carbon formation. Using a previously established network of elementary surface reactions [30,31], reaction pathways on Pt- and Ni-based catalysts were theoretically analyzed. The nature and concentration of carbon deposited were investigated by temperature-programmed oxidation and electron microscopy. From the combination of the experiments and the theoretical calculations, a reaction mechanism with special focus on pathways for buildup and removal of carbon deposits has been established for both metals.

2. Experimental

2.1. Synthesis

The Ni-hexaaluminates were synthesized following ref. [19]. Stoichiometric amounts of the metal nitrates (La, Ni, Al) were dissolved in water and then transferred into a solution of polyethyleneglycole (PEG) in isopropanol. After drying, the sample was calcined in air at 873 K (2 h) and 1473 K (8 h), to yield Ni-hexaaluminate (confirmed by X-ray diffraction). The Pt/ZrO₂ catalyst has been synthesized and supplied by *hte GmbH*.

2.2. Chemisorption measurements

The fraction of catalytic active sites on the Pt/ZrO₂ catalyst was determined by TPO, according to the procedure described in [30]. The Ni dispersion measurements were done on samples pre-reduced in a stream of H₂ at 1073 K and transferred into an automatized Sorptomatic 1990 system where the samples were reduced for another 3 h at 101.3 kPa of H₂ at 673 K. The measurement was conducted at 308 K after evacuation of the system to less than 0.1 Pa. Each pressure increment (range 0.57–1.02 kPa) was equilibrated for 3–5 min. After the first run, the sample was evacuated for 1 h to a pressure below 0.1 Pa, a second isotherm was measured. By extrapolating the linear part of the difference between the two isotherms to zero pressure, the amount of adsorbed H₂ was calculated. The dispersion of Ni was determined assuming a dissociative H₂ adsorption (stoichiometry of 1 for H/Ni_{surface}) [32].

2.2.1. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

A high-resolution FE-SEM (JEOL JSM 7500 F) with EDX (Oxford) was used to study the samples by SEM. TEM images were collected on a JEM-2010-JEOL microscope equipped with a LaB₆ electron source. The emerging electrons were accelerated with a voltage of 120 kV. The resolution of the microscope was 0.2 nm. The samples were dispersed in ethanol using an ultrasonic bath and subsequently applied drop wise to a copper grid supported film. The preparation methods for electron microscopy were identical for both techniques.

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