A) Overview

We successfully employed our setup (home-built at ETH and previously demonstrated in *J. Am. Chem. Soc.* 2019, 141, 34, 13497–13505, as described in the proposal) for the in situ/operando measurements described in our proposal, under methanol synthesis relevant conditions (helium, carbon dioxide, hydrogen). The robustness of the setup, and the cautious implementation of the experiments enabled to meet all safety requirements. As a result, we encountered no safety issues throughout the duration of the experiments. Furthermore, the valuable help from the beamline staff and the well-equipped beamline (especially the potential for hassle-free operation between XAS, PDF, and XRD), ensured the success of our proposed experiments and yielded valuable time-resolved information. The data obtained have been preliminary analyzed and are expected to give valuable insights into the dynamic evolution of the electronic and coordination environment of the metal sites under reaction conditions. Overall, the successful outcome of this beam cycle paves the way for future investigations into the dynamic behavior of binary and ternary supported metal catalysts for the methanol synthesis reaction.

B) Quality of measurement/data

Excellent XAS, XRD, and PDF data quality was obtained (XAS experiments were performed in fluorescence mode for the samples and in transmission mode for references) for all tests conducted across different metal edges (*e.g.*, Cu K edge, Zn K edge, Pt L3 edge, and Pd K edge), despite the low metal loading (0.5-0.75 wt%) and even upon heating to mild temperatures (573 K) under different feeds (CO_2:H_2 4:1, He only) and elevated pressure (15 bar). The highly valuable component of the beamline to switch from XAS to XRD in an automated and hassle-free fashion proved key to following the rapid changes in oxidation state and coordination environment of all phases upon annealing from room temperature to 573 K and exposure to different feed compositions (*e.g.*, He only, or under CO_2+H_2 mixtures), a particularly valuable feature for our studies.

C) Status and progress of evaluation

Clear trends in the evolution of the electronic and structural properties were observed across different samples, under various reaction conditions. Preliminary data analysis enabled to decouple contributions of transient metal species and gave insights into the kinetics of the metal speciation dynamics under different reactive environments. More detailed analysis is ongoing to accurately resolve changes in the oxidation and coordination environment of the metal sites.

On a separate note, but not any less important, the robustness of the setup was confirmed in this beam cycle. No leaking of H_2, CO_2, and He was observed at any point throughout the duration of the experiments. All connections (and especially the ones around the capillary reactor) were frequently tested with He leak detectors (especially after changing samples), while flowing He through the whole tubing, which ensured that no leaking would

occur during in situ/operando experiments. In conclusion, we are convinced that operando XAS analysis of metal sites under methanol synthesis conditions can be safely conducted and provides valuable insights into the metal species dynamic behavior.

D) Results

The large amount of data obtained is currently being analyzed using Athena and Artemis software to determine the change in electronic and coordination environment of the metal site (metal edges include Cu, Zn, In, Pt, Pd) induced by the different feed mixtures and across a broad temperature range (spanning from room temperature to 573 K). Our findings have helped us obtain strong evidence about the state of the metal sites under reaction conditions, which can educate our theoretical investigations, and clearly identify their role in the reaction mechanism. Upcoming beamtime will help us elucidate the individual role of these components in more complex (multimetallic) systems and under hybrid feeds (*i.e.*, including CO and CO_2 in the reactants mixture). These results are currently analyzed and coupled with other experimental observations and will be included in separate manuscripts that are expected to provide solid foundation for future investigations on the development of promising methanol synthesis catalysts.