



	Experiment title: Combined <i>operando</i> XRD, Raman and XAS studies of bismuth molybdate catalysts for selective propylene oxidation	Experiment number: MA-3461
Beamline: BM31	Date of experiment: from: 12/04/2017 to: 18/04/17	Date of report: 05.09.2017
Shifts: 18	Local contact(s): Michela Brunelli	<i>Received at ESRF:</i>
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Report:

The selective oxidation of propylene towards acrolein is an important reaction in the chemical industry, since acrolein is a precursor for large scale production of the amino acid methionine or acrylic acid as polymer building unit. Catalysts used for this process are based on bismuth molybdates [1]. Depending on the ratio of Bi/Mo, three bismuth molybdate phases may occur: γ -Bi₂MoO₆, β -Bi₂Mo₂O₉ and α -Bi₂Mo₃O₁₂. However, there is an ongoing discussion about the stability and activity of the three phases under working conditions. In our group, we have recently found that the preparation method, including co-precipitation, hydrothermal synthesis and flame spray pyrolysis, significantly effects the catalysts performance [2-3]. Furthermore, there is a strong debate about the redox-role of molybdenum and bismuth within the mechanistic cycle and their reducibility. In order to reveal the working properties of bismuth molybdates, *in situ* and *operando* X-ray spectroscopy present a valuable tool and have not been performed on such systems. XAS is especially suitable since it is sensitive to amorphous intermediates and to the very local order. However, for a valid interpretation, a combination with XRD, which gives information on the crystalline bismuth molybdate phases, is crucial and accessible at BM31. Originally, we intended to further combine XAS and XRD with Raman spectroscopy. Unfortunately, the Raman spectrometer is not available at BM31 like it was in former times at BM01B. Thus, the proposed experiment had three objectives: (1) to probe the reducibility of molybdenum and bismuth by performing temperature-programmed reduction experiments in a helium/propylene atmosphere, (2) to study the stability of phases under various conditions and (3) to compare the properties of the highly active β -Bi₂Mo₂O₉ prepared by different methods. Samples of γ -Bi₂MoO₆, β -Bi₂Mo₂O₉ and α -Bi₂Mo₃O₁₂ were prepared by flame-spray pyrolysis and hydrothermal synthesis. For *operando* studies, they were filled in capillary reactors, available at BM31. By using a gas blower, the capillaries with the catalyst material could be heated and helium, oxygen, water, and propylene could be dosed *via* a gas distribution system brought from KIT.

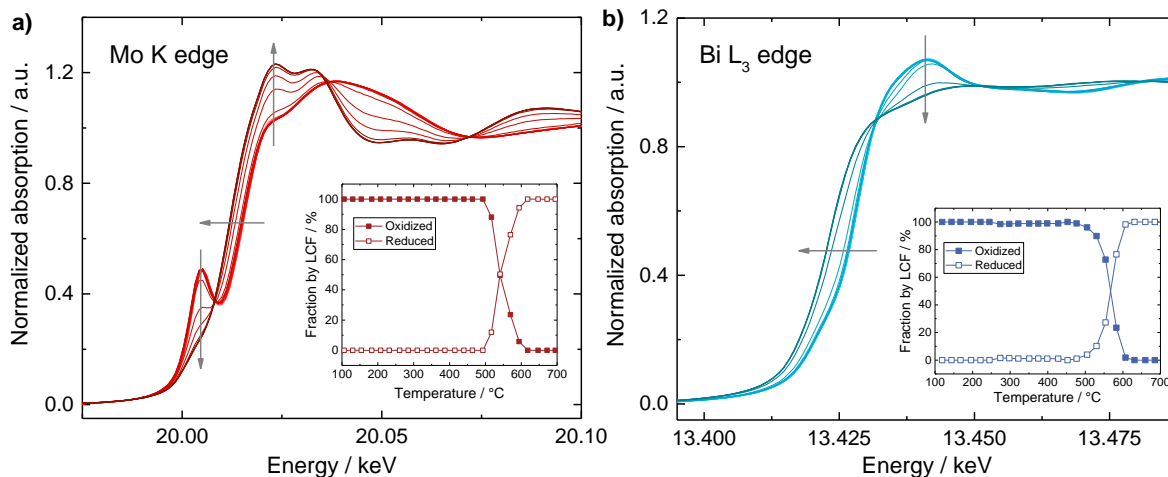


Figure 1: *In situ* XANES of Mo K (a) and Bi L₃ (b) edge of α -Bi₂Mo₃O₁₂ during temperature-programmed reduction in propylene.

