Bio-inorganic hybrid catalyst combining enzyme aggregates and catalytic hollow spheres for the green epoxidation of olefins

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1. Introduction

In line with green chemistry principles, Vennestrom *et al.*[1] proposed the chemoenzymatic epoxidation of olefins by sequential catalysis using glucose oxidase (GOx) - for *in situ* production of H_2O_2 - and microporous titanosilicalite-1 (TS-1) (**Fig. 1**). The direct immobilization of GOx on the catalyst was also proposed but the epoxide production was notably limited by the low enzyme loading. Here, we propose a new strategy (**Fig. 2**) for the preparation of a hybrid catalyst that combines all the features of TS-1 with a high loading of GOx. The method is based on the aerosol-assisted self-assembly of TS-1 nanocrystals to form hollow spheres with tailored texture and good epoxidation activity. These spheres are subsequently loaded with the enzymes which are then cross-linked to secure their entrapment. Upon optimization of the working conditions, we show that it is possible to reach much higher epoxide productivity.

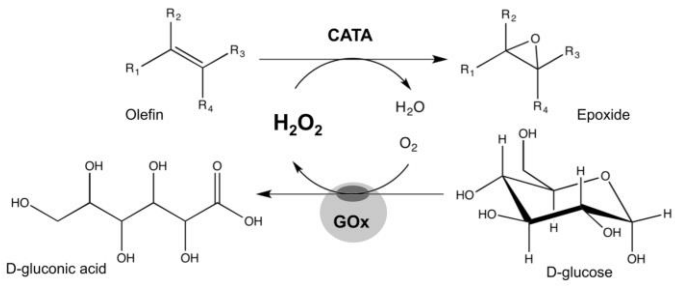

Figure 1. Chemo-enzymatic olefin epoxidation using a TiO_2-SiO_2 epoxidation catalyst (**CATA**) together with glucose oxidase (**GOx**).

2. Experimental

Hybrid catalyst preparation. 1) The inorganic catalyst was prepared by the aerosol technique[2] from a colloidal TS-1 suspension mixed with a silica precursor solution ("**TS-1_Aer**", **Fig. 2 a**). The material was fully characterized (*see below*) and the catalytic performance was tested for the conversion of allyl alcohol in H_2O at 45°C. 2) Cross-Linked Enzyme Aggregates (CLEAs)[3] were formed after impregnating **TS-1_Aer** with a solution of free GOx ("**GOx-CLEAs@TS-1_Aer**", **Fig. 2 b**). The enzyme loading was evaluated by TGA whereas the activity was monitored using an optical oxygen sensor.

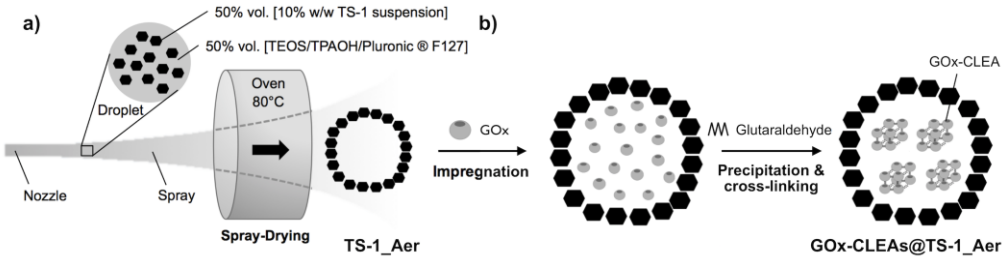

Figure 2. Procedures for the preparation of a) **TS-1_Aer** and b) **GOx-CLEAs@TS-1_Aer**.

Chemo-enzymatic epoxidation of allyl alcohol. The reaction medium (conditions in **Fig. 4**) was fed with pure oxygen using an oxygen permeable membrane. Acidification by gluconic acid was compensated by automatic titration with NaOH. Glucose conversion was evaluated by the amount of base added, whereas H_2O_2 concentration was followed by a colorimetric assay.

3. Results & Discussion

TS-1_Aer particles display a hollow sphere morphology (**Fig. 3 a**). PXRD, XPS, ICP-AES, and SEM confirmed that these structures are made of well-preserved TS-1 nanocrystals embedded in a mesoporous silica matrix (10–20 nm pore size, N_2 physisorption). **TS-1_Aer** is almost as active as pure TS-1 (**Fig. 3 b**) and also fully selective for the epoxide.

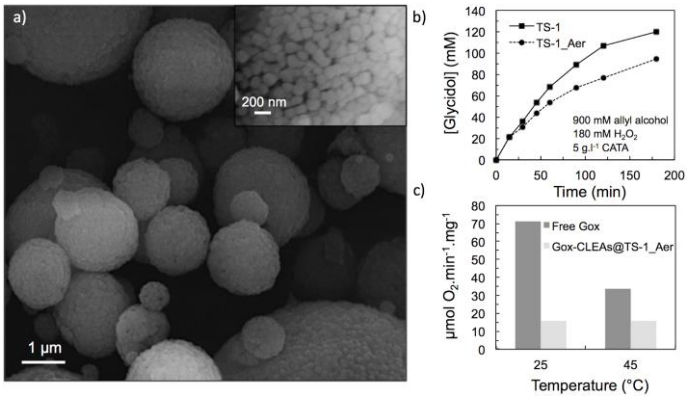

Figure 3. a) SEM image of **TS-1_Aer**. Inset: embedded TS-1 crystals. b) Conversion of allyl alcohol. c) Activity of free and immobilized GOx.

The experimental enzyme loading in the hybrid is 44 $mg.g^{-1}$ (nominal = 50 $mg.g^{-1}$). SEM analysis demonstrated that GOx-CLEAs were properly encapsulated. They were also shown to withstand temperature of 45°C (**Fig. 3c**).

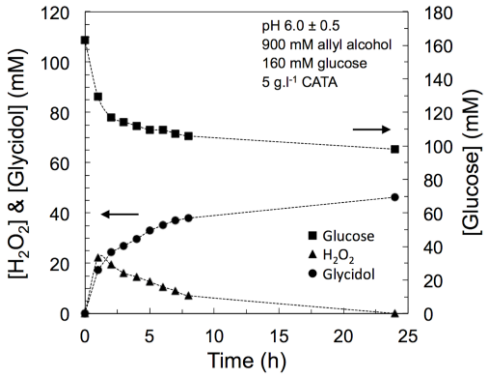

Figure 4. Chemo-enzymatic epoxidation of allyl alcohol in H_2O at 45°C with **GOx-CLEAs@TS-1_Aer**.

For the cascade reaction (**Fig. 4**), the glycidol concentration was 46 mM (24h) with a selectivity estimated to be above 70%. No enzyme leaching was observed, as confirmed by a hot filtration test and a Bradford assay on filtrated reaction medium.

4. Conclusions

Such hybrid chemo-enzymatic heterogeneous catalysts constitute a valid approach to run cascade reactions in green conditions, where the entrapped enzyme and the surrounding catalytic sphere are put at work simultaneously.