

Unravelling the structural changes of Bi-Mo-Co-Fe-O catalysts during selective olefin oxidation by complementary *operando* synchrotron-based techniques

L. Klag¹, A. Gaur¹, T. L. Sheppard^{1,2}, J.-D. Grunwaldt^{1,2}

¹Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

²Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

grunwaldt@kit.edu, abhijeet.gaur@kit.edu

Keywords: *operando* characterization, XAS, XRD, mixed metal oxides, selective oxidation

The selective oxidation of propylene and isobutene are key reactions in chemical industry for large-scale production of various intermediates (e.g., Acrolein).[1] Typically, these are catalysed by bismuth molybdate based multicomponent systems (e.g., Bi-Mo-Fe-Co-W-K-Si-O), which exhibit a high structural complexity, forming composites of active, selective, inert and promoter phases.[2] However, the roles and interactions of individual (mixed) metal oxide phases during selective olefin oxidation are still under strong discussion.[3] In the past, academic research commonly focused on simplified model systems (e.g., 2-component Bi-Mo-O) to get a fundamental understanding of catalytic function.[4] Based on this knowledge, the next step towards the 4-component system, Bi-Mo-Co-Fe-O, is very promising, as it provides a suitable representation of complex metal oxide phases mixtures and superior catalytic performance.[5] To study structure-activity relationships in such complex, dynamic systems, various complementary and advanced characterization methods are needed that probe the catalyst under operating conditions.[6] We investigated the structural evolution of Bi-Mo-Co-Fe-O catalysts by the means of *synchrotron-based operando* X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD) and *laboratory-based* Raman spectroscopy under different gas atmospheres. While *operando* XAS allowed to monitor structural changes of each metal individually at Mo K-, Bi L₃-, Co K- and Fe K-edges (Fig. 1), *synchrotron-based* XRD with Rietveld refinement (Fig. 2) gave qualitative and quantitative insights into crystalline catalyst phases (e.g., Bi₃FeMo₂O₁₂ formation). Complementary *operando* Raman spectroscopy completed the understanding of the catalyst workings by probing contribution and stability of non-crystalline species during selective propylene and isobutene oxidation.

Determining the structural transformations within these systems under different gas atmospheres by an *operando* approach was crucial to reveal the role of individual catalyst phases, their dynamic behaviour, and interaction with other phases. Comparing characterization data obtained for selective propylene and isobutene oxidation allowed us to define the catalyst working principles more accurately in terms of active or selective metal oxide phases. Finally, studying 4-component systems is essential for closing knowledge gaps between the functionality of model systems, and complex industrially-applied catalysts, and thus contributes to a knowledge-based catalyst design and improvement.

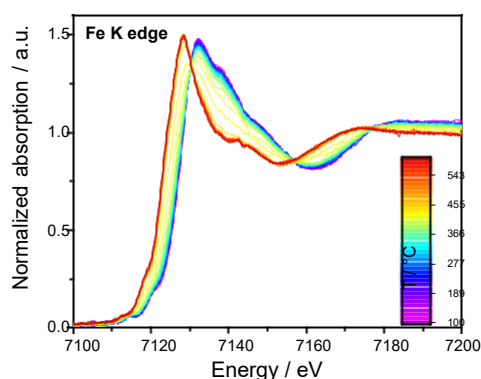


Figure 1 Structural evolution of Bi₁Mo₁₂Fe₃Co₈O_x derived from XAS at the Fe K edge during selective isobutene oxidation.

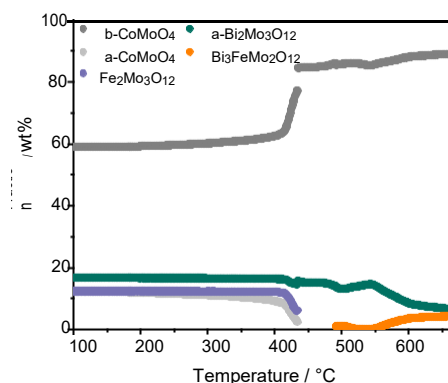


Figure 2 Structural evolution of Bi₁Mo₁₂Fe₃Co₈O_x derived from synchrotron-XRD during selective isobutene

[1] J. Haber, *Handbook of Heterogeneous Catalysis*, Wiley-VCH, Germany, **2008**, 3350-3384.

[2] Y. Moro-Oka, W. Ueda, *Adv. Catal.* **1994**, *40*, 233-273.

[3] P. Sprenger, W. Kleist, J.-D. Grunwaldt, *ACS Catal.* **2017**, *7*, 5628-5642.

[4] P. Sprenger, M. Stehle, A. Gaur, A. Gänzler, D. Gashnikova, W. Kleist, J.-D. Grunwaldt, *ACS Catal.* **2018**, *8*, 6462-6475.

[5] M. Stehle, A. Gaur, S. Weber, T. L. Sheppard, M. Thomann, A. Fischer, J.-D. Grunwaldt, *J. Catal.* **2022**, *408*, 339-355.

[6] L. Klag, T. L. Sheppard, J.-D. Grunwaldt, *ChemCatChem* **2023**, *15*, e202201276.