



Experiment title: Combined operando XRD/XAS/Raman investigation of copper migration and phase composition in working copper-zeolite composite catalysts for direct dimethyl ether synthesis

Experiment number:
CH-4339

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Shifts:	Local contact(s): Dr VAN BEEK Wouter	<i>Received at ESRF:</i>

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Report:

Summary

The structure of copper-zeolite hybrid catalysts was studied during direct dimethyl ether synthesis from syngas using a combination of synchrotron based time-resolved X-ray diffraction and X-ray absorption. This report represents the first study of the structure of direct DME catalysts performed at the realistic reaction conditions (high pressure and temperature). Copper is present in metallic form under the reaction conditions. No copper oxidation was detected. Copper sintering seems to be a major mechanism of the hybrid catalyst deactivation during the first hours of the reaction.

The accomplishment of the proposal has led to a manuscript published in Applied Catalysis A and another one submitted to Angew. Chem. Int. Ed and. The results were disclosed in the invited keynote lecture at the 12th European congress on catalysis (Europacat 12, Kazan, 2015) and 24th Meeting of North American Catalysis Society (24NAM, Pittsburgh, 2015).

The target of the experiment was an operando XRD/XANES/EXAFS investigation of the evolution of the structure of copper-zeolite hybrid catalysts at the genuine conditions of direct DME synthesis. In particular, the experiments focused on the identification of copper oxidation state and copper sintering during the high pressure reaction conditions.

Dimethyl ether (DME) is one of the most promising environmentally optimized alternatives to the conventional fossil fuels (gasoline or diesel fuels) due to its high cetane index (> 55), low emission of CO, NO_x, particulates and reduced noise. DME is manufactured from syngas (H₂/CO mixture) which can be generated either from renewable (e.g. biomass) or fossil resources. In the conventional two stage DME synthesis, syngas is first converted into methanol. Then in the second stage, methanol is dehydrated to DME. In that technology, the maximum syngas conversion to methanol is limited by thermodynamics, especially at high temperatures. Direct DME synthesis, which was recently developed, overcomes these thermodynamic constraints. In the direct DME synthesis, the reaction occurs in a single reactor under high pressure and

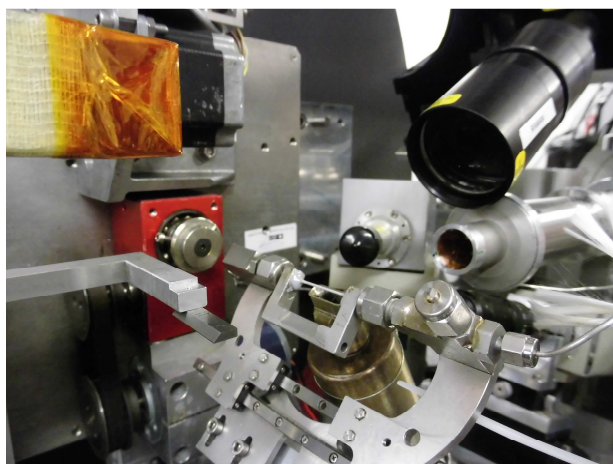


Figure 1. Operando setup used for simultaneous measurement of XANES/EXAFS and XRD during direct DME synthesis from syngas

temperature over a bifunctional catalyst which contains simultaneously active phases for carbon monoxide hydrogenation and methanol dehydration. The most important challenge of direct DME synthesis is catalyst deactivation which reduces catalyst life time and DME productivity. The information about deactivation mechanisms occurring in bifunctional Cu/ZSM-5 catalysts is rather contradictory, because of the lack of direct characterization techniques operating under the harsh reaction conditions.

A series of copper zeolite copper-zeolite hybrid catalysts for the synchrotron experiments with different stability were prepared in our laboratories by kneading. They were characterized by a number of characterization techniques, such as XRD, XPS, TPR, TEM; their catalytic performance in terms of carbon monoxide conversion and stability was evaluated in our laboratories in fixed bed reactors at 260-300 °C and pressure of 20 bar (H₂/CO=2).

The synchrotron experiments conducted in the ESRF involved simultaneous measuring XRD patterns, XANES spectra and EXAFS using a quartz capillary operando cell-catalytic reactor (Figure 1). A similar catalytic operando cell was previously used for investigation of the structure of working cobalt Fischer-Tropsch catalysts [1]. Prior to the catalytic tests the catalysts were reduced in hydrogen at 290°C. Then, the catalysts were exposed to syngas (H₂/CO=2) at total pressure of 20 bar at 260°C, while continuously measuring XRD, XANES/EXAFS at Cu K-edge. The analysis of the reaction products was conducted using a mass spectrometer.

