Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Supporting information

Unwanted effects of X-rays in surface grafted copper (II) organometallics and copper exchanged zeolites, how they manifest, and what can be done about them?

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Figure S1 gives some salient examples of Cu K-edge XANES obtained during these studies.

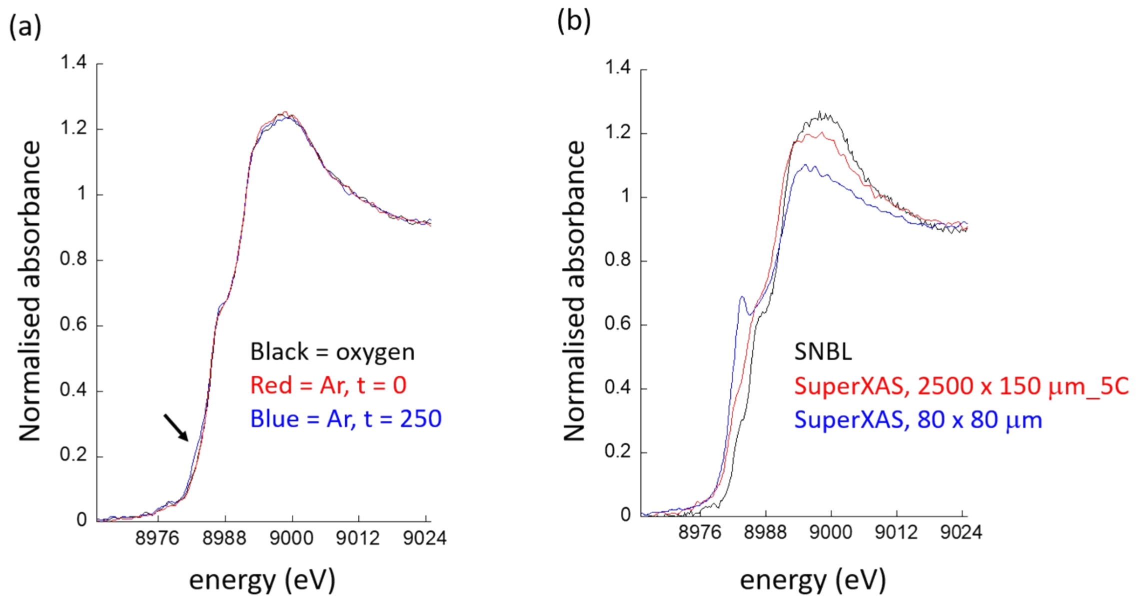
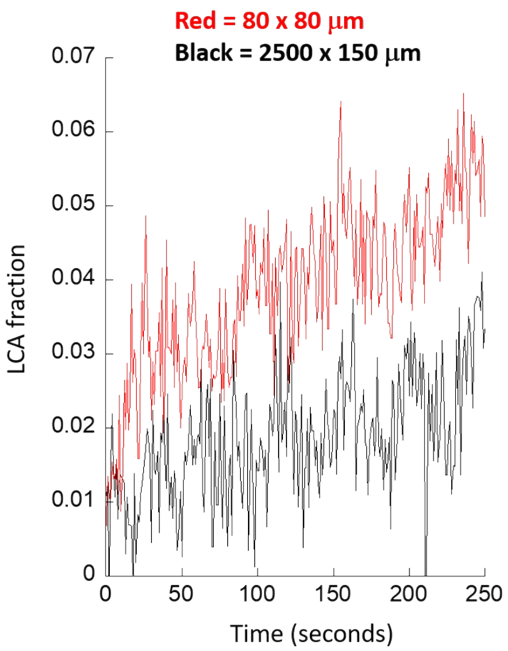


Figure S1 (a) shows Cu K-edge XANES spectra obtained on SuperXAS, using the nominal standard beamline focus of 80 x 80 μm, for three different cases: post high temperature activation, under oxygen at 413 K (black); at the switch (t = 0) from oxygen to argon (red); and 250 seconds after the switch to argon has occurred. The formation of Cu^{I} is indicated by the black arrow. (b) Comparison of Cu K-edge XANES obtained at the end of exposure to methane at 413 K in three different cases: Cu/MOR measured at SNBL (black, 17 seconds); Cu/MOR measured at SuperXAS using the nominal beamline standard focus (80 x 80 μm^2) and no attenuation (blue, a single acquisition of 0.5 seconds); and, (red, an average of 34 scans of 0.5 seconds duration = 17 seconds) at SuperXAS but with a defocused (2500 x 150 μm^2) beam and 5 mm of carbon attenuation.

