

Local Coordination Environment and Dispersion of Ti in Zeolite Derived Oxidation Catalysts

Proposal Code: 31-01-143 (11 February 2021 - 15 February 2021)

Lukas Lätsch, ETH Zurich, Department of Chemistry and Applied Biosciences, Zurich, Switzerland

Due to the COVID-19 pandemic the beamtime was performed remotely (e.g. all experiments were performed through the local beamtime scientists Dr. Wouter van Beek and Dragos Stoian). All samples were shipped in advance either as powder in vials (for non-air sensitive samples) or in sealed capillaries (for air and moisture sensitive samples). Temperature sensitive samples were shipped in sealed capillaries and cooled with dry ice.

In this beamtime we aimed at studying the local coordination environment and the dispersion of titanium in zeolite derived oxidation catalysts by generating a library of Ti K edge XANES from a series of molecular compounds and zeolites with great variation of structure and properties. In total, we were able to measure 26 different zeolites, 15 molecular compounds and 15 materials obtained from grafting molecular precursors on silica surfaces and subsequent thermal treatment. Overall, the Ti loading varied between 0.4 wt% and 3 wt% for the zeolites / silica materials. Because of the low weight loadings in some samples, measurements were carried out with a fluorescent scheme of detection using a silicon drift diode with associated digital electronics. Capillaries were mounted in a frame and translated vertically (in Z) for overnight measurements (for setup, see Fig. 1). The non-air sensitive samples were pressed as pellets (diluted with cellulose and pressed with ca. 1 ton for 10-15 seconds) and measured automatically using a rotatable wheel.

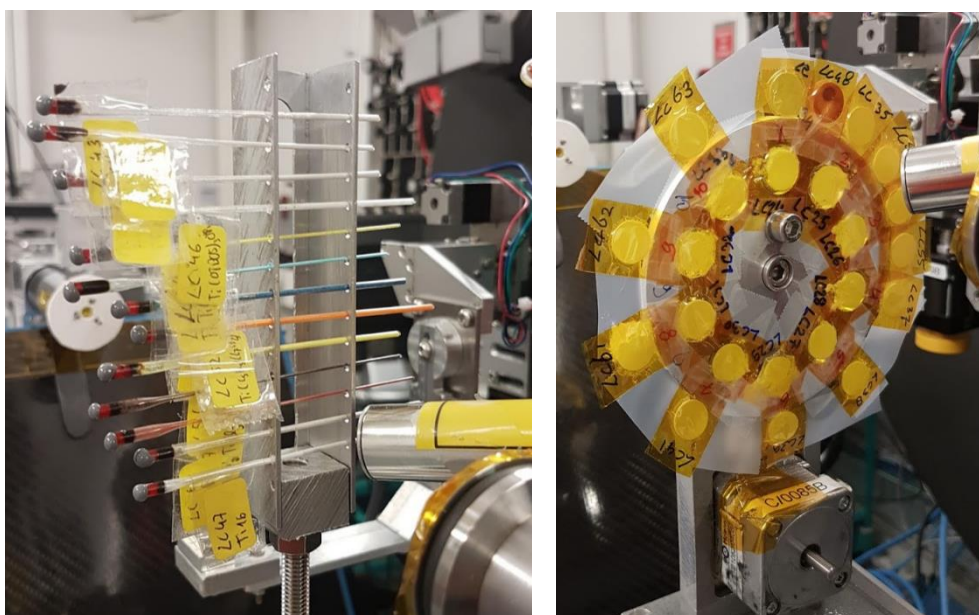


Figure 1: Capillaries containing air and moisture sensitive samples mounted on a frame (left) and pressed pellets from non-air sensitive samples mounted on a rotatable wheel (right) for automatic/overnight measurements.

Zeolites prepared via different synthetic pathways and with differing Ti weight loading (1-3 wt.%) showed very different spectroscopic signatures in terms of pre-edge, edge position and whiteline features (for examples see Fig. 2). All zeolites were measured as pellets and the data quality obtained was very good. Molecular reference samples were measured in sealed capillaries (due to their sensitivity towards air and moisture) and produced good quality data as well (for examples see Fig. 3),

suitable for benchmarking of our ongoing computational studies. Finally, we investigated heterogeneous model systems obtained via the surface organometallic chemistry approach. These samples were the most challenging due to their low Ti w% loading (ca. 0.4 wt%) – yet their measurement was successful (for examples see Fig. 4.).

