Novel tools for correlation between chemical activity and in situ structural evolution of catalyst particles in gas environment

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In the last years, in situ transmission electron microscopy (TEM) with gas environment has been used as a powerful tool to visualize structure changes of catalyst particles under heterogeneous catalysis conditions.[1, 2] However, in order to obtain a detailed understanding of the catalytic activity, it is crucial to correlate structural changes with chemical activity analysis, for instance using mass spectrometry and calorimetry. The possibility to perform direct correlation under industrially relevant, high-pressure and high temperature conditions will help us to link structure evolution and catalytic properties.

In this work, we studied the activity of palladium nanoparticles during the catalytic oxidation of methane and other gases using a FEI Titan TEM operated at 300 kV combined with a DENSsolutions Climate in situ gas & heating system. Carbon monoxide and methane, in different ratios, were used as reactive gases (Fig. 1, upper graph). The structure changes of palladium nanoparticles during the catalytic reaction were recorded using in situ STEM (Fig. 1, STEM images). Simultaneously, the catalyst performance was analyzed by monitoring the reaction products (CO_2, CO) using the mass spectrometer (Fig. 1, lower graph). During the experiments, the changes in CO_2 and CO product content while decreasing the oxygen composition were clearly visible. This indicates a decrease in the activity of the catalytic reaction, which corresponds well with the in situ STEM movie. Furthermore, chemical analysis via mass spectrometry and physical analysis via TEM imaging were combined with in situ calorimetry using power data from the MEMS-based heating device (sample carrier). It was observed that at certain experimental conditions the catalytic reaction exhibits oscillatory behavior that are strongly sensitive to the chemical environment, like methane concentration. (Fig. 2).

The correlation between TEM data, chemical analysis of the catalytic reaction, gas composition, temperature and calorimetric data provides an intuitive tool helping us to probe the structure-property relationship of catalytic particles in the reactive environment, which can be easily applied to other heterogeneous catalytic reactions.

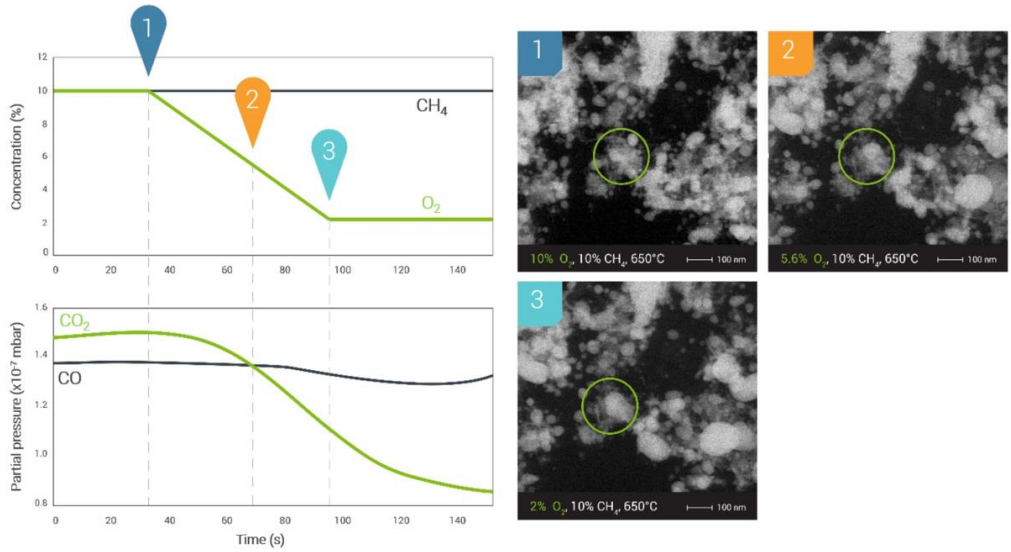

Figure 1: Upper graph shows the applied gas conditions during the in situ experiment, where we lowered the O_2 concentration from 10% to 2%. Simultaneously, the mass spectrometry data in the lower graph shows a decrease in CO_2 and CO reaction products. STEM images on the right (snapshots from the in situ STEM

movie) correspond with the different conditions, showing changes in the morphology of the palladium catalyst (encircled region).

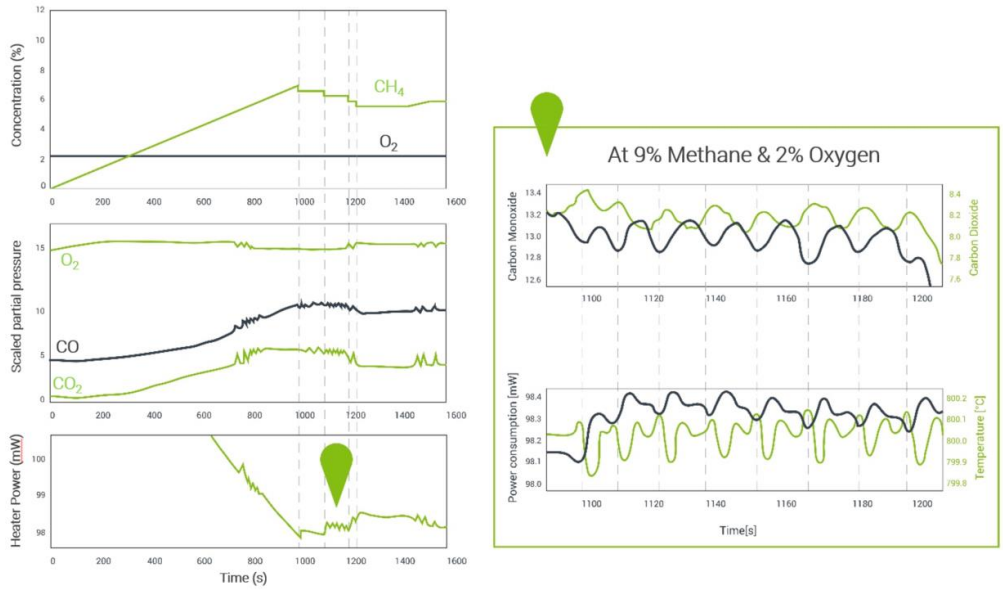

Figure 2. Top left graph shows the input reactant gas composition, with an increase ramp in CH_4 concentration from 0% to 10% while O_2 was kept stable at 2%. Middle graph shows the corresponding mass spectrometer signal, where oscillations are visible, showing that the catalytic reaction exhibits oscillatory behavior between a high- and low-activity phase. The oscillations observed in the mass spectrometer signal correspond with spikes in the MEMS heater power data (lower graph). Inset graphs on the right show the high temporal resolution of the mass spectrometer and corresponding MEMS power data, of the oscillations which occur at 9% CH_4 and 2% O_2.

[1] Y. Jiang, H. Li, Z. Wu, W. Ye, H. Zhang, Y. Wang, C. Sun, Z. Zhang, *Angew. Chem. Int. Ed.* **2016**, *55*, 12427.
[2] X. Zhang, J. Meng, B. Zhu, J. Yu, S. Zou, Z. Zhang, Y. Gao, Y. Wang. *Chem. Comm.* **2017**, *53*, 13213.