



Redox dynamics of Ni catalysts in CO₂ reforming of methane



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ABSTRACT

The influence of redox dynamics of a Ni/MgAl oxide catalyst for dry reforming of methane (DRM) at high temperature was studied to correlate structural stability with catalytic activity and coking propensity. Structural aging of the catalyst was simulated by repeated temperature-programmed reduction/oxidation (TPR/TPO) cycles. Despite a very high Ni loading of 55.4 wt.%, small Ni nanoparticles of 11 nm were obtained from a hydrotalcite-like precursor with a homogeneous distribution. Redox cycling gradually changed the interaction of the active Ni phase with the oxide support resulting in a crystalline Ni/MgAl₂O₄-type catalyst. After cycling the average particle size increased from 11 to 21 nm – while still a large fraction of small particles was present – bringing about a decrease in Ni surface area of 72%. Interestingly, the redox dynamics and its strong structural and chemical consequences were found to have only a moderate influence on the activity in DRM at 900 °C, but lead to a stable attenuation of carbon formation due to a lower fraction of graphitic carbon after DRM in a fixed-bed reactor. Supplementary DRM experiments in a thermobalance revealed that coke formation as a continuous process until a carbon limit is reached and confirmed a higher coking rate for the cycled catalyst.

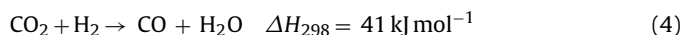
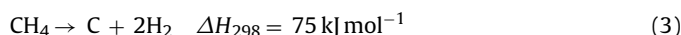
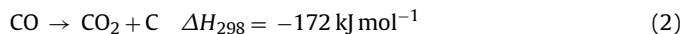
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1. Introduction

Fossil power generations emit large amounts of the greenhouse gas CO₂ [1,2]. For the energetic utilization of anthropogenic CO₂, dry reforming of methane (DRM, Eq. (1)) is an interesting option to convert these two greenhouse gases into syngas (CO/H₂ mixtures) [3]. DRM can be integrated in the well-established downstream syngas chemistry leading to synthetic fuels like alcohols or hydrocarbons [4]. Reforming with CO₂, rather than steam reforming with H₂O yields syngas with lower H₂/CO ratios, which is especially attractive for oxo synthesis (hydroformylation) of aldehydes from alkenes and possibly also for Fischer–Tropsch synthesis of long-chain hydrocarbons [5,6].

Apart from expensive noble metals, abundant nickel based catalysts are known to be highly active in the dry reforming reaction, but suffer from fast deactivation by coking [7,8] that can even lead to reactor blocking. Carbon deposition originates mainly from the exothermic Boudouard reaction (Eq. (2)) or from methane

decomposition (Eq. (3)). Additionally, a deviation from the expected CO:H₂ ratio of 1:1 composition is usually observed due to the reverse water gas shift reaction (Eq. (4)). We have recently reported that mitigation of coking over a Ni-based catalyst is possible by operating the reaction at elevated temperatures of 900 °C [9]. This effect is likely due to the thermodynamic suppression of the Boudouard reaction at such high reaction temperature. Thus, operation at high temperature might be an attractive option for the application of cheap Ni-based catalysts for the DRM reaction.



While Ni-based catalysts are extensively studied in this reaction [10,11], most reports have looked at reaction temperatures up to around 800 °C. It is thus desirable to learn more about the coking behavior, the structural and catalytic stability at higher temperature where only limited information is available in the literature.

Several attempts have been made to suppress coke formation on Ni catalysts using different supports. The addition of basic promoters such as CaO or MgO to Ni/Al₂O₃ catalysts can increase the activity and reduce carbon formation [12,13]. The Lewis basicity of

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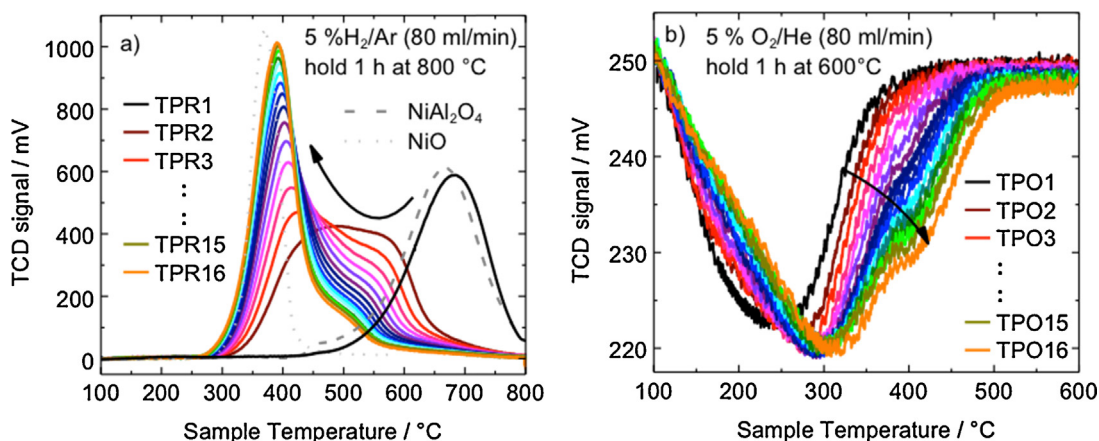


Fig. 1. TPR cycles of Ni/MgAl oxide catalyst calcined at 600 °C and of NiAl₂O₄ (dark gray dashed line) and NiO (light gray dotted line) as references (a); TPO cycles of Ni/MgAl oxide catalyst (b).

these promoters enhances the chemisorption of CO₂ [14], a characteristic that is proposed to reduce the Boudouard reaction by shifting the equilibrium toward CO. The relation of carbon deposition and the catalyst structure was studied by Chen and Ren [15] for a Ni/Al₂O₃ catalyst. They reported on the influence of strong Ni–Al₂O₃ interactions on the catalytic properties during DRM. The formation of a NiAl₂O₄ spinel was found to have a suppressing effect on the carbon formation. Furthermore, the reduction of NiAl₂O₄ compared to NiO results in smaller Ni crystallites [16].

