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Studying a bifunctional Cu/ZnO-zeolite catalyst for direct production of dimethyl ether with *in situ* ptychography and ETEM

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Recently, it was shown that hard X-ray ptychography offers a resolution below 10 nm¹. Hence, it is promising for investigation of catalysts *in situ*, as the high penetration depth allows measurements inside a reactor. Due to the possibility to measure under controlled environmental conditions (elevated temperature, gas flow, pressure) and to gain a high resolution, it can be used as a complementary tool to electron microscopy. To understand structure-activity relationships during catalytic application, *in situ* studies are required and microscopic studies have to be performed at different length scales², whereby the meso scale can be well covered by X-ray microscopy and the nanoscale by Environmental Transmission Electron Microscopy (ETEM). The present study comprises the development of *in situ* cells for hard X-ray microscopy and its combination with ETEM to study structural changes both in the nm scale and in the 20-500 nm scale on a bifunctional core-shell catalyst. The catalyst consists of a methanol producing core of CuO-ZnO/Al₂O₃ surrounded by a ZSM-5 zeolite shell,³ which promotes methanol dehydration to form dimethyl ether (DME). This bi-functional catalyst shifts the chemical equilibrium to the formation of DME and enhances the selectivity to it^{3,4}. Upon reductive activation, the CuO in the catalyst core is reduced, which leads to a shrinkage of the Cu containing crystallites⁵. This may in turn affect the activity and bifunctional operation of the catalyst. Therefore, the stability and behaviour of the core-shell interface was studied during redox cycles with respect to volume changes of the Cu containing crystallites.

In situ ptychography studies were performed in a specialized *in situ* cell⁶ (see Figure 1) compatible with ptychographic measurements which were performed at the nanofocus endstation of the beamline P06 at PetraIII. For reduction and re-oxidation, pre-mixed gas mixtures (4% H₂/He) and synthetic air (20% O₂/N₂) were used. The reduction and re-oxidation processes were studied at 250°C and 350°C respectively. For ETEM studies, the reduction was performed at 1 mbar (H₂) and re-oxidation at 3 mbar (O₂) at 250°C and Scanning Transmission Electron Microscopy-High Angle Annular Dark Field (STEM-HAADF) images were performed using a FEI Titan E-Cell 80-300 ST TEM operated at 300 kV.

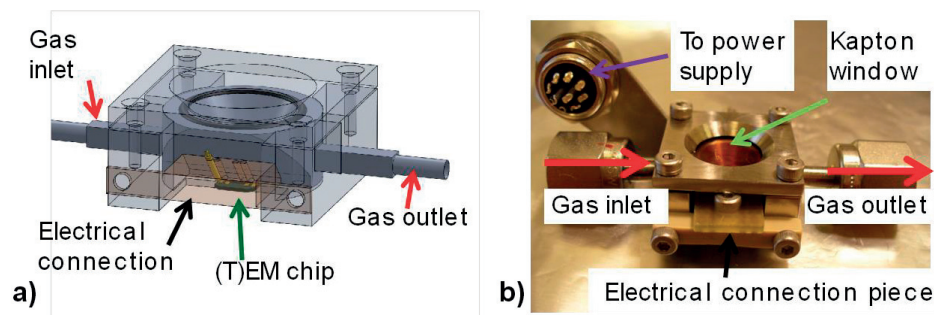


Figure 1: a) Schematic representation and b) photograph of the *in situ* cell used for ptychography.

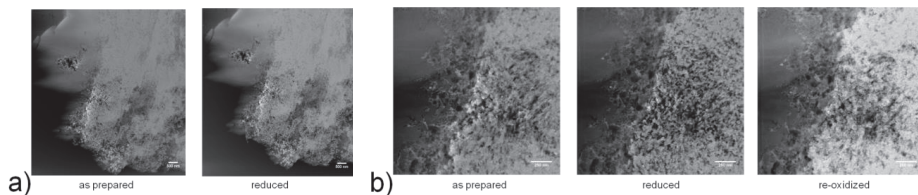


Figure 2: a) STEM-HAADF overview images of the examined core-shell areas, b) example of STEM-HAADF images revealing the separation of the core material, while the interface to the shell remains stable.

Selected STEM-HAADF images are presented in Figure 2. In the overview images (Figure 2a)), hardly any changes could be observed between the as prepared and the reduced state. On a magnified area (Figure 2b)), changes in the core material became obvious when the sample was reduced and re-oxidized. However, the shell stayed stable although the core material became more separated in the reduced state, which could be explained by volume shrinkage of the Cu containing crystallites.

In contrast to the measurements under model conditions in the ETEM, the sample could be studied during activation under realistic conditions (atmospheric pressure) by applying *in situ* ptychography. A series of images at different temperature steps and gas atmospheres is presented in Figure 3. No obvious changes occurred at lower temperature, but at T~350°C, changes became visible. These included movement of the Cu containing areas as well as structural changes in the Cu free area, albeit the shell stayed stable and was not influenced by the redox processes in the core material, in agreement with the results obtained by STEM.

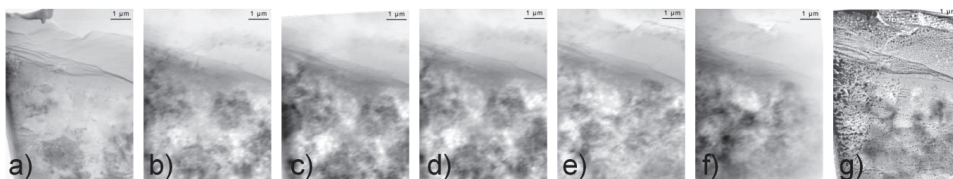


Figure 3: a) Inverted *ex situ* BSE-SEM image (vacuum), b-f) *in situ* ptychograms (phase contrast) b) room temperature in He, c) 250°C in H₂, d) 250°C in O₂, e) 350°C in H₂, f) 350°C in O₂, g) inverted *ex situ* BSE-SEM image after the *in situ* treatment at PetraIII, P06.

The activation of a bifunctional core-shell catalyst was studied by complementary ETEM and *in situ* ptychography. By ETEM under model-like conditions, the results indicate a stable core-shell structure which was not influenced by redox processes occurring inside the core. Applying *in situ* ptychography measurements, the activation was studied for the first time under realistic conditions. The results support the presence of a stable core-shell interface which is not influenced by processes inside the core. Despite the relatively lower resolution of X-ray microscopic methods compared to electron microscopy, this study demonstrates the complementarity and potential of *in situ* ptychography for studying active catalytic processes under realistic conditions. Additionally, further studies by X-ray tomography on the whole catalyst grain are going to be performed.

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