The fast edge changing possibilities at BM31 allowed us to measure XAS at Mo K and Bi L₃ edges almost simultaneously. Thus, temperature programmed reduction in propylene/helium atmosphere allowed us to study the reduction behavior of bismuth and molybdenum in the same heating cycle. As shown in Figure 1, α -Bi₂Mo₃O₁₂ shows reduction of both molybdenum (Mo⁶⁺ → Mo⁴⁺) and bismuth (Bi³⁺ → Bi⁰), whereas molybdenum is getting reduced at ca. 30 K lower temperature. This indicates an easier reduction of molybdenum, which is in line with the proposed mechanistic behavior by Zhai *et al.* [4]. Similar experiments have been conducted for other bismuth molybdate phases showing versatile results. Under TPR and oxidative

conditions, we observed phase transformations by both XAS and XRD. Their extent depended on the synthesis method and type of bismuth molybdate phase. Thus, their reactive stability depends on both. For instance, as shown in Figure 2, γ -Bi₂MoO₆ transformed after the TPR to its high temperature form. Under reducing conditions, only MoO₂ reflections are present, which is in line with XAS results. In general, β -Bi₂Mo₂O₉ was more stable under working conditions than other phases. Only a combination of XAS and XRD allowed to evaluate the results and assign the changes e.g. in molybdenum coordination to a distinct crystalline phase.

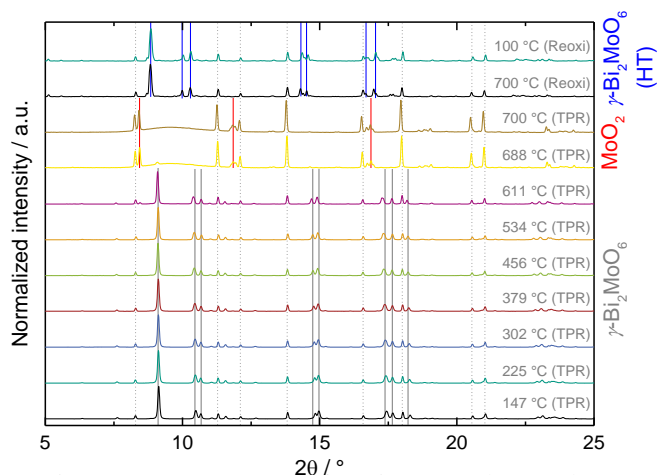


Figure 2: *In situ* XRD of γ -Bi₂MoO₆ shows phase transformation after TPR in propylene to its high temperature phase (dashed lines = α -Al₂O₃).

In the present study, we could successfully combine XRD and XAS to study the behavior of various bismuth molybdates in propylene oxidation. For the first time, we were able to unravel the redox-role of the specific elements under realistic conditions and gain insight on the phase stability. A detailed discussion of the obtained results is underway [5].

Publications

- [1] Y. Moro-Oka, W. Ueda, Adv. Catal. 40 (1994) 233-273.
- [2] K. Schuh, W. Kleist, M. Høj, V. Trouillet, P. Beato, A. Jensen, J.-D. Grunwaldt, Catalysts 5 (2015) 1554-1573.
- [3] K. Schuh, W. Kleist, M. Høj, V. Trouillet, A.D. Jensen, J.-D. Grunwaldt, Chem. Commun. 50 (2014) 15404-15406.
- [4] Z. Zhai, A.B. Getsoian, A.T. Bell, J. Catal. 308 (2013) 25-36.
- [5] P. Sprenger, M. Stehle, A. Gaur, A.M. Gänzler, D. Gashnikova, W. Kleist, J.-D. Grunwaldt, in preparation.