In this work we present an attempt to relate structural stability and redox dynamics of a Ni catalyst with its coking propensity. The catalyst under study contains 55.4 wt.% Ni supported on a mixed Mg, Al oxide that was obtained from a co-precipitated hydrotalcite-like precursor as described in a previous report [9]. The structural and redox stability of the catalyst was tested by subjecting the precursor either to only one calcination and reduction treatment or to multiple TPR/TPO cycles. It has been recently shown that the calcination conditions can have substantial effects on the catalytic performance of Ni/La₂O₃–ZrO₂ catalysts in the low-temperature DRM reaction [17]. On Ni/Al₂O₃ catalysts, Guillaume et al. [18] have observed significant structural and chemical changes of Ni/Al₂O₃ catalysts as a consequence of such redox cycling. They found, that Ni is initially incorporated in a spinel phase formed with the support and that redox cycling at low temperatures progressively extracts metallic Ni from the spinel-type structure. While their catalysts were tested in sequential cracking of acetic acid, we have tested our materials for their DRM activity and coke formation rates in a tubular plug-flow reactor and in a magnetic suspension thermobalance. With this approach the effect of structural ageing as simulated by repeated TPR/TPO cycles can be decoupled from the structural effect induced by coking, e.g. by enhanced metal mobility during carbon filament growth.

2. Results and discussion

2.1. Catalyst preparation and characterization

We have shown recently [9] that Ni nanoparticles supported on a matrix of Mg and Al oxide can be obtained by the preparation of hydrotalcite-like compounds (htl) as well-defined precursor materials. The resulting catalysts are characterized by a homogeneous metal distribution and very small Ni particles that are embedded and therefore stabilized at high temperatures in a Mg,Al mixed oxide matrix. The catalyst used here was prepared via a hydrotalcite-like (htl) precursor of the nominal composition Ni_{0.5}Mg_{0.17}Al_{0.33}(OH)₂(CO₃)_{0.17}·mH₂O. The precursor compound

can easily be prepared from metal nitrates in a phase-pure form by pH-controlled co-precipitation [9]. The Ni content of 50 mol% (metal based) corresponds to a 55.4 wt.% Ni loading in the final catalyst. The 1:2 ratio of Mg to Al in the oxidic matrix was chosen to enable MgAl₂O₄ spinel formation, a sintering-stable ceramic compound. The platelet-like precursor particles provides a specific BET area of 131 m² g_{cat}⁻¹. The calcination was performed at 600 °C. We have previously shown that this temperature is sufficient to completely decompose the hydrotalcite-like precursor [9]. The calcination in air leads to an increase to 213 m² g_{cat}⁻¹ due to shrinkage of the platelets. The characterization details of the phase pure precursor and the calcined product are described in our previous study [9].

The reduction behavior of the calcined material has been investigated using TPR. A single broad peak was observed in the temperature range between 450 and 850 °C. The TPR profile reflects a one-stage process with a maximum at 685 °C (Ni50-TPR1, Fig. 1a). On the basis of the TPR profile with a peak maximum around 700 °C a reduction temperature of 800 °C was chosen for the following experiments. At this temperature the reduction of Ni will be complete after a subsequent holding period of 1 h. The catalyst obtained after reduction at 800 °C is labeled Ni50-TPR1 in this study. It is characterized by small Ni particles of 11 nm, which are partially embedded in an oxide matrix with a high specific Ni surface area of 25 m² g_{cat}⁻¹ (Table 1, Fig. 3) [9]. The elemental distribution (Fig. 6a), determined by TEM-EDX at different locations is rather homogeneous and the average molar composition is close to the nominal values (Ni/Mg/Al: 57/14/30 (±5); nominal 50/17/33). A comparison of the TPR profile with the reduction profile of a NiAl₂O₄ reference material, suggests on a first sight the presence of Ni²⁺ in a NiAl₂O₄ phase formed during the first calcination (TPO0). However, the corresponding XRD pattern revealed the presence of a rock salt-type oxide MO (M = Ni, Mg) and a small fraction of Al₂O₃ (Fig. 2a). The reflexes in general are relatively broad indicating a low crystallinity. An unambiguous discrimination of NiO and MgO is difficult due to very similar lattice constants and the low crystallinity of the obtained material. Though, the presence of NiO seems more likely regarding higher angles > 100° 2θ, where the differences are more distinct due to the widening of the d-space (see inset Fig. 2a). Thus, although the formation of NiAl₂O₄ in nickel/alumina catalysts during oxidation is reported in many publications [16,19–22], our catalyst might be better described as a NiO phase that is strongly interacting with the oxide matrix. Based on XRD, a spinel phase seems to be absent or X-ray amorphous, as no peaks corresponding to MgAl₂O₄ or NiAl₂O₄ are detectable (Fig. 2a). However, the interpretation of the XRD results is usually difficult. Zieliński [16]

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