Activation of a Cu/ZnO methanol catalyst studied with \textit{in situ} ASAXS

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Catalysts for methanol synthesis are of vital importance for many applications in industrial chemistry, and may quickly become very important as a key component of the "hydrogen society". Presently, the best catalysts for methanol synthesis are based on Cu as the catalytic active component, supported on ZnO substrate particles. The catalyst should maintain a high porosity and surface area.

This system is however, prone to substantial deactivation under methanol synthesis conditions (220° C, CO, CO\textsubscript{2}, H\textsubscript{2} reactant gas) for reasons that are not clearly understood. Although it is generally acknowledged that Cu metal is the catalytic active component, its exact state and how it interacts with the substrate is not well described, which hampers speculation on mechanisms for deactivation.

We have previously reported on ASAXS studies of dynamical effects in a methanol model catalyst as a function of reactant gas oxidation potential \cite{1}. This model catalyst consist of ZnO with 5 \% Cu loading, formed by coprecipitation of Cu,Zn hydroxy carbonates, followed by calcination at 300° C. The catalyst is activated by slow heating to 220°C in a gas mixture of CO, CO\textsubscript{2}, H\textsubscript{2} in argon. We report here on our latest studies of this activation process.

Recent results from \textit{in situ} resonant powder diffraction and \textit{in situ} electron energy loss spectroscopy \cite{2} indicate that Cu may be completely or partially dissolved in ZnO in the calcined catalyst, and that the catalytic active, nanometer sized, Cu metal particles are formed during the reduction process. Upon reoxidation it appears that Cu does not form the tenorite CuO phase, but instead adopts the ZnO wurtzite structure (either dissolved in ZnO or as an epitaxial layer). In order to determine the distribution of Cu after calcination, after reduction, and after reoxidation, we studied these processes in an \textit{in situ} ASAXS experiment at the B1 (JUSIFA) beamline. The experimental setup is described in \cite{3}.

The measured scattering cross sections are separated into partial structure factors as formulated in the Bhatia-Thornton expression \cite{4}, defining a topological contrast structure factor $S_{NN}$, a compositional contrast structure factor $S_{CC}$, and a correlation structure factor, $S_{NC}$ \cite{5}.

The ASAXS measurements of the as-prepared sample, yield a negative compositional partial structure factor. This might signify the lack of phase separation between CuO and ZnO, but this and other suggestions are presently under investigation. If the compositional partial structure factor actually represents a homogeneous distribution of Cu in ZnO, it may be viewed as a "diluted" representation of the composite particle scattering cross section.

After reduction, the separated (positive) compositional partial structure factor clearly display the formation of Cu particles (Fig. 1), with a radius of gyration about 2 nm (cf. \cite{1}).

When the sample is reoxidised \textit{in situ}, the particulate contribution to the compositional partial structure factor disappears, indicating that the Cu particles are redispersed onto (or into) the substrate particles. Comparison with the separated structure factors from the as-prepared sample, does however suggest that the sample state is not completely reversible. Evidently, the analysis is still in progress.
Figure 1: Separated partial structure factors from scattering cross section of reduced (activated) methanol model catalyst, consisting of ZnO substrate particles with 5% Cu loading.

References