



	Experiment title: Structure performance correlation in bi-functional M-Mo ₂ C (M=Ni, Fe) catalysts for DRM reaction	Experiment number: CH-5229
Beamline: BM31	Date of experiment: from: 15.11.2017 to: 20.11.2017	Date of report: 09-10-2020
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Names and affiliations of applicants (* indicates experimentalists): Alexey Kurlov*, Paula M. Abdala*, Agnieszka Kierzkowska*, Athanasia Tsoukalou*, Muhammad Awais Naeem*, and Christoph Müller Laboratory of Energy Science and Engineering, Institute of Energy Technology, ETH Zurich, Leonhardstrasse 27, 8092 Zurich, Switzerland		

Report:

Abstract 1

The two-dimensional morphology of molybdenum oxycarbide (2D-Mo₂CO_x) nanosheets dispersed on silica is found vital for imparting high stability and catalytic activity in the dry reforming of methane. Here we report that owing to the maximized metal utilization, the specific activity of 2D-Mo₂CO_x/SiO₂ exceeds that of other Mo₂C catalysts by ca. 3 orders of magnitude. 2D-Mo₂CO_x is activated by CO₂, yielding a surface oxygen coverage that is optimal for its catalytic performance and a Mo oxidation state of ca. +4. According to ab initio calculations, the DRM proceeds on Mo sites of the oxycarbide nanosheet with an oxygen coverage of 0.67 monolayer. Methane activation is the rate-limiting step, while the activation of CO₂ and the C–O coupling to form CO are low energy steps. The deactivation of 2D-Mo₂CO_x/SiO₂ under DRM conditions can be avoided by tuning the contact time, thereby preventing unfavourable oxygen surface coverages.

Abstract 2

Molybdenum carbide (β -Mo₂C) supported on carbon spheres was prepared via a carbothermal hydrogen reduction (CHR) method from delaminated nanosheets of molybdenum(VI) oxide (d-MoO₃/C). The carburization process was followed by combined in situ XANES/XRD analysis revealing the formation of molybdenum oxycarbide Mo₂C_xO_y as an intermediate phase during the transformation of d-MoO₃/C to β -Mo₂C/C. It was found that Mo₂C_xO_y could not be completely carburized to β -Mo₂C under a He atmosphere at 750 °C, instead a reduction in H₂ is required. The β -Mo₂C/C obtained showed activity and stability for the dry reforming of methane at 800 °C and 8 bar. In situ XANES/XRD evaluation of the catalyst under DRM reaction conditions combined with high resolution TEM analysis revealed the evolution of β -Mo₂C/C to Mo₂C_xO_y/C. Notably, the gradual oxidation of β -Mo₂C/C to Mo₂C_xO_y/C correlates directly with the increased activity of the competing reverse water gas shift reaction.^[2]

- [1] A. Kurlov, E. B. Deeva, P. M. Abdala, D. Lebedev, A. Tsoukalou, A. Comas-Vives, A. Fedorov, C. R. Müller, *Nat. Commun.* **2020**, *11*, 4920.
- [2] A. Kurlov, X. Huang, E. B. Deeva, P. M. Abdala, A. Fedorov, C. R. Müller, *Nanoscale* **2020**, *12*, 13086-13094.