



	<b>Experiment title:</b> XAS study of coke formation and surface oxidation tolerance of bimetallic Ni-Fe catalyst on dry reforming	<b>Experiment number:</b> CH-4340
<b>Beamline:</b> BM01B	<b>Date of experiment:</b> from: 01.04.2015 to: 06.04.2015	<b>Date of report:</b> 24-06-2015  <i>Received at ESRF:</i>
<b>Shifts:</b> 15	<b>Local contact(s):</b> Wouter van Beek	
<b>Names and affiliations of applicants</b> (* indicates experimentalists):  Sung Min Kim*, Sena Yüzbasi*, Paula M. Abdala*, Qasim Imtiaz* and Christoph Müller Laboratory of Energy Science and Engineering, Institute of Energy Technology, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland		

## Report:

The results of these studies have been published in: J. Am. Chem. Soc. 2017, 139, 1937–1949.

**Title: Cooperativity and Dynamics Increase the Performance of NiFe Dry Reforming Catalysts**

**Authors:** Sung Min Kim, Paula Macarena Abdala, Tigran Margossian, Davood Hosseini, Lucas Foppa, Andac Armutlulu, Wouter van Beek, Aleix Comas-Vives, Christophe Copéret, and Christoph Müller\*,  
Laboratory of Energy Science and Engineering, Department of Mechanical and Process Engineering, ETH Zurich, Leonhardstrasse 21, Zurich 8092, Switzerland Department of Chemistry and Applied Sciences, ETH Zurich, Vladimir Prelog Weg 1-5, Zurich 8093, Switzerland §Swiss-Norwegian Beamlines, European Synchrotron Radiation Facility (ESRF), BP 220, Grenoble 38043, France

**ABSTRACT:** The dry reforming of methane (DRM), i.e., the reaction of methane and CO<sub>2</sub> to form a synthesis gas, converts two major greenhouse gases into a useful chemical feedstock. In this work, we probe the effect and role of Fe in bimetallic NiFe dry reforming catalysts. To this end, monometallic Ni, Fe, and bimetallic Ni-Fe catalysts supported on a Mg<sub>x</sub>Al<sub>y</sub>O<sub>z</sub> matrix derived via a hydrotalcite-like precursor were synthesized. Importantly, the textural features of the catalysts, i.e., the specific surface area (172–178 m<sup>2</sup>/gcat), pore volume (0.51–0.66 cm<sup>3</sup>/gcat), and particle size (5.4–5.8 nm) were kept constant. Bimetallic, Ni<sub>4</sub>Fe<sub>1</sub> with Ni/(Ni + Fe) = 0.8, showed the highest activity and stability, whereas rapid deactivation and a low catalytic activity were observed for monometallic Ni and Fe catalysts, respectively. XRD, Raman, TPO, and TEM analysis confirmed that the deactivation of monometallic Ni catalysts was in large due to the formation of graphitic carbon. The promoting effect of Fe in bimetallic Ni-Fe was elucidated by combining operando XRD and XAS analyses and energy-dispersive X-ray spectroscopy complemented with density functional theory calculations. Under dry reforming conditions, Fe is oxidized partially to FeO leading to a partial dealloying and formation of a Ni-rich NiFe alloy. Fe migrates leading to the formation of FeO preferentially at the surface. Experiments in an inert helium atmosphere confirm that FeO reacts via a redox mechanism with carbon deposits forming CO, whereby the reduced Fe restores the original Ni-Fe alloy. Owing to the high activity of the material and the absence of any XRD signature of FeO, it is very likely that FeO is formed as small domains of a few atom layer thickness covering a fraction of the surface of the Ni-rich particles, ensuring a close proximity of the carbon removal (FeO) and methane activation (Ni) sites.

