

Keywords: Dry Reforming of Methane, Nickel Catalyst, Carbon Formation, Thermogravimetric Measurements, Catalyst Deactivation

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ABSTRACT

Dry Reforming of methane (DRM: $\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2$) is an attractive catalytic process for the industrial syngas (CO/H_2) production from CO_2 . Coke formation due to side reactions decreases the catalyst lifetime and can lead to irreversible damage of reformer reactors. The selectivity of a catalyst towards coke formation during DRM can be studied by gravimetric measurements under reaction conditions using a DynTHERM magnetic suspension thermobalance by Rubotherm. Accurate thermogravimetric measurements allow to understand the kinetic of carbon growth on the catalyst and optimizing the reaction conditions leading to minimum coking by retaining the high activity towards syngas.

INTRODUCTION

Many reforming technologies have been introduced in response to the increasing demand for syngas, including dry (carbon dioxide) reforming of methane (DRM: $\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2$), the more traditional steam methane reforming (SMR: $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$), and partial oxidation of methane (POM: $\text{CH}_4 + \text{O}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$). However, investment calculations show that DRM has an essential cost advantage over SMR. In DRM, a highly endothermic reaction, noble metal-based catalysts are very active and stable. Active base-metals, in particular Ni-based catalysts, have a low cost and wide availability but are more prone to fast deactivation by coking, oxidation and poisoning. The carbon deposition originates mainly from the endothermic methane decomposition ($\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$) and Boudouard reactions ($2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$) and may cause damage of reformers. A new noble-metal free Ni-based catalyst is designed and its coking behavior has been studied at the Fritz-Haber-Institute of the Max-Planck-Society, Berlin.

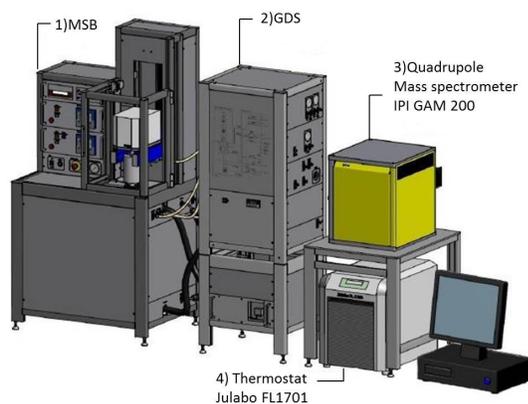


Figure 1. Schematic view of the DynTHERM Thermogravimetric Analyzer Setup including Magnetic Suspension Balance, Gas Dosing System and MS for gas analysis.

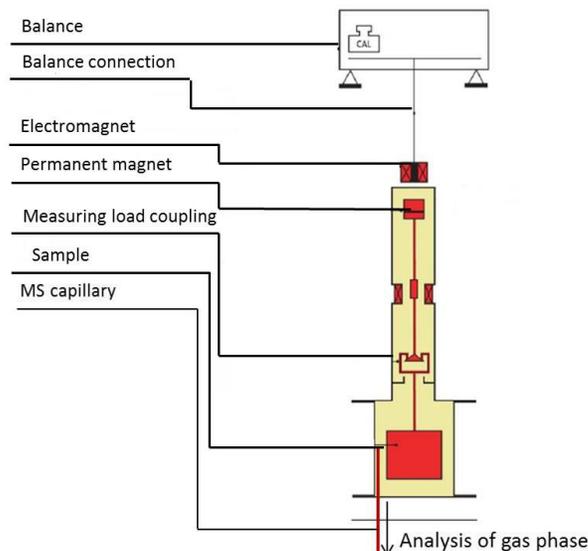


Figure 2: Scheme of thermogravimetric measuring cell.

EXPERIMENTAL

The measurements were performed on the Dyn-THERM Thermogravimetric Analyzer by Rubotherm. Maximum operating conditions of this instrument are 1100 °C and 40 bar. For fast analysis of the evolving gas phase the system was coupled to an online mass spectrometer (IPI GAM 200) using a thin capillary (0.25 mm) that ends directly under the sample crucible. A schematic view of the setup and the scheme of the measuring cell are given in Figure 1 and Figure 2.

RESULTS AND DISCUSSION

The Ni/MgAlO_x catalyst with traces of Co was synthesized according to the well-established route described elsewhere [1] from a hydrotalcite-like precursor obtained by co-precipitation. The elemental analysis of the studied catalyst is presented in the table 1.