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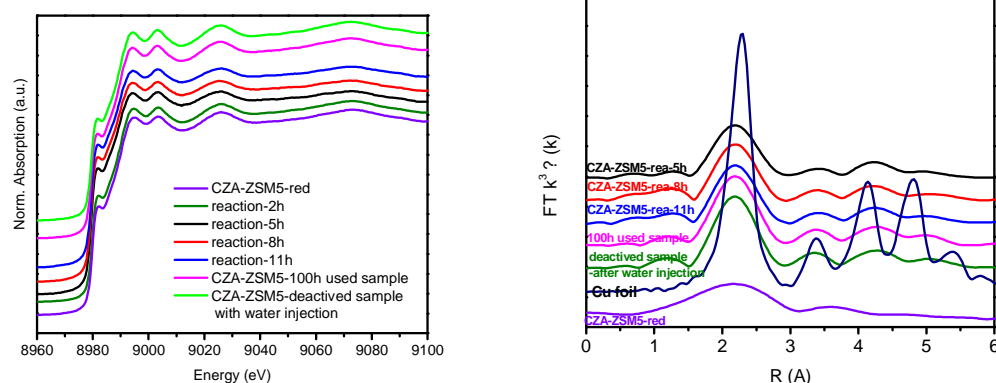


Figure 2. Cu K-edge XANES spectra (left) and EXAFS Fourier transform moduli (right) measured during direct DME synthesis over Cu-zeolite hybrid catalysts

The Cu K-edge XANES spectra and relevant EXAFS Fourier transform moduli of the reduced and working catalysts in comparison with Cu foil are shown in Figure 2. Cu foil shows the absorption edge at 8979 eV and two resonance features at 8993 and 9003 eV. The absorption at the edge at 8979 eV corresponds to 1s to 4p electronic transitions. The XANES shapes for the reduced and working catalysts are almost identical and similar to reference foil indicating the presence of mainly metallic Cu in the sample at the reaction conditions. Interestingly, the XANES spectra do not evolve as a function of time of stream. This suggests that metallic copper remains the dominant copper phase during direct DME synthesis over copper zeolite-hybrid catalysts. Several authors attribute catalytic activity of copper catalysts in methanol synthesis either to metallic copper or Cu^+ ions [2]. Our results suggest that the concentration of Cu^+ ions under the reaction conditions is well below the detection limit of the XANES technique (<5%).

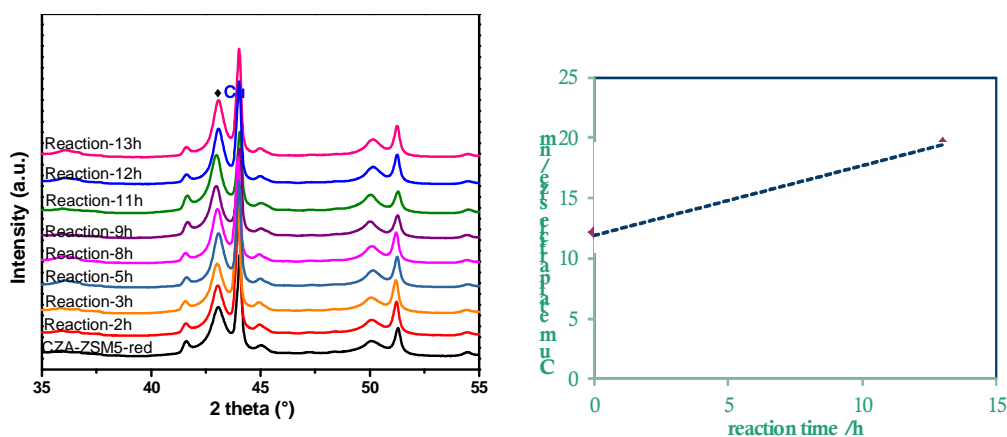


Figure 3. Operando XRD patterns (left) and evolution of the sizes of copper metallic particles (right) during the direct DME synthesis over copper-zeolite hybrid catalysts.

stream. This suggests modification of copper local coordination during the reaction which can be tentatively assigned to copper sintering. Previously, we observed [3] an increase in the copper nanoparticle size in the used catalysts for direct DME synthesis using STEM-EDX analysis.

Figure 3 displays operando XRD patterns measured over Cu-zeolite hybrid catalysts during the direct DME synthesis experiment using a position sensitive detector. The patterns exhibit several XRD peaks attributed to copper metallic species, zeolite and a sample holder. The patterns slowly evolve with time-on stream, showing narrowing the peaks attributed to metallic copper phases, which indicates sintering of copper particles from 12 to 20 nm (Figure 3, right). The in-situ results were consistent with post-reaction characterization.

Thus, a combination of XANES/EXAFS/XRD is indicative of the following phenomena occurring during direct DME synthesis over copper zeolite hybrid catalysts:

- Metallic copper is a major phase in different copper zeolite catalysts for direct DME synthesis from syngas under the reaction conditions.
- Copper sintering seems to be a major mechanism of deactivation of copper zeolite hydride catalysts.

The accomplishment of the proposal has led to two manuscripts published in Applied Catalysis A and submitted to Angew. Chem. Int Ed. The results were also disclosed in the invited keynote lecture at the 12th European Congress on Catalysis (Europacat 12, Kazan, 2015) and 24th Meeting of North American Catalysis Society (24NAM, Pittsburgh, 2015)

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In agreement with XANES, EXAFS (Figure 2) is also indicative of the presence of copper metallic species in the working copper zeolite catalysts. Interestingly, the width of the peak in EXAFS Fourier transform moduli attributed to Cu-Cu first coordination in metallic copper decreases with time on