Simultaneous SAXS and WAXS Measurements for *in situ* Investigations of Fischer-Tropsch Synthesis

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The Fischer-Tropsch synthesis (FTS) is a set of chemical reactions that forms hydrocarbon chains from a mixture of CO and H_2. The outcome can be used for petroleum substitutes, such as synthetic diesel (see for example [1]). Typically, cobalt nanoparticles of diameter 6-200 nm are used as catalyst, and optimal particle size as well as high temperature and pressure are required for the reactions to work well. After the syngas (H_2/CO) is introduced to the system, a change in the catalytic activity is observed during the first few hours. Until present, a correlation between these changes to the structure of the catalyst particles has not been found (it is very difficult using for example environmental transmission electron microscopy). On this basis, we decided to test if it is possible to use *in situ* small-angle X-ray scattering (SAXS) for monitoring the gross structural features of the nanoparticles. Due to their penetrating properties, X-rays provide a suitable probe for studying catalysts during reactions.

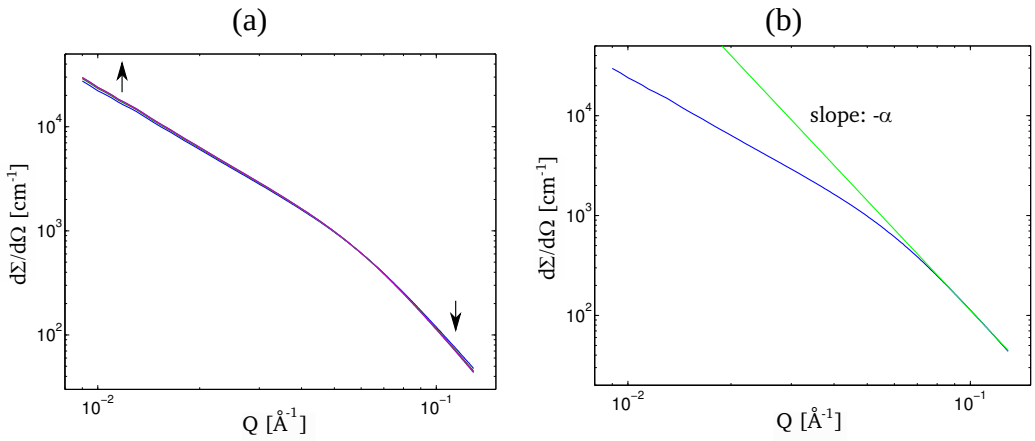

Figure 1: (a) Measured SAXS patterns from cobalt nanoparticles immediately before and some time after introducing syngas (H_2/CO). In order to quantify changes, a straight line has been fitted to the data at large Q (as illustrated in (b)), for all the measured SAXS patterns.

The SAXS/WAXS experiments were performed at the HASYLAB beamline B1, using an X-ray energy of 16.0 keV and with a distance between the sample and the SAXS detector of 3575 mm. The sample atmosphere and temperature is summarised in figure 2(a). The exposure time of the reapeated measurements were 3 minutes. For each of the SAXS patterns the slope α was fitted to the measured data in the large Q region (Porod analysis), and the result is shown in figure 2(b). Wide-angle X-ray scattering (WAXS) was used to check that the cobalt oxide nanoparticles were

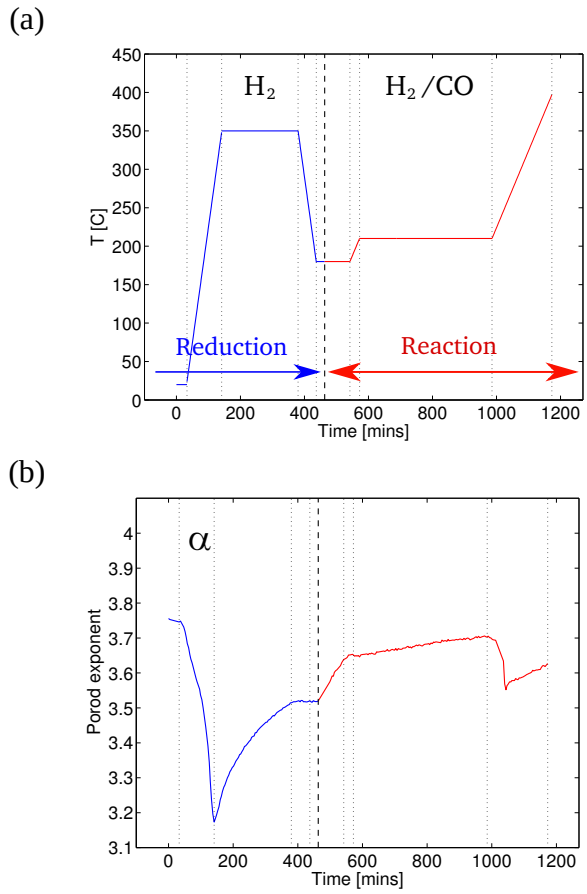

Figure 2: (a) Experimental conditions for the Co nanoparticle catalyst sample. Left of dashed line; reduction (H_2). Right: reaction (H_2/CO). (b) The Porod exponent, α, measured for the conditions indicated in (a). Note the sudden increase in α after the syngas (H_2/CO) is introduced.

properly reduced to metallic Co.

We found that combined SAXS and WAXS is well suited for studying catalyst particles during the reactions since information about size, shape and surface structures of the catalyst particles can be obtained *in situ*. These experiments showed that there is a change in the Porod slope α after gas-change from H_2 to syngas, which means that there is a change in shape, or of surface structure, of the catalyst particles. To the best of our knowledge, this is the first time a correlation has been found between the reported change in catalytic activity during the first few hours after introducing syngas and a measurable parameter that depends on the shape and surface structure of the particle.

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References

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