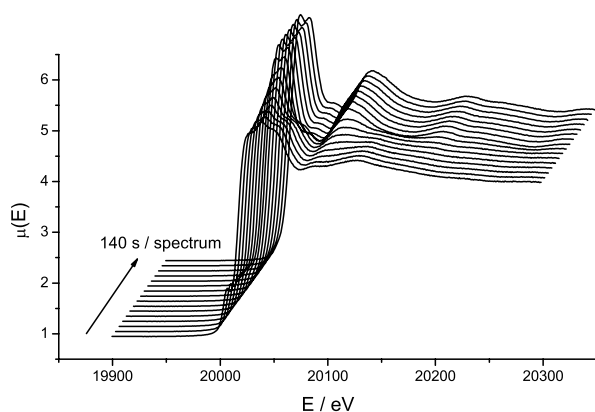


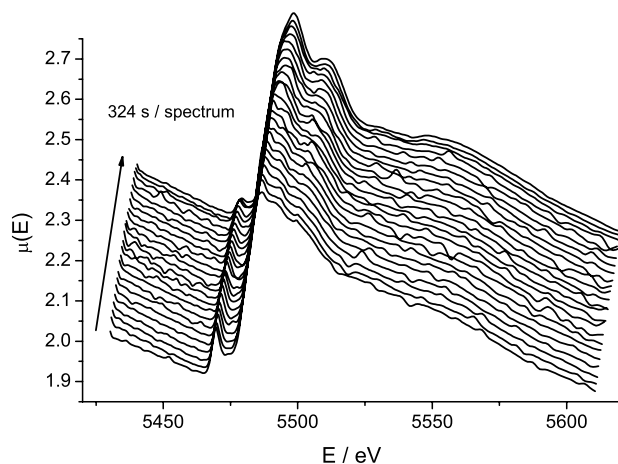
Figure S1:



Caption:

Sample *in situ* spectra of a $V_{2.5}Mo_{7.5}O_z$ spray dried catalyst at 480 °C, taken at the Mo K-edge during reduction with 5% ACR in He. Each line corresponds with a single XAS spectrum with a recording time of 140 s. The spectra are displaced horizontally and vertically for better readability. One can immediately recognize the disappearing pre-peak feature at around 20000 eV, and several strong changes in other XANES features.

Figure S2:



Sample *in situ* spectra of a $V_{2.5}Mo_{7.5}W_{0.5}O_z$ spray dried catalyst at 450 °C, taken at the V K-edge during reduction with 5% ACR in He. Each line corresponds with a single XAS spectrum with a recording time of 324 s. The spectra are displaced horizontally and vertically for better readability. The changes are much less pronounced, compared to fig. S1. However, these spectra also show the disappearance of a pre-peak around 5675 eV, and shifts in other characteristic XANES features.²²