A combined XRD, XPS and DFT study into the structural and electronic effects of X-ray radiation on prototypical catalysts

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X-rays are essential in a wide variety of advanced characterisation techniques to probe properties of matter. However, interactions of X-rays with crystalline matter are known to induce a range of changes. Despite the undesirable consequences of radiation being well documented in biological macromolecular crystallography since it was first studied in the 1960s [1,2], knowledge of the effect of this ionising radiation on small molecular crystals, which are integral in catalytic applications for instance, remains incredibly limited.

In recent years the advent of modern microfocused laboratory sources and the shift towards higher brilliance synchrotron sources has exacerbated the problem of unwanted radiation effects, increasing the necessity for a better understanding of its influence on matter and characterisation results. The main aims of observing changes caused by irradiation are not only to design and implement preventative measures, but also to fully understand the radiation damage process and how it occurs in the materials being studied.

In this study, a combined experimental and computational approach of synchrotron powder X-ray Diffraction (XRD at beamline I11 at the Diamond Light Source) and laboratory-based X-ray Photoelectron Spectroscopy (XPS) is implemented to understand changes to the structure, the local chemical environments, as well as the electronic structure of a family of prototypical catalysts. These have the general formula [M(COD)X] [2] where M= Ir, Rh, COD= cyclooctadiene and X= Cl. Observations from experiments are complemented with theoretical calculations from Density Functional Theory using the CASTEP code [3]. Approaching this topic through the combination of these three advanced techniques allows for a compelling, novel multi-modal way to probe effects of X-ray irradiation, by way of a direct correlation of structural changes with changes of the chemical state of the metal. The progression of radiation-induced changes to these small molecular crystals is monitored over considerable timescales. In addition, the X-ray induced effects relative to absorbed radiation dose will be discussed. These values of X-ray dose are obtained using a recent development in the RADDOSE-3D utility [4] for radiation dose estimation in small molecular systems [5]. This is the first known application of RADDOSE to XPS experiments.

There is enormous potential to extend this application of XRD, XPS and theory beyond this family of organometallic catalysts, to follow X-ray induced effects and apply conclusions drawn, to other small molecular systems of significant scientific and industrial relevance.

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