Table 1: Elemental Analysis of the Calcined Catalyst

Element	Wt, %
Al	11.6
Co	0.03
Mg	5.1
Ni	54.7
O	28.6

Upon reduction the calcined precursor loses around 20% of mass including residual carbonate and adsorbed water (Figure 3). The reduced catalyst was subjected to DRM conditions and the effects of varying temperatures and flows have been explored (Figure 4). At 850 °C and a flow of 120ml/min no significant increase in catalyst mass was detected within 6hr, indicating low carbon formation. Decreasing temperature to 800 °C results in the continuous mass gain with 8%/hr decelerating to 2%/hr after 5 hrs on stream. Switching to a pure Ar atmosphere for 30 min leads to a stable value of mass indicating the absence of weak bonded surface groups that could be purged away by a continuous Ar flow. At 900 °C previously formed carbon reacts with CO₂ according to the reverse Boudouard reaction and mass decreases.

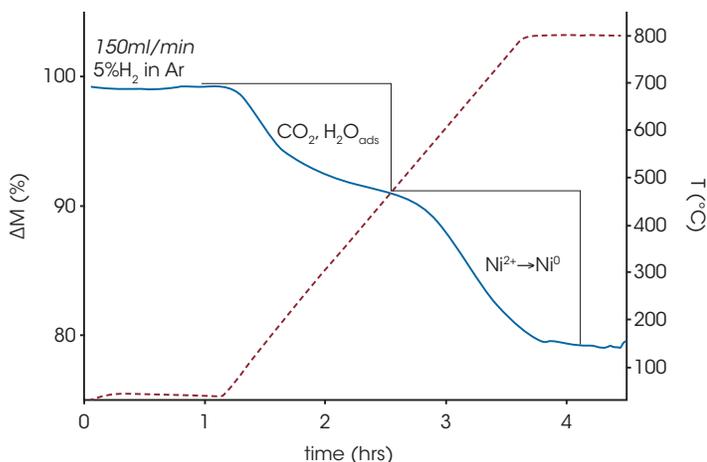


Figure 3: Weight loss of the Ni/MgAlO_x precursor during temperature programmed reduction

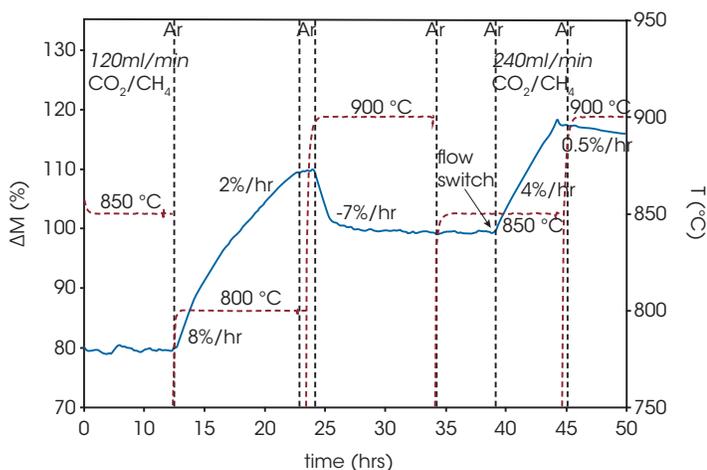


Figure 4: Reduced Ni/MgAlO_x catalyst at different DRM conditions. Argon flow was applied during change of operating conditions. See text for results from IPI online MS measurements.

The weight loss within next 5 hours is accompanied with a slight increase in CO intensity recorded by the mass spectrometer. During the following isothermal period at 900 °C and subsequent segment at 850 °C, no weight changes were detected. However, upon increasing the flow

by 100%, the coking process tremendously takes place with the rate of 4%/hr. The consecutive temperature growth to 900 °C leads to the slow consumption of the formed carbon.

During carbon growth at 800 °C and 850 °C the MS traces of the observed components do not demonstrate any significant changes in intensity. This fact implies that deactivation of Ni/MgAlO_x catalyst probably is related to the type of carbon deposits rather than the total amount of carbon. Comprehensive information on different types of carbon and activity data is presented in upcoming papers [2,3].

CONCLUSION AND OUTLOOK

These results clearly show that two different temperatures regimes exist for this catalyst. At high temperature, the catalyst possess good stability and does not undergo severe sintering and coking, while at lower temperatures coking becomes favorable and the catalyst continuously produces carbon.

It could be shown that the Rubotherm DynTHERM TGA provides valuable data on the coking behavior and enables accurate monitoring of the dynamics of carbon growth during complex DRM processes.

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