	Experiment title: XAS study of coke- and sintering-tolerant Al_2O_3 or TiO_2 coated Ni/SiO_2 catalysts on dry reforming of methane	**Experiment number**: 01-01-1001
Beamline: BM01B	**Date of experiment**: from: 29.09.2016 to: 05.10.2016	**Date of report**: 08-02-2017 *Received at ESRF:*
Shifts: 15	**Local contact(s)**: Wouter van Beek	

Names and affiliations of applicants (* indicates experimentalists):

Sung Min Kim*, Paula M. Abdala*, Manouchehr Nadjafi*, Pedro Castro-Fernández*
and Christoph Müller
Laboratory of Energy Science and Engineering, Institute of Energy Technology,
ETH Zurich, Leonhardstrasse 21, 8092 Zurich, Switzerland

Report:

The aim for this project was to examine the chemical and structural changes occurring in Ni/SiO_2 (Ni) and Al_2O_3-coated Ni/SiO_2 (Al-Ni) catalysts, during the dry reforming of methane (DRM). DRM is a promising process to convert two greenhouse gases (CH_4 and CO_2) into a synthesis gas (H_2/CO) that is a key feedstock for liquid fuels produced via Fischer-Tropsch or methanol synthesis. Ni-based catalysts exhibit a high activity, comparable to noble metals, but are prone to carbon deposition and sintering. In preliminary tests, we have observed an improvement in sintering and coke resistance of Ni catalysts when coated with a thin layer of Al_2O_3 by atomic layer deposition (ALD).

In order to elucidate the role of the Al_2O_3 overcoat in catalyst performance, we have carried out combined Ni K-edges XAS and XRD measurements of coated and uncoated Ni catalysts during reduction and under DRM conditions. The data were acquired under the following conditions:

(a) As-synthesized (dried) coated and uncoated catalysts were calcined in air (10 ml/min). XAS and XRD measurements were collected during calcination from room temperature to 800°C.

(b) The calcined catalysts were reduced using a gas mixture containing 5 vol.% H_2 and 95 vol.% He (10 ml/min). XAS and XRD measurements were collected during temperature programmed reduction (TPR) from room temperature to 850°C.

(c) DRM of the reduced catalysts at 750°C using 9 ml/min of 50 vol.% of CH_4 and 50 vol.% of CO_2 mixed with 1 ml/min of He.

The catalysts were placed in the center of a quartz capillary reactor and the effluent gases were analyzed by mass spectroscopy. XANES and XRD data collected during calcination and reduction are shown in Fig. 1. Bragg reflections from NiO were only observed in the calcined catalysts, whereas also $NiAl_2O_4$ was observed in the ALD coated catalyst. The formation of $NiAl_2O_4$ indicates a strong interaction between Ni and the Al_2O_3 layer.

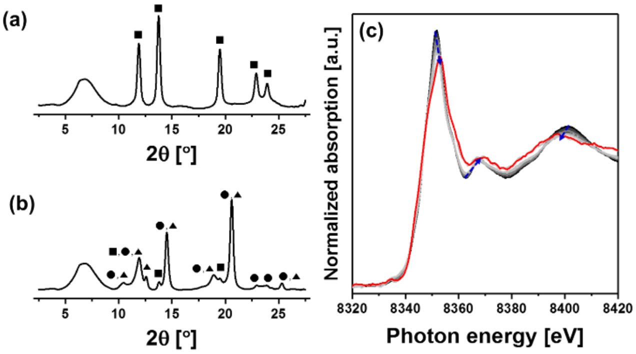

Fig. 1. Normalized diffractograms of (a) uncoated and (b) coated catalysts after calcination. The following compounds were identified: (■) NiO, (●) $NiAl_2O_4$, (▲) Al_2O_3. (c) *In-situ* XANES of coated catalysts during calcination.

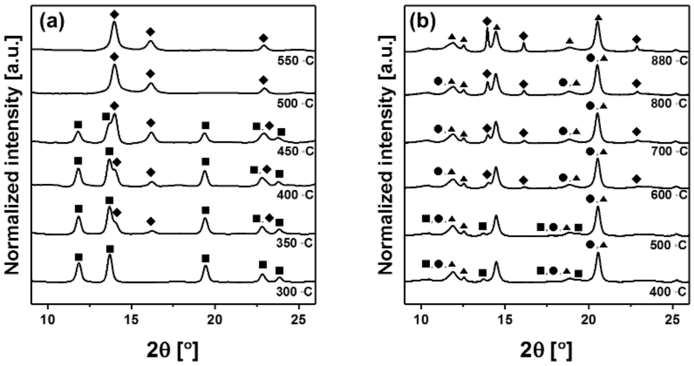

Fig. 2. Selected *in-situ* XRD data (λ=0.5060 Å) of (a) Ni/SiO_2 and (b) Al_2O_3-coated Ni/SiO_2 during reduction. The following compounds were identified: (■) NiO, (●) $NiAl_2O_4$, (▲) Al_2O_3, (◆) Ni.

