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Catalysis in complex media

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Summary

Over recent decades, mechanistic studies in manganese catalysed oxidation catalysis in organic solvents has provided a broad insight into the mode of action of the catalysts and various parameters that control the outcome of the catalysis. However, understanding the behaviour of these catalysts in complex aqueous media has received much less attention due to the analytical complexity of these systems. The catalysis systems based on manganese salt and the tmtacn ligand with hydrogen peroxide is a typical example. Mn-tmtacn based catalysts have been applied in bulk catalysed oxidation processes, *e.g.*, raw cotton bleaching as well as domestic cleaning. In this thesis, the aim was to understand at a molecular level, how and why these Mn-tmtacn base catalysts work in complex aqueous media and develop the necessary analytical techniques to probe such complex systems. A solid mechanistic understanding of the effect of additives, buffers, pH and oxidation state of the manganese catalysts was established through these studies.

In chapter 1, the solution chemistry of manganese based complexes of interest to oxidation catalysis in both biological as well as chemical processes was discussed.

In chapter 2, the application of the DCDR (drop coating deposition Raman) method in the analysis of reaction mixtures during (organic) synthesis and to monitor the progress of catalyzed reactions is explored. Although, DCDR spectroscopy has seen recent application in the study of biological fluids, its application in other areas was not explored. The model substrate 4-vinylbenzoic acid (VBA) which is moderately water soluble, was chosen for this study as it undergoes catalytic epoxidation in water quantitatively. The marker bands (*ca.* 1600 cm^{-1}) of the phenyl and alkene groups are convenient for monitoring the reaction by Raman spectroscopy (Figure 1). In previous studies the inhomogeneity of deposited samples has presented challenges to the application of DCDR in large molecules such as proteins. However, the present study shows that with drop coating of small molecules, *e.g.* in the deposition of compounds of substantially differing solubility, essentially homogeneous deposition was achieved. The reproducibility of the Raman spectra obtained by the DCDR technique was examined and showed relatively little variance (<2%). Using this method enabled the screening of catalyzed reactions where the volume and mass available are also limited. The time taken for the solvent (*i.e.* H_2O) to evaporate and the deposit to form is a potentially limiting factor in the time resolution that can be achieved using the DCDR method. Comparison of DCDR with in-line Raman and at-line ^1H NMR spectroscopy shows good agreement. A key advantage of using this method to monitor the catalytic reaction is that the rapid drying of the sample in this method results in quenching of the reaction, which allows for analysis after the reaction at a later time. For reactions that proceed over relatively long periods (*i.e.* >1 h), applying the DCDR method enables at-line analysis of large numbers of reactions relatively inexpensively both in terms of facilities required and time, in comparison with commonly employed techniques such as GC and HPLC or in-line monitoring.

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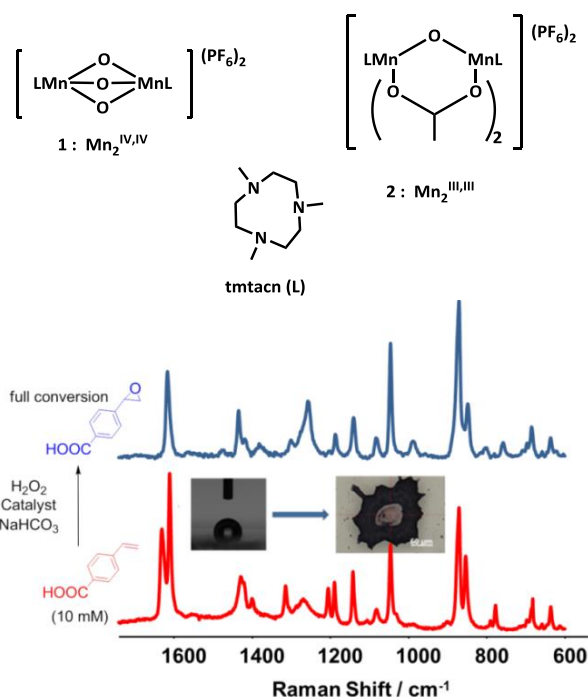


Figure 1 Left) $[\text{Mn}^{\text{IV,IV}}_2(\text{O})_3(\text{tmtacn})_2](\text{PF}_6)_2 \cdot \text{H}_2\text{O}$ (1), $[\text{Mn}^{\text{III,III}}_2\text{O}(\text{CH}_3\text{COO})_2(\text{tmtacn})_2](\text{PF}_6)_2$ (2) and the ligand, tmtacn (*N,N',N''*-trimethyl-1,4,7-triazacyclononane). Right) Raman spectra (λ_{exc} 785 nm) of (a) VBA (4-vinylbenzoic acid) and (b) OBA (4-(oxiran-2-yl)benzoic acid) obtained on a treated hydrophobic surface. Regions of most interest are noted.

