New experimental setup for on-line monitoring of mixed oxide catalyst synthesis at the µ-Spot Beamline at BESSY II

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New classes of heterogeneous oxidation catalysts often contain complex oxides like vanadyl pyrophosphates (VPO), mixed MoVTe(Nb)-oxides (so-called MoVTe´s) and other Mo or V containing mixed oxides which are often used for the activation of alkanes [1]. During synthesis of the catalyst precursors the preparation method, as well as the nature of used components and the reaction conditions play an important role. However, the influence of these parameters is not fully understood and systematically investigated. To elucidate how different synthesis parameters affect the structure and crystallinity of the precursors and, consequently, the structure and performance of the final catalysts, sophisticated methods for the on-line monitoring of the synthetic process are necessary.

Against this background a new setup was established to perform simultaneously *Wide-* and *Small-Angle X-ray Scattering (WAXS/SAXS)* and *Raman* spectroscopic experiments during the synthesis of Mo based mixed oxide catalyst precursors at the µ-spot beamline at BESSY II. From the scattering experiments information about the precipitate could be derived, such as state of agglomeration of particles, crystallite size, and phases formed during the precipitation. The Raman spectroscopic measurements provide additionally structural information of the precipitate and the anions in solution.

The synthesis of the mixed oxide precursors has been carried out in an Erlenmeyer flask. The suspension was pumped within a closed circuit of flexible tubes through two capillary glass tubes, one used for the Raman measurements, the other for the scattering and back to the flask. A borosilicate capillary with an inner diameter of 5 mm and a wall thickness of 100 µm (Hilgenberg, Malsfeld, Germany) was used as measuring cell for the X-ray scattering. The Raman spectroscopic measurements were performed by focussing the laser beam onto the suspension in a glass tube (commercial borosilicate glass). The measurements were carried out using a fiber optical RXN-Spectrometer (Kaiser Optical Systems, 785 nm Laser) with a Laser power of 70 mW.

To test the performance of the experimental setup some measurements were implemented comprising the precipitation of various metal molybdates by mixing solutions of ammonium heptamolybdate (AHM) and metal nitrates of iron, nickel or bismuth at different pH values. While the changes of molybdate species within solution and precipitate were observed by Raman spectroscopy, the appearance and vanishing of Bragg reflexes could be detected simultaneously. This is nicely seen during mixing of AHM and bismuth nitate/HNO_3 solutions at ambient temperature. Bragg reflexes appear during reaction indicating the formation of a crystalline precipitate. The typical ν(Mo=O) band shifts from 940 to 949 cm^{-1} which is due to the formation of a bismuth molybdate phase. After addition of H_3PO_4 the band at 949 cm^{-1} looses intensity and a new one at 971 cm^{-1} appears. This is accompanied by the disappearance of the Bragg reflexes, i.e. a vanishing of the crystallinity of the precipitate. Differences in the scattering intensity at low scattering vectors confirm a dependence of the particle size on the preparation conditions.

References

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