

## University of Groningen

### Catalysis in complex media

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## Overview and perspectives

Each chapter in this thesis describes an approach in understanding the mechanisms by which Mn-tmtacn based catalysts in oxidation and bleaching process.

Raman spectroscopy is one of the few spectroscopic tools that can achieve the level of detailed structural information required to follow reactions in real time. The insensitivity of Raman spectroscopy to water makes it a key technique in studying complex aqueous systems. In chapter 2 the focus was on the development of spectroscopic analysis techniques capable of probing components present in aqueous catalytic systems at low concentrations. The DCDR technique<sup>1</sup> was used to monitor reaction progress in the catalytic epoxidation of alkenes by manganese catalysts in water both quantitatively as well as qualitatively. These catalysed reactions are highly suited to the DCDR technique. For other reactions control experiments must be made to ensure that the observations made here hold for those reactions also, especially with regard to homogenous deposition of reaction components over the sampled area. Extension of this method to non-aqueous conditions can be explored in future studies.

In chapter 3, the pH dependent aqueous and non-aqueous coordination chemistry of  $[\text{Mn}_2^{\text{III,IV}}(\mu\text{-CH}_3\text{COO})(\mu\text{-O})_2(\text{Me}_4\text{dtne})](\text{PF}_6)_2$  was investigated by UV/vis absorption, Raman and electron paramagnetic resonance (EPR) spectroscopies, as well as cyclic voltammetry. It was demonstrated the key role played by dissociation of the  $\mu$ -carboxylato ligand, at high pH, in oxidation catalysis, *e.g.*, in the bleaching of chrysin containing aqueous solutions with  $\text{H}_2\text{O}_2$ . Since the behaviour of the complex was established in a homogenous system and this complex has shown good performance in cotton bleaching<sup>2</sup> especially at relatively high pH (11-11.5), the focus can be shifted now to non-homogenous systems, in particular in the investigation of the behaviour of the complex in presence of unbleached cotton sample.

The first challenge in the mechanistic studies in complex processes is to find a suitable model compound. In chapter 4, morin and chrysin, both flavonoid compounds, were compared and contrasted as a model substrate under conditions relevant to bleaching. Morin is shown to be unstable in aqueous bicarbonate solution due to the photo degradation under exposure to UV light, pH sensitivity and reactivity with  $\text{O}_2$  and introduces specific complications in the kinetic analyses carried out in bleaching studies. In contrast, chrysin turned out to be a more suitable model for mechanistic studies in oxidations with catalysts, *e.g.*, manganese complexes, with  $\text{H}_2\text{O}_2$  due to reduction of the complexity of analysis since it shows little pH sensitivity in the pH range of interest and no photo degradation or reactivity with oxygen. A detailed understanding of the mechanism using chrysin as a model compound and identification of the products formed under bleaching conditions can provide useful insights, which can improve the performance of the catalyst under commercial conditions.

In chapter 5, a key challenge was to establish where the oxidation chemistry takes place in a two phase system. From the data obtained, it was concluded that oxidation chemistry was localised in the aqueous phase in two phase reactions where heptane, toluene or styrene is the organic phase. The oxidation chemistry under two phase conditions with **1** is restricted to the aqueous layer, which holds implications for the use

of these catalysts in two phase applications and especially in the use of phase transfer catalysts and indeed maximising interfacial area is likely to be key to reactivity.

Reactions in emulsions are difficult to monitor with any spectroscopic method due to the dimension of the micelles and the scattering of light derived from the optical anisotropy of the mixture. The development of a spectroscopic real-time analysis technique capable of probing complex multiphase systems can provide major advantages in obtaining molecular information from the system non-invasively.

Although in chapter 6, an understanding of the effect of additives and other reaction parameters on the activity of the manganese catalysts in the oxidation of substrates and decomposition of  $H_2O_2$  has been explored, more information about the aqueous chemistry of the complex  $[Mn_2^{IV,IV}(\mu-O)_3(Me_3tacn)_2](PF_6)_2$ , and its analogue  $[Mn_2^{III,III}(\mu-CH_3COO)_2(\mu-O)(Me_3tacn)_2](PF_6)_2$  under the same conditions needs to be gained in order to understand why the activity of the catalyst in catalysis changes with varying the reaction parameter. Through the combination of techniques such as UV/vis absorption, Raman and EPR spectroscopies and cyclic voltammetry, we may be able to understand at molecular level why in aqueous media, factors such as pH, buffers and additives, e.g., sequestrants, affect the activity of manganese- $Me_3TACN$  based catalysts. This knowledge will facilitate application of these systems in new areas of oxidation catalysis, by allowing inhibition routes to be identified and circumvented.

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