**Electronic Support Information**

**Stability of a bifunctional Cu-based core@zeolite shell catalyst for DME synthesis under redox conditions studied by ETEM and *in situ* X-ray ptychography**

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This Electronic Support Information (ESI) provides additional basic characterization of the bifunctional catalyst and further information on the study of the stability of the CuO/ZnO/Al2O3@ZSM-5 core‑shell catalyst studied by ETEM and *in situ* X-ray ptychography during reduction (activation) and reoxidation.

Figure S1 shows top-view SEM images of the as-prepared catalyst, revealing a closed shell of micrometer sized zeolite crystals, which also cause sharp reflexes in the X-ray powder diffraction pattern depicted in Figure S2. Figure S2 also reveals broad reflexes for the core material consisting of CuO and ZnO.

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Figure S1: Top-view scanning electron micrographs of the core-shell material showing the homogeneous coverage of the core with the zeolite shell. SE-micrographs were taken by a Carl Zeiss Ultra55 microscope at 2 kV acceleration voltage.

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Figure S2: Powder X-ray diffraction pattern of the core-shell catalyst. Pattern obtained from a Phillips X'pert Pro Diffractometer using Cu-Kα radiation. Reference patterns taken from the ICDD-Database (International Center for Diffraction Data).

Figure S3 shows the Fourier Ring Correlation (FRC) analysis to estimate the spatial resolution obtained by *in situ* X-ray ptychography (van Heel & Schatz, 2005). The intersection of the FRC with the 1/2-bit threshold curve indicates a spatial resolution of 28 nm.

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Figure S3: FRC plot to estimate the spatial resolution obtained by *in situ* X-ray ptychography at RT while probing with a photon energy of 9032 eV (first image in Figure 4, top row).

Figure S4a and b show the BSE‑SEM images before and after *in situ* X-ray ptychography. Blue horizontal lines, as well as light blue and red arrows, indicate the same sample positions before and after treatment. By comparison of SEM images before and after the *in situ* X-ray ptychography experiments, no effects related to beam damage could be observed, except that the resin (top right corner in Figure S4) did not resist the high temperatures during the *in situ* treatment.

Figure S5 shows the BSE-SEM image after the treatment and the EDX maps for Cu, Al, Si and Pt. By comparison of Figure S4a and b with Figure S5b, one can conclude, that the Cu containing material of the core is localized at a different position after the treatment. Furthermore, the bright “dots” distributed all over the BSE‑SEM image after the treatment could be related to platinum, as shown in Figure S5d. In fact, the platinum used for fixation of the sample on the Protochips E‑ChipTM, was unstable probably during the highest reaction conditions and was therefore deposited in the neighboring area.

F:\paper_conferences\paper\draft_CuZn-ZSM5\Figures\ptychosample_SEM2.tifFigure S4: BSE-SEM image a) before the *in situ* X-ray ptychography treatment and b) after the *in situ* X-ray ptychography treatment.

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Figure S5: a) BSE-SEM image of the sample after the *in situ* treatment and EDX maps for b) Cu, c) Al, d) Si and e) Pt.

Figure S6a shows a TEM image of a core‑shell interface of another sample recorded in a conventional TEM under vacuum conditions, while Figure S6b shows the same area of the sample probed by *in situ* X-ray ptychography at 8.920 keV under ambient pressure and a flow of He. A comparison reveals, that a similar resolution can be obtained by both methods. For such thick samples, X-ray ptychography reveals a higher contrast, which can be seen in the central part of Figure S6b. However, the areas on the borders of the image were not in the field of view of the X-ray beam. They are affected by reconstruction artifacts, shown by an “out of focus” appearance of the outer parts of the image.

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Figure S6: a) Merged bright field TEM image a core‑shell interface recorded in a conventional TEM under vacuum conditions. The vertical line shows the position where the two images were merged. b) Corresponding phase contrast image recorded by *in situ* X-ray ptychography at approximately 1 bar under a flow of He (3 ml/min).

Since the presented microscopic studies involve several steps of sample preparation, the sample appearance can potentially be changed on different levels although the techniques are commonly applied in microscopy. First, during polishing of the embedded sample, mechanical stress could potentially introduce ruptures in the structure. However, preliminary tests revealed that the sample seems to remain stable, as mostly an intact connection of the core and the shell was observed. The next preparation step was Ar ion milling which could potentially lead to formation of defects in the crystal or material redeposition, but no visible effects were found for this sample. For the *in situ* X-ray ptychography experiment, the sample was transferred to the Protochips E‑ChipTM by a FIB-SEM equipped with a sample manipulator. Potential damage could be caused by Ga bombardment extended to regions of interest, Pt and material redeposition or Ga implantation during fixation on the chip and releasing the sample from the micromanipulator, respectively. Before *in situ* X-ray ptychography, no Pt contamination was observed, but a slight amount of Ga distributed over the sample. However, after the most severe *in situ* treatment (350°C, change of gas atmosphere), the Pt used for fixation covered the sample surface, as shown in Figure S4b and S5d. For future experiments, this could be circumvented by either using adhesive forces for fixation or cooling down to room temperature for changing of the gas atmosphere. Apart from the resin which did not resist the high temperatures during the *in situ* treatment, no damage of the sample was observed independent if the area was probed by X-rays or not, which leads to the conclusion that the exposure of the sample to the X-ray beam did not lead to visible beam damage. Also for ETEM experiments, no noticeable beam damage could be observed, but a slight carbon deposition where the beam was parked for STEM imaging, was found.

References:

van Heel, M. & Schatz, M. (2005). Fourier shell correlation threshold criteria. J. Struct. Biol. **151**(3), 250-262.