In chapter 3 a range of spectroscopic techniques were employed to gain insight into the aqueous and non-aqueous chemistry of the complex $[\text{Mn}_2^{\text{III,IV}}(\mu\text{-CH}_3\text{COO})(\mu\text{-O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$, which has been demonstrated as an exceptionally active catalyst in the bleaching of raw cotton and especially wood pulp at high pH (> 11), including UV/vis absorption, Raman and EPR spectroscopies and cyclic voltammetry (Figure 2). Although the solid state and magnetic properties of these complexes have been examined in detail, the speciation of manganese complexes in solution and especially in water has received relatively little attention. This lack of speciation analysis means that the mechanism(s) by which these complexes activate H_2O_2 are still largely unknown. The data indicate that dissociation of the μ -acetato bridge is essential to the catalysts activity and rationalises the inhibitor effect of sequestrants such as DTPA on its performance.

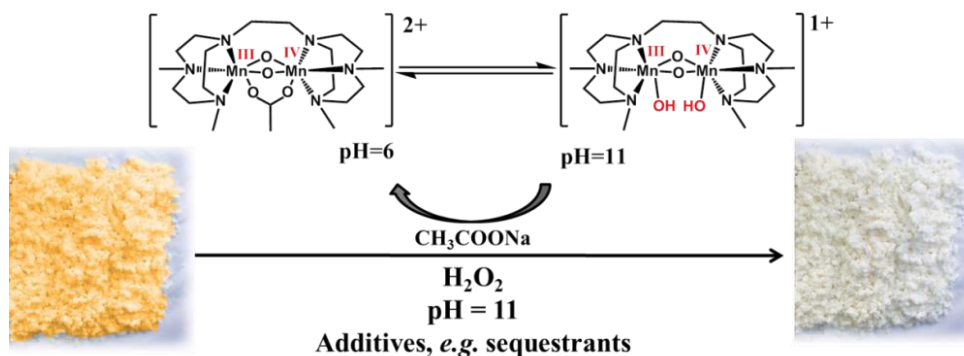


Figure 2 Equilibrium between $[\text{Mn}_2^{\text{III,IV}}(\mu\text{-CH}_3\text{COO})(\mu\text{-O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$ (Me_4dtne = 1,2-bis(4,7-dimethyl-1,4,7-triazacyclonon-1-yl)ethane) and the acetate dissociated form present at high pH.

In chapter 4, focus turns to identifying a suitable model compound to allow for the study of the behaviour of the manganese catalysts under conditions relevant to cotton bleaching (*i.e.* alkaline aqueous media). First a well-known, albeit problematic, model compound (morin) for the colourants present in raw cotton is discussed, in particular with regard to its limitations. It is found that despite being oxidised readily, morin is subject to metal catalysed oxidations with oxygen, that are accelerated by photochemical activation. In contrast, chrysin, which does not bear an OH at the C-3 position is introduced which is essentially unreactive towards photooxidation. As chrysin is oxidised only by H_2O_2 in the presence of a catalyst and not by oxygen, it provides more reliable information in regards to modelling the colourants in cotton and thus allows for mechanistic studies of the action relevant to bleaching catalysts to be carried out under homogenous conditions (Figure 3).

