Coupled X-ray scattering and Raman spectroscopy investigations on the synthesis of Mo-based oxides at the µ-spot Beamline at BESSY

Radnik J.[1], Bentrup U.[1], Armbruster U.[1], Schneider M.[1], Martin A.[1], Brückner A.[1], Leiterer J.[2] Emmerling F.[2]

[1] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Außenstelle Berlin Richard-Willstätter-Str. 12, 12489 Berlin, Germany, **e-mail:** joerg.radnik@catalysis.de

[2] Bundesanstalt für Materialforschung und -prüfung, Richard-Willstätter-Str. 11, 12489 Berlin, Germany, **e-mail:** franziska.emmerling@bam.de

Mo or V containing mixed oxides belong to a new class of heterogeneous catalysts with a high potential for the partial oxidation of alkanes [1]. During the synthesis of catalyst precursors the preparation method, the nature of used components as well as the reaction conditions are an important factor. However, the influence of these parameters is not fully understood and systematically investigated. For such investigations combining X-ray scattering with Raman spectroscopy seems to be promising: 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 on the precipitate and the anions in solution. Such an experimental setup combining X-ray scattering and Raman spectroscopy was recently established at the µ-spot beamline at BESSY [2]. The influence of different synthesis parameters on the structure and crystallinity of the catalyst precursors has been elucidated. Therfore, this might affect the structure and performance of the final catalysts.

The synthesis of the Mo-oxide precursors has been carried out in an Erlenmeyer flask. Afterwards the suspension was pumped within a closed circuit of flexible tubes through two capillary glass tubes, one used for the Raman measurements, the second one for the scattering experiments and back to the flask. The experimental setup is described in detail elsewhere [2].

Several measurements were included to investigate the precipitation of metal molybdates by mixing solutions of ammonium heptamolybdates (AHM) and metal nitrates of nickel, iron and bismuth. After mixing, Bragg reflexes appear indicating the formation of a crystalline precipitate. Simultaneously, a Raman band at 957 cm^{-1} could be observed, typical for $[Mo_8O_{26}]^{4-}$. After addition of H_3PO_4 at room temperature this band looses intensity and a new one at 979 cm^{-1} appears which could be correlated to $[PMo_{12}O_{40}]^{3-}$ showing the formation of a Keggin structure. At the same time, the intensity of the Bragg reflexes decreases. After heating to 50°C, the Bragg reflexes disappeared. This indicates a loss of crystallinity of the precipitate. The increasing intensity at lower scattering vectors below 10 nm^{-1} indicates changes in the formation of particles. Raman spectra show, that the Keggin structure is predominant at these conditions.

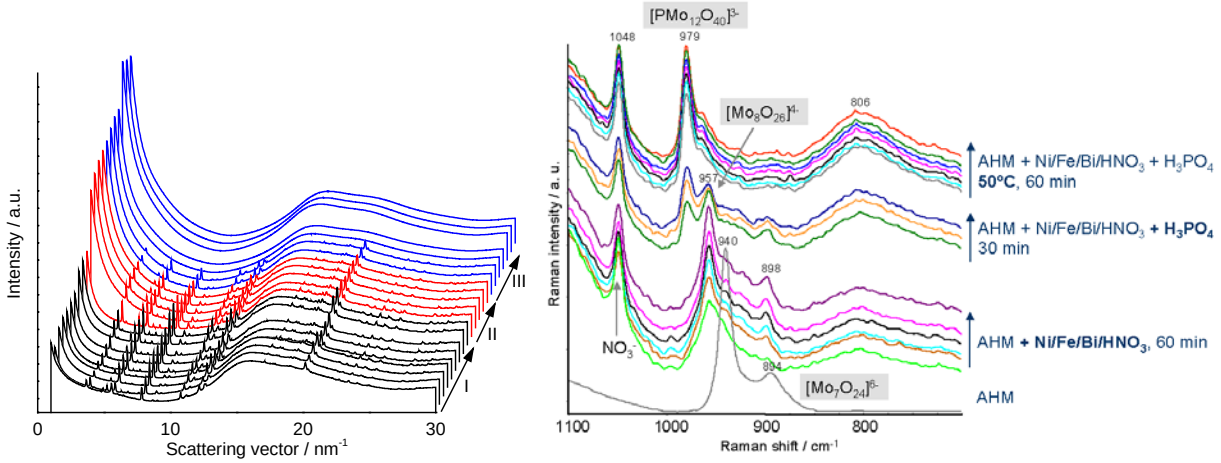

Fig. 1: X-ray scattering curves (left) after mixing the nitrates with AHM (I, black), addition of H_3PO_4 (II, red) and increasing the temperature to 50°C (III, blue) and Raman spectra (right) obtained simultaneously.

References

[1] F. Schüth, *Chem.Ing.Tech.* 2005, 77, 1399-1416.

[2] J. Radnik, U. Bentrup, U. Armbruster, M. Schneider, A. Martin, A. Brückner, J. Leiterer, F. Emmerling, „New experimental setup for online-monitoring of mixed oxide catalyst synthesis at the µ-spot beamline at BESSY“, Poster, ESRF Workshop “Time resolved and in-situ study of heterogeneous catalysts and catalytic process using X-rays: current possibilities and future prospects”, 5-7 February 2008