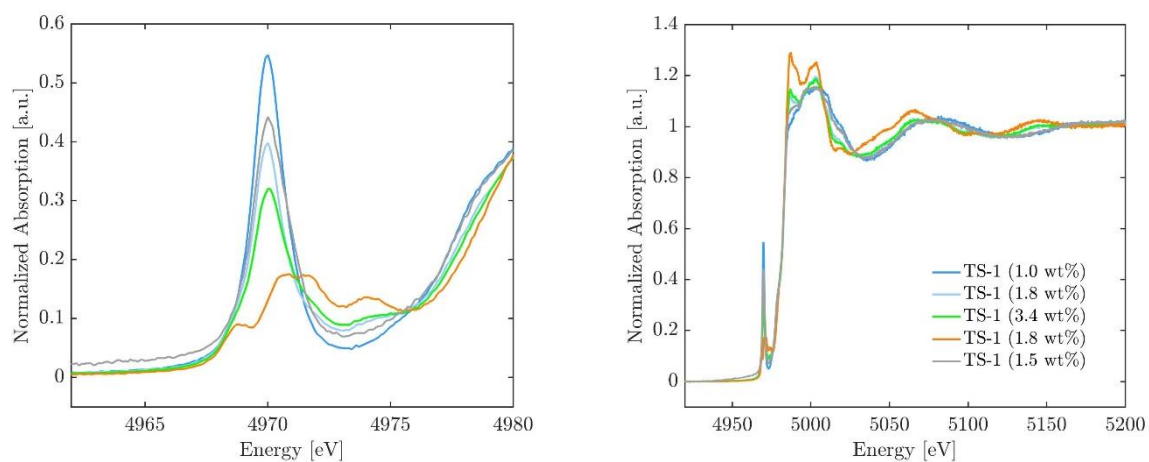


Figure 2: Ti K edge XAS of TS-1s prepared via different routes and with differing Ti weight loading.

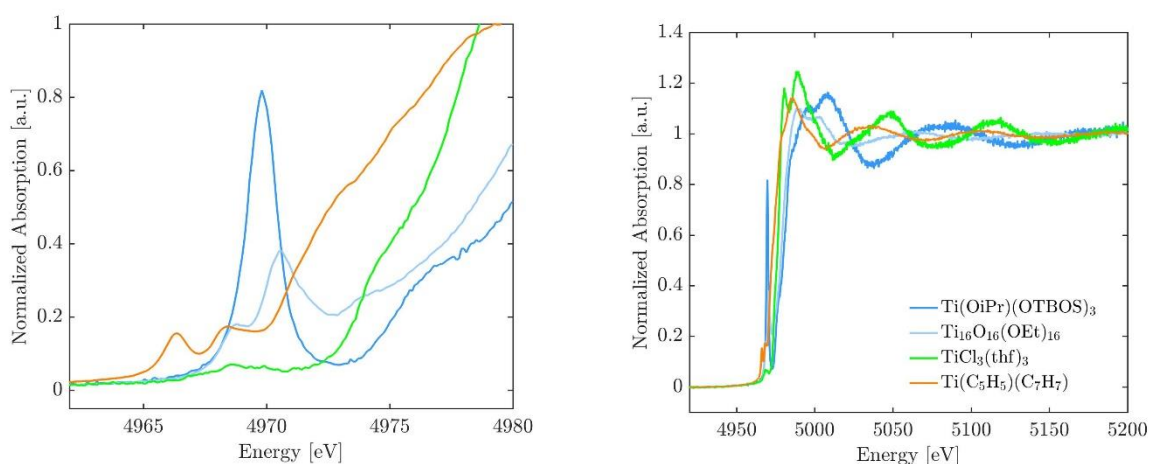


Figure 3: Ti K edge XAS of molecular references that will serve for computational benchmarking.

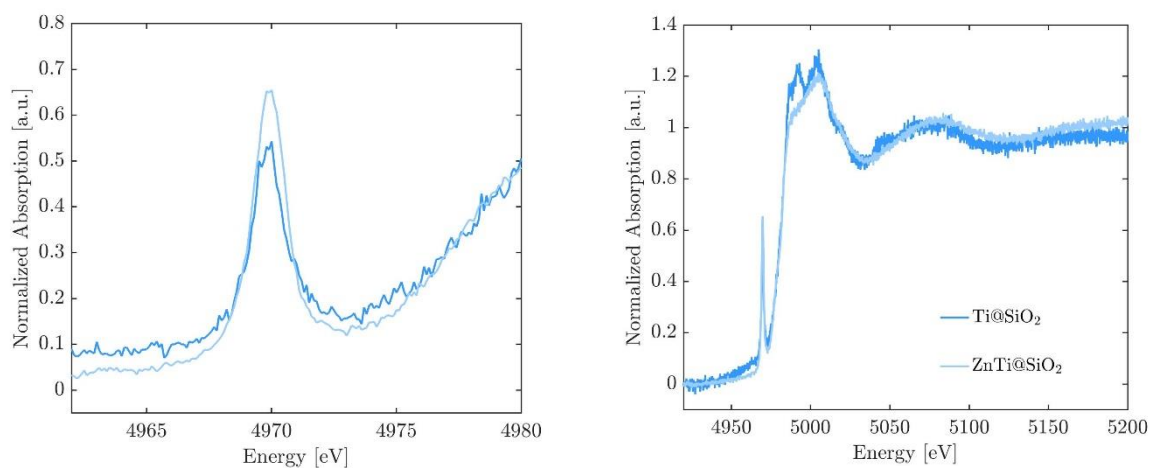


Figure 4: Ti K edge XAS of heterogenous model systems obtained via the surface organometallic chemistry approach.