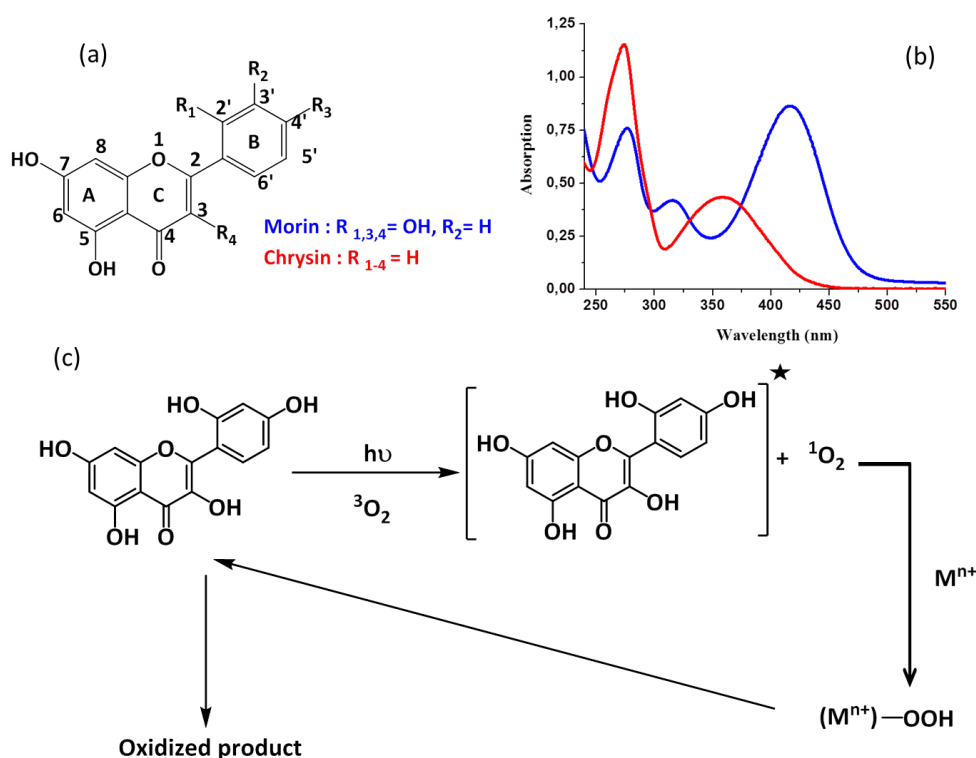


Figure 3 (a) General structure and numbering scheme of flavonoids under investigation. (b) UV/vis absorption spectra of morin and chrysin. (c) Proposed mechanism for light induced degradation of morin catalysed by metal ions with O₂.

In chapter 5, the activity of the complex $[\text{Mn}_2^{\text{IV,IV}}(\mu\text{-O})_3(\text{tmtacn})_2](\text{PF}_6)_2$ and its analogues in the oxidation of alkenes under two phase reaction conditions (*i.e.* organic/aqueous), is investigated (Figure 4). A central question in such processes, that is addressed here, is as to where, *i.e.* in which phase, the catalysed reaction takes place. Studying the activity of the Mn-tmtacn complexes in the oxidation of both hydrophilic and hydrophobic alkenes under two phase conditions was carried out in an effort to answer these questions with several approaches taken to identify in which phase the catalytic reaction takes place. Evidence is presented for the localisation of catalysed oxidation in the aqueous phase of a two phase system, with the second phase either n-heptane, toluene or an alkene such as styrene. These data indicate that oxidation chemistry under the two

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phase conditions presented is restricted to the aqueous layer and that the use of a phase transfer catalyst in these systems is not required. Answering this question is important in the industrial application of these catalysts, as the use of phase transfer catalysts for example would have a negative effect if the complexes are inactive in the organic layer.

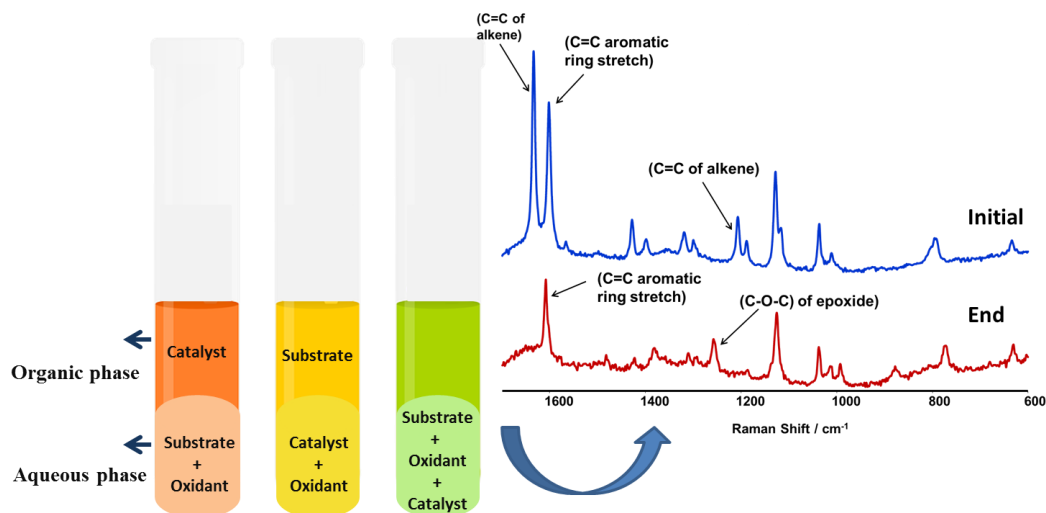


Figure 4. Approach taken in the present study and example of in line monitoring of an aqueous phase by Raman spectroscopy.

In chapter 6, the activity of Mn-tmtacn catalyst in single phase reactions is investigated. The goal is to understand at a molecular level, the effect of additives and other reaction parameters on the activity of the manganese catalysts in the oxidation of substrates and decomposition of H_2O_2 . The epoxidation of styrene sulfonate and the oxidation of chrysin in water as model substrates in the pH ranges 6-9 and 10-11, respectively, and catalysed by Mn-tmtacn complexes are compared and contrasted. Although control over solution pH in such systems requires the addition of buffering agents, commonly used buffers are not innocent in regard to the reactivity of the catalysts. In addition, it was demonstrated that the initial structure of the complex has a profound effect on the activity of the catalyst