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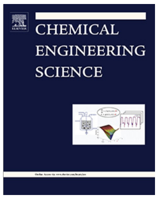

From model compounds to applications: Kinetic studies on the activation of dioxygen using an iron complex in a SuperFocus mixer

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HIGHLIGHTS

- An iron system that could be used for selective oxidation reactions.
- Mechanistic studies using stopped-flow and continuous flow.
- A recyclable reaction KIT system applicable in industrial settings.

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ABSTRACT

It was demonstrated previously that a system consisting of a dinuclear iron complex with the ligand HPTB (*N*,*N*,*N*′,*N*′-tetrakis[2-benzimidazolylmethyl]-1,3-diamino-2-propanol) reacts with dioxygen to form a peroxido complex that may be used for the oxidation of organic substrates. Detailed kinetic studies using stopped-flow techniques and a SuperFocus mixer clearly demonstrate that this complex has a high potential for future applications in catalytic selective oxidation processes in industry. Especially for that reason a reaction KIT system for easy handling was developed that allows to start with a stable iron(III) complex that is reduced (activated) prior to its oxidation with dioxygen.

1. Introduction

Oxidation reactions play an important role for the synthesis of organic compounds in chemical industry. In that context, the German Catalysis Society (GECATS) published a paper in 2015 on catalytic oxidation as a key technology (German Catalysis Society, 2015). However, using dioxygen from air as an oxidant together with a catalyst for selective oxidation of organic substrates is still a difficult task to accomplish. The goal to perform such reactions under ambient conditions in water, thus avoiding dangerous explosive mixtures of volatile organic solvents and air, only can be achieved in a cooperation between research chemists and chemical engineers. In contrast such reactions occur quite easily in nature catalyzed for example by non-heme iron enzymes (Bollinger and Krebs, 2006; Que and Tolman, 2008; Tshuva and Lippard, 2004; Zhang et al., 2005; Kryatov et al., 2005; Costas et al., 2004). Quite important is methane monooxygenase (MMO), an iron enzyme that is capable to oxidize methane with dioxygen from air under ambient conditions (Lee et al., 1993; Tinberg and Lippard, 2011; Shu et al., 1997; Rowe et al., 2007; Valentine et al., 1999; Siegbahn, 2001; Dong et al., 1997). Efforts to perform this reaction in the lab using metal complexes achieved conversions up to three percent (Wang et al., 2017; Schwarz, 2011; Shilov and Shteinman, 2012; Hammond et al., 2012; Sun et al., 2014; Hermans et al., 2009). This reaction has been numbered as one of the 10 most important challenges in catalytic reactions in the past. In contrast, reversible binding of dioxygen to hemerythrin (Projahn et al., 1995), a non-heme protein that is an oxygen carrier for marine invertebrates was successfully modelled previously (Tshuva and Lippard, 2004; Kryatov et al., 2005; Feig et al., 1996; Hartman et al., 1987; Dong et al., 1993; Hayashi et al., 1992; Ookubo et al., 1996). An interesting example for this biological system is the dinuclear iron complex with the ligand **HPTB** (*N*; *N*; *N*′,*N*′-Tetrakis[2–benzimidazolylmethyl]-1,3-diamino-2-propanol) (Feig et al., 1996; Dong et al., 1993; Feig and Lippard, 1994;

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Menage et al., 1990). The reaction of the iron(II) HPTB complex, $[Fe_2(HPTB)Cl_3]$ (**1**), with dioxygen to form the peroxido complex $[Fe_2(HPTB)O_2Cl_2]Cl$ (**2**) is shown in Fig. 1 (R = H, X = Cl^-). In contrast to other iron complexes that can activate dioxygen, complex **2** is quite stable under ambient conditions in protic solvents and therefore allows a detailed analysis of its reactions. Furthermore and quite unusual for iron complexes, **2** can be formed repeatedly if its decomposition product is reduced to **1** and reoxidized again with dioxygen (Miska et al., 2017).

The dinuclear iron peroxido complex, was structurally characterized previously (R = Ethyl, X = $Phenyl_3PO$, anions = BF_4^-) (Dong et al., 1996). In particular, the reaction and the product were met with special interest; it was shown that this iron system is also capable of oxidizing organic substrates. Thus, even simple hydrocarbons such as methane, ethane or cyclohexane could be oxidized, however using hydrogen peroxide as an oxidant (together with additives) and with bad yields (Nizova et al., 2002).

Current investigations on oxygenation reactions showed the potential of complex **2** (Fig. 1) as "peroxide shuttle". Here an aqueous solution of hydrogen peroxide is replaced by the peroxide complex **2** thus avoiding decomposition reactions of hydrogen peroxide to dioxygen and water. With the use of **2** as co-catalyst, it was possible to oxygenate cyclohexane to the corresponding ketone with dioxygen at room temperature (Schindler and Miska, 2017). Therefore it was important to investigate complex **1** further in view of regeneration and dioxygen activation.

Industrially, oxygenation reactions can be performed within large bubble columns. They enable easy contacting of air, which is used as oxidizing agent, and the liquid phase. As a result, they are especially capable to deal with large liquid holdups and long liquid phase residence times for applications without the need for a narrow residence time distribution. However, hydrodynamics and the mass transport mechanism within these processes overly the overall kinetics are still poorly investigated.

