In situ ASAXS investigations of dynamic nano-scale structural changes in a Cu/ZnO based methanol catalyst

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One of the most successful catalysts for methanol synthesis basically consists of nanometer sized metallic Cu particles dispersed on a ZnO support material with high surface area. This system has been studied for a number of years and exhibits some interesting dynamical effects, correlated to composition of the reactant gas feed. EXAFS measurements have indicated a change in apparent coordination number of Cu atoms that is correlated with methanol production rate, as a function of oxidation potential of the reactant gas. The change in coordination number has been interpreted as a reversible morphological change of the Cu crystallites [1]. This interpretation is supported by recent results from in situ TEM investigations on a Cu/ZnO model catalyst [2]. At least two mechanisms may be responsible for the observed dynamic effects. Adsorbates (e.g. H\(_2\)O) may change the surface free energy of the nano crystallites, and partial reduction of the support surface may change the interface interaction energy.

The present study aims at investigating these effects using anomalous small angle X-ray scattering (ASAXS) on model catalysts and real catalyst materials under realistic working conditions i.e. at a temperature of 220° C in a flow of synthesis gas (5% CO, 5% CO\(_2\) in H\(_2\)). The oxidation potential of the gas is varied by addition of 4-5 % water vapour. The study is initially focused on the same model system as the one used for EXAFS measurements, consisting of 5 weight % Cu on ZnO. The experiments are performed at the JUSIFA (B1) ASAXS beamline at HASYLAB. After temperature programmed reduction of the catalyst CuO in situ, ASAXS data are acquired under methanol synthesis conditions (see above). This entails recording the scattering curve at 10 different energies in close proximity to the absorption edges for Cu and Zn. Following Haubold et al. [3], the scattering cross section can be formulated in terms of partial structure factors:

\[
\frac{d\sigma}{d\Omega}(\vec{q}, E) = |f(E)|^2 S_{NN}(\vec{q}) + |\Delta f(E)|^2 S_{CC}(\vec{q}) + 2 \text{Re}\left\{\int f^* \Delta f S_{NC}(\vec{q})\right\}
\]

known as the Bhatia-Thornton expression [4] where \(S_{NN}\), \(S_{CC}\) and \(S_{NC}\) represents the partial structure factors for topological and chemical contrast, and their correlation, respectively.

![Figure 1: Partial structure factors, separated by in situ ASAXS during methanol synthesis in 'wet' syngas.](image-url)
With scattering cross sections measured at 10 energies, this formulation corresponds to an overdetermined system of linear equations that may be solved by appropriate least squares methods. Figure 1 shows the solution for the scattering cross section measured with the catalyst in 'wet' synthesis gas (~5 % water vapour). The high-q part of the scattering curve can be fitted by the unified exponential/power-law approach (Fig. 2) suggested by Beaucage [5], where the structural level (one size distribution) is characterised by an exponential regime, followed by a power-law regime:

$$I(q) = G \cdot \exp\left(\frac{-q^2 R_G^2}{3}\right) + B \left[\frac{\text{erf}\left(q R_G \sqrt{6}\right)}{q}\right]^P$$

Figure 2: Separated chemical contrast structure factors measured under 'wet' and 'dry' conditions. Full lines represent the unified exponential/power-law fits (corresponding fit parameters in the table below).

<table>
<thead>
<tr>
<th>Gas type</th>
<th>$G$</th>
<th>$B$</th>
<th>$R_G$ [Å]</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>'Dry'</td>
<td>74290</td>
<td>5.28</td>
<td>20.8</td>
<td>1.1</td>
</tr>
<tr>
<td>'Wet'</td>
<td>149900</td>
<td>6.27</td>
<td>22.8</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The small increase in particle radius, may be indicative of a change from dome-shaped to more spherical Cu particles, as has been observed with in situ TEM. This interpretation can be substantiated if the observation is reproducible and reversible. Further experiments and analysis are in progress.

References