These illustrate the types of data obtained and some of the processes and differences between beamlines observed, some of which may arise as a result of the rather different manners (for example, types of monochromators, ion chambers employed, and degrees of oversampling) by which the spectra are obtained. However, as internal standards used for determining the concentrations of Cu^{I} and Cu^{II} by LCA analysis were obtained at each beamtime, these spectral differences do not impact upon the analyses undertaken nor the conclusions derived from them.

Figure S2 then shows rates of appearance of Cu^{I} during the switch from flowing oxygen to Argon, that must precede reaction with methane, for activated Cu/MOR at 413 K. The two cases shown correspond to the fully focused beam at SuperXAS (80 x 80 μm^2, red)



and to a defocused, but not further attenuated, beam of 2500 x 150 μm^2 (black).

Figure S2. Cu^{I} evolution as a function time, derived from a two-component LCA analysis of time resolved Cu K-edge XAFS, during switching from a flow of oxygen to a flow of argon for Cu/MOR at 413 K and for two different dimensions (as indicated) of the SuperXAS X-ray beam.

The evolution of Cu^{I} under the influence of the X-ray beam and under nominally "inert" conditions occurs linearly with time. Given the loading of copper in the Cu/MOR (ca.

682 μmolg^{-1}) observed rate of Cu^{I} formation correspond to ca 0.1 μmolg^{-1}s^{-1} (@ 80 x 80 μm^2) and 0.04 μmolg^{-1}s^{-1} (@ 2500 x 150 μm^2). In this case, therefore, a factor ca. 58 change in the applied brilliance results in only a factor ca. 2.5 diminution in the apparent rate of formation of Cu^{I}.

The X-ray induced perturbation to the system is, therefore, of a considerably decreased magnitude than is observed during subsequent exposure of the Cu/MOR to the "reactive" methane flow. Nonetheless, and even in this "inert" case, a measurable perturbation, which comes with unknown ramifications for the speciation of the copper present, still occurs as a function of X-ray dose.

Figure S3 gives two examples of the induction of Cu^{I} during the required switch to an inert gas flow from an oxygen feed prior to methane being introduced to the system for Cu/MAZ. As for Cu/MOR the sample was previously activated (723 K in oxygen) before cooling in oxygen to the eventual reaction temperature of 413 K.

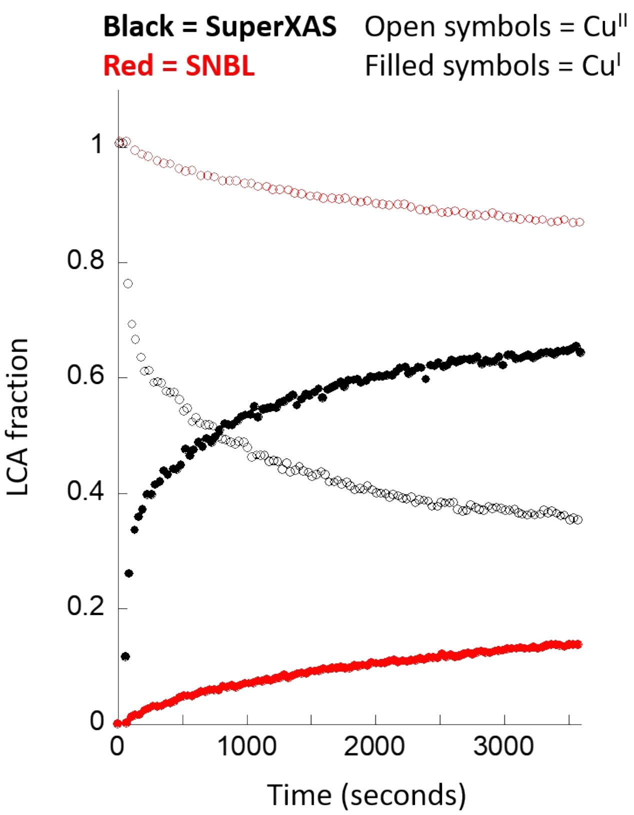


Figure S3. Time dependent formation of Cu^{I} (filled symbols) and consumption of Cu^{II} (open symbols) during the reaction of activated (723 K in oxygen) Cu/MAZ with methane at 413 K measured at SNBL (red) and SuperXAS (black).

In the Cu/MAZ system, as with the Cu/MOR case, significant disparities in apparent behavior of the zeolite are also observed. It is, however, interesting to note that in the case of Cu/MAZ no significant Cu^{I} is found in either case at t= 0, in contrast to Cu/MOR. That this is the case implies that, the Ar purge step in the reaction sequence does not lead to auto reduction of the copper in the case of MAZ whereas it does in Cu/MOR.

Thereafter the difference in behavior observed between the non-focused SNBL and the significantly more brilliant SuperXAS manifest in the same way; that is to say significantly greater rates of reaction, and very different end levels of Cu^{I} formation/Cu^{II} consumption.