

N°601 / OC

TOPIC(s) : Homogenous, heterogenous and biocatalysis / Clean reactions

Catalytic hollow spheres as vessels for Cross-Linked Enzyme Aggregates - Paving the way to efficient chemo-enzymatic reactions

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PURPOSE OF THE ABSTRACT

With the advent of green chemistry, industrial chemical processes have to be re-designed in order to perform reactions in a more sustainable fashion. Biocatalysis has recently been the focus of many studies which aimed at carrying out reactions with low waste production, low energy consumption and possibly starting from bio-sourced substrates [1]. Nowadays, there are strong incentives to construct heterogeneous-enzyme hybrids [2], allowing to recover the enzymes and to increase their stability. Moving further, the functionality of the support itself could be exploited to allow for one-pot tandem or domino catalytic systems. The idea is to combine the heterogeneous catalyst and the enzyme in a single reusable chemo-enzymatic active solid [3,4]. However, only a few studies investigated such hybrid systems, possibly because of the poor stability of many heterogeneous catalysts under aqueous conditions.

In 2010, Vennestrøm et al. proposed the chemo-enzymatic formation of epoxides by tandem catalysis using free glucose oxidase and TS-1 zeolite [5]. In this case, the water-stable crystalline zeolite uses the hydrogen peroxide produced in situ by the enzyme to oxidize an olefin into its epoxide. The direct immobilization of the enzyme on the surface of TS-1 was also proposed but the epoxide production was limited by the low enzyme loading on the external surface of zeolite crystals.

Here, we propose a new strategy for the preparation of a GOx/TS-1 hybrid catalyst that allows to combine all the features of the zeolite with a high enzyme loading. The method is based on the aerosol-assisted [6] self-assembly of TS-1 crystals to form hollow mesoporous zeolite microspheres ("TS-1_Aer", Fig. 1a) with tailored texture and good epoxidation activity in water. The latter spheres were loaded with various amounts "X" of enzymes which were then cross-linked (Cross-Linked Enzyme Aggregates, CLEAs [7]) to secure their entrapment ("GOx_X@TS-1_Aer", Fig. 1b). Thus, the hollow spheres were used both as catalysts and as vessels for the enzyme.

TS-1_Aer particles displayed a hollow sphere morphology (Fig. 2a) with size in the 0.5-8 micrometers range. PXRD, XPS, ICP-AES, and SEM confirmed that these structures were made of well-preserved TS-1 crystals embedded in a mesoporous (10-20 nm pore size, inset Fig. 2a) silica matrix. This catalyst was shown to be almost as active as pure TS-1 for the conversion of allyl alcohol with hydrogen peroxide in water (Fig. 2b) and fully selective towards the epoxide product.

The enzyme immobilization yield was in the 80-100% range for enzyme loadings between 5 and 50 mg/g (Fig. 2c), with more than 99% of the activity coming from the solid phase (see an illustration of the immobilization procedure in inset of Fig. 2c). Entrapped CLEAs were less active than the free enzyme but were shown to withstand a temperature of 45°C. Besides, the enzymes had little effect on the epoxidation activity (Fig. 2b).

Upon optimization of the working conditions for these new hybrid structures, we show that significant epoxide

production was obtained via the cascade reaction (Fig. 2d). The glycidol yield reached 23% (37 mM) after 24h whereas the glucose conversion was 36%. The selectivity for glycidol product was ca. 64%. No enzyme leaching was observed, as confirmed by a Bradford assay on filtrated reaction medium. The experimental data were fitted using a mathematical model (dotted lines in Fig. 2d).

In conclusion, we show that aerosol-made hollow zeolite microspheres - with zeolitic crystals embedded in a porous silica shell - can be used as vessels to load high amounts of enzymes entrapped in the form of Cross-Linked Enzyme Aggregates. The results presented give a promising insight into the production of epoxides using tandem catalysis. The method combines efficiently the advantages of heterogeneous and bio-catalysis; it opens new perspectives for performing chemo-enzymatic reactions in a green fashion.

FIGURES

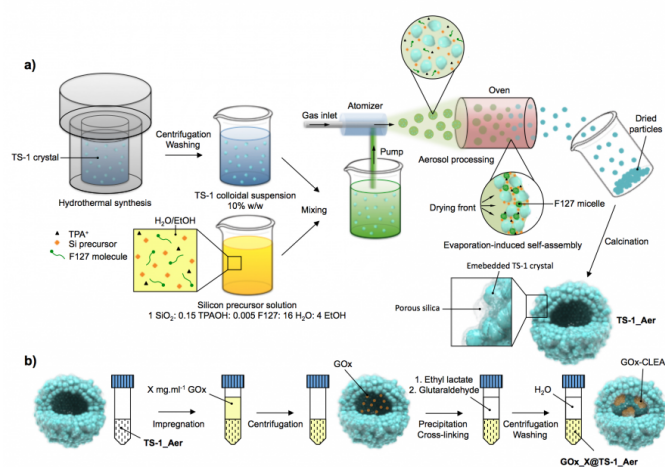


FIGURE 1

Figure 1

Preparation routes used for a) the formation of hollow zeolite microspheres with embedded TS-1 crystals using the aerosol method (TS-1_Aer), b) the immobilization of GOx on the aerosol-made material by the formation of entrapped CLEAs (GOx_X@TS-1_Aer).

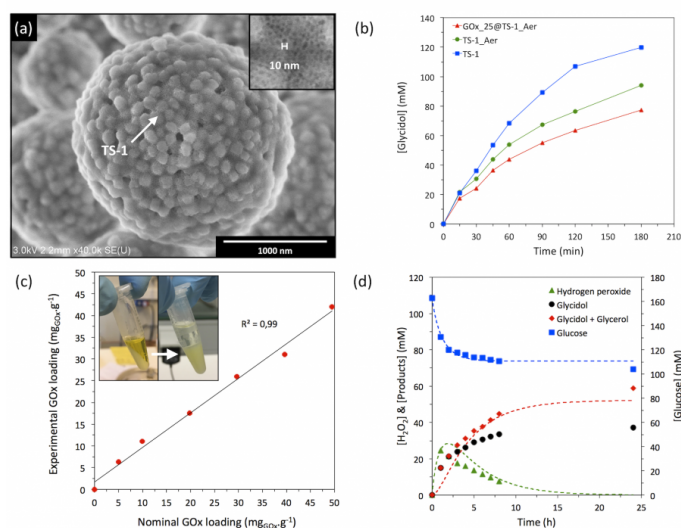


FIGURE 2

Figure 2

a) SEM-FEG micrograph of TS-1_Aer; b) Catalytic performance of the catalysts in the conversion of allyl alcohol at 45°C; c) Experimental vs. nominal enzyme loadings in TS-1_Aer; d) Chemo-enzymatic epoxidation of allyl alcohol with GOx_25@TS-1_Aer at 45°C.

KEYWORDS

Olefin epoxidation | Aerosol assisted sol-gel | Cascade reaction | Enzyme immobilization

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