Figure 2a plots the XAENS data at the Ni K-edge for the reduced and reacted catalysts. We could not observe any significant difference to Ni foil for both the reduced and reacted catalysts independent whether they were coated or not. This indicates that the deactivation of the uncoated catalyst is not due to changes in the oxidation state of the active site Ni. Turning to XRD measurement under DRM conditions, we observed Bragg reflections of graphite in the uncoated catalyst, whereas such reflections were not observed for the coated catalyst. These findings indicate that the formation of coke is the main deactivation mechanism for the uncoated catalysts.

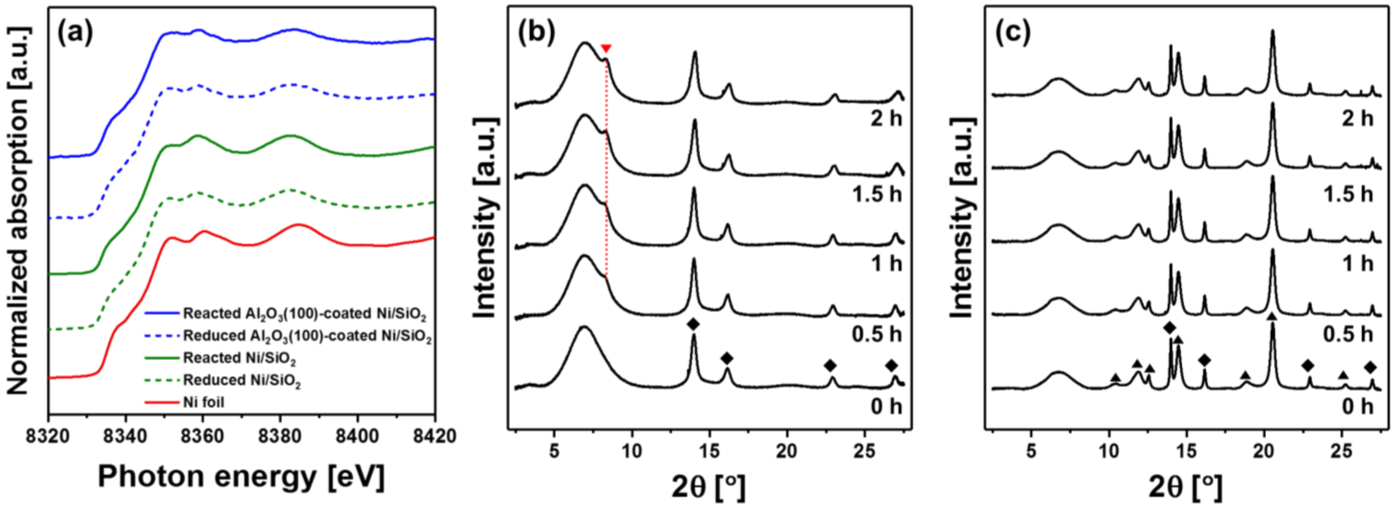

Fig. 2. (a) XANES of the reduced and reacted catalysts under DRM conditions, and diffractograms (λ=0.506 Å) of (a) the uncoated and (b) coated catalyst during DRM. The XANES of Ni foil was included for reference. The following compounds were identified: (▲) Al_2O_3, (◆) Ni and (▼)graphite.

In summary, operando XAS and XRD measurement allowed us to draw the following conclusions: i) Strong Ni-Al_2O_3 interaction due to the formation of $NiAl_2O_4$, ii) deactivation of uncoated Ni due to the formation of graphitic carbon. Combining our operando XAS/XRD results with ex-situ characterizations performed in our lab, we observe that the strong interaction between Ni and Al_2O_3 improves the sintering resistance of Ni, with smaller Ni particles, leading to a lower degree of coke deposition. A more detailed analysis of the data acquired is still under progress and a manuscript for publication is in preparation.