Time resolved and resonance Raman spectroscopy in the elucidation of mechanisms in transition metal catalyzed oxidative transformations

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The search for new and better reactivity has driven the development of 1st row transition metal catalysis over the last several decades, not least in the field of oxidation catalysis. Our group has focused on manganese and iron based catalysts for both fine chemical and bulk applications, and more recently on Ni(II) based catalysts, employing environmentally benign oxidants. A key challenge faced in catalyst development and in optimisation is to move from catalyst discovery to catalysis design. However, design requires understanding of the fundamental mechanisms that underpin catalysis. In this lecture I will discuss our recent efforts in elucidation of reaction mechanisms and the consequences of a lack of mechanistic understanding at the system level (i.e. considering all reaction components and their interplay). In particular, the synergy that can be achieved between theoretical and experimental methods to delve deep into understanding not just the catalytic cycle but also the broader context of the catalytic reaction. The choice of spectroscopic techniques, and especially time resolution, used to study individual reactions will be emphasised.

Figure 1. Reaction progress monitoring with Raman spectra showing the consumption of H$_2$O$_2$ as well as resonance enhanced Raman scattering from an intermediate formed with the mixing time from the catalyst (0.1 mM) and H$_2$O$_2$ (100 mM) acetonitrile at $l_{\text{exc}}$ 785 nm (a) before, and 0.5 s (blue) and 2 s (red) after addition of H$_2$O$_2$, and (b) time dependence of intensity of the band at 1598 cm$^{-1}$ (intermediate, red) and at 870 cm$^{-1}$ (H$_2$O$_2$, black).

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