Many of these investigations within bubble columns were performed in non-reactive mode to gain insight into the hydrodynamics only (Jimenez et al., 2013; Jimenez et al., 2014; Saito and Toriu, 2015; Rollbusch et al., 2015; Bozzano and Dente, 2001; Nagami and Saito, 2013; Joshi et al., 2017; Wegener et al., 2014). Regarding the fact that large bubble columns contain a high gram scale amount of one-time usable reactive chemicals, a system which is recyclable would be desirable. Therefore, the formation and reactivation of the previous mentioned dinuclear iron peroxido complex **1** and **2** was investigated. Due to the fact that the influence of hydrodynamic conditions and mass transport within a bubble column is quite challenging the reactivated complex system was investigated and compared within a commercially available stopped-flow system and a home built continuous-flow system (Super Focus mixer) to gain insight into the reaction mechanism, the handling of the reaction KIT system and to check the applicability for larger industrial settings, e.g. bubble columns.

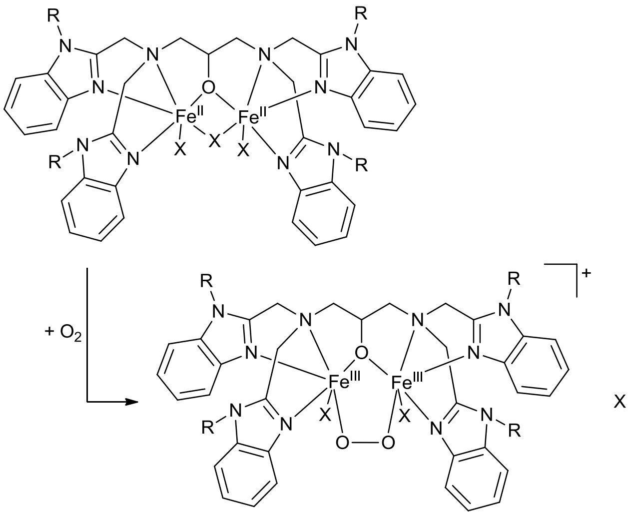

Fig. 1. Binding of molecular dioxygen by $[Fe_2(HPTB)Cl_3]$ (1) forming a binuclear peroxido intermediate (2) with X = Cl^- and R = H.

Hence, for studies on the reaction kinetics of the formation of the dinuclear peroxido complex a lab scale reactor with defined hydrodynamic conditions and without mass transport limitations is preferred. In particular, microstructured devices are suitable for such an application. First, they handle only small amounts of the reactants. Second, very fast microstructured mixer designs allow spatial separation of the mixing process and the reaction. For this work, a special design is used: The so called SuperFocus mixer recently described by Schurr et al. (2016). The SuperFocus mixer is a continuous flow apparatus that is based on the principle of reducing the diffusional path length to speed up the mixing process. The mixer was initially developed by Hessel et al. (2003; 2005). A schematic drawing is shown in Fig. 2.

Two different fluids enter alternatingly into a conical mixing zone. The resulting lamellae are focused and thus, the width of the lamellae, which corresponds to the characteristic diffusional path length, is diminished. After the focusing zone the fluid is entering into the mixing channel with 0.5 mm width, where the reaction takes place. The SuperFocus mixer used for this work is similar to the one presented by Schurr et al. (2016). The structure of the mixer is etched into silicon and the cover plates are made of glass. Thus, the mixer provides optical access to adapt in-situ process analysis tools to it, i.e. UV/Vis spectroscopy.

2. Experimental

2.1. Methods

2.1.1. Continuous-flow SFM setup

The experimental setup was derived from the one presented by Schurr et al. (2016). The two reactants, the methanol solution saturated with pure oxygen at ambient temperature and pressure and the methanol solution containing the $[Fe_2(HPTB)Cl_3]$ complex of 2.0 $mmol\cdot L^{-1}$, are fed into the SuperFocus mixer by a syringe pump. A detailed description of the design of the silicon-glass composite of the mixer is shown in Schurr et al. (2016). In their work two mixers were used differing in the length of the mixing channel. For our work we used the mixer with a channel length of 200 mm. At a distance of 81 mm or 157 mm from the outlet of the focusing zone multiple UV/Vis spectra were taken with the optical setup, shown in Fig. 3. The light of a halogen lamp (1) is directed via light

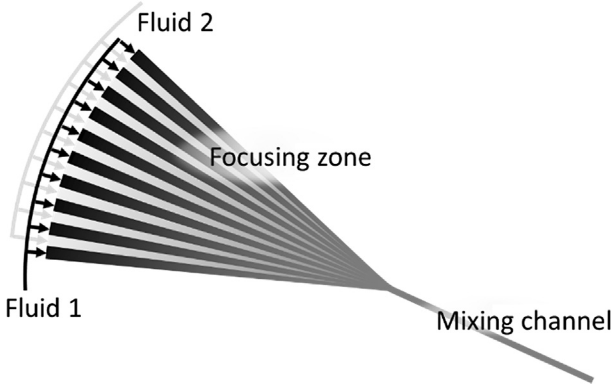

Fig. 2. Schematic of the SuperFocus mixer.

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