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Zeolite-Coated Porous Arrays: A Novel Strategy for Enzyme Encapsulation

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Zeolite Beta-coated stainless steel supports with gradient porosity are employed as filter-panels for lipase encapsulation. Enzyme encapsulation on the stainless steel porous discs is achieved via vacuum infiltration. Subsequently, two lipase-encapsulated zeolite Beta-coated stainless steel discs are attached using an adhesive. The zeolite Beta layer on the stainless steel discs largely prevents lipase leaching in comparison to the stainless steel discs without a zeolite layer. The activity of the lipase-encapsulated, attached zeolite Beta-coated stainless steel porous discs depends on the thickness of the zeolite Beta layer. It is shown that the biocatalytic performance of the lipase-encapsulated, attached zeolite Beta-coated stainless steel supports with a zeolite Beta layer thickness of ≈0.7–1 µm is better than the lipase-encapsulated, attached zeolite Beta-coated stainless steel supports with a zeolite Beta layer thickness of ≈2–3 µm in the lipase-catalyzed transesterification of vinyl propionate with 1-butanol using *n*-hexane as solvent.

1. Introduction

Due to their high activity, specificity, and ability to work under mild pH and temperature conditions, enzyme-based catalysts have become increasingly important in industrial applications, e.g., in fine chemical or pharmaceutical synthesis, food processing, and bioremediation. In particular, the use of enzymes as industrial biocatalysts has been significantly increased in sustainable organic synthesis.[1] However, enzymes in their native form experience low operational stability and are difficult to recovery and reuse. In order to overcome these drawbacks, enzyme immobilization has been routinely performed on various carriers by different immobilization methods.[2] Inorganic porous solids due to their environmentally benign nature and superior physicochemical properties such as high surface area, chemical, thermal, and mechanical stability, etc., have been considered prime candidates for enzyme immobilization. Several porous supports, including microporous and mesoporous zeolites,[3] as well as ordered mesoporous materials[4] have been studied extensively for the enzyme immobilization. Recently, we applied periodic mesoporous organosilicas (PMOs) as host materials for the enzyme immobilization.[5] In comparison to mesoporous solids, microporous zeolites have limited potential applications in enzyme immobilization due to their narrow pore sizes (<2 nm) with respect to the large size (usually, >3 nm) of the enzyme molecules. In general, selection of the porous materials for enzyme immobilization was mainly guided by their physicochemical properties and the interaction of enzyme and support. These porous materials have been applied for enzyme immobilization only in a particulate form. In contrast to powders, structured inorganic porous supports (e.g., porous stainless steel disc supports) offer several outstanding advantages, such as low pressure drop, low diffusion limitations, and easy scale-up for a given biocatalytic process. In addition, they possess high surface area as well as high mechanical, chemical, and thermal stability. The application of structured supports, such as ceramic materials,[6] alumina and stainless steel supports[7] for enzyme immobilization has been reported initially a few decades ago. Since then, numerous articles have been published on the immobilization of different types of enzymes using structured inorganic solids, such as ceramic supports,[8] porous alumina or hybrid membranes,[9] and stainless steels supports.[10] On the other hand, the literature concerning the application of the zeolite-coated materials for enzyme immobilization is very scarce.[11]

In contrast to the methods proposed for enzyme immobilization on zeolite membranes,[11] we present an alternative novel method for the application of zeolite-coated stainless steel supports containing gradient porosity as filter-panels for the encapsulation of lipase from *Thermomyces lanuginosus* (TLL) with a size of 3.5 nm × 4.5 nm × 5.0 nm[12] (see **Figure 1**). In this work, zeolite Beta was employed for the coating. Zeolite Beta consists of a 3D pore network with straight (0.77 nm × 0.66 nm)

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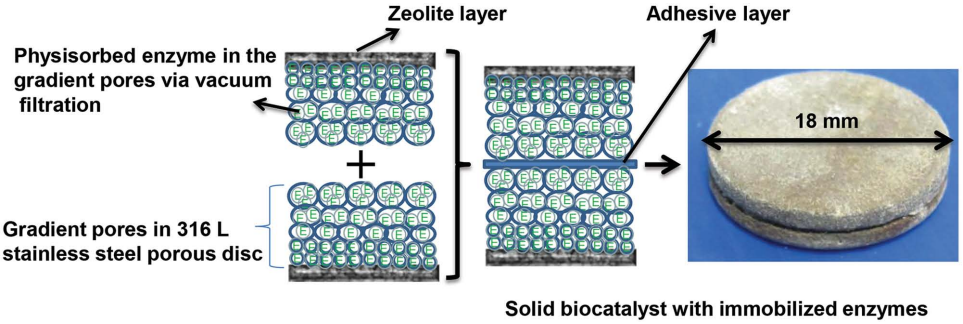

Figure 1. Schematic representation (left) and a photograph (right) of zeolite Beta-coated stainless steel porous discs used as filter-panels for lipase encapsulation.

and crossed (0.56 nm × 0.56 nm) 12-membered ring channels. Aluminum-containing zeolite Beta possesses both Brønsted and Lewis acid sites due to the presence of framework and non-framework aluminum species, respectively. Hence, it has been applied as a potential catalyst in several Brønsted as well as Lewis acid catalyzed reactions.[13] Initially, zeolite Beta (*BEA) was coated on the sintered side of the stainless steel porous discs via multiple in situ crystallization (MISC) method, which is known to give (defect-free) thin layers. Thereafter, TLL was encapsulated in the gradient pores of the stainless steel discs using vacuum infiltration. Subsequently, two lipase-encapsulated zeolite Beta-coated stainless steel supports were attached using an adhesive. In this approach, the encapsulated enzyme molecules are freely mobile like in their native form within the gradient pores of stainless steel discs, while the zeolite layer on top of the discs acts as a protective layer against enzyme leaching.

2. Results and Discussion

2.1. Lipase Leaching Tests

At first, enzyme leaching tests were carried out with the attached, noncoated lipase-immobilized stainless steel porous discs and attached, zeolite Beta-coated stainless steel porous discs having a zeolite layer with a thickness of ≈0.7–1 µm. Prior to the leaching tests, TLL was immobilized onto the stainless steel supports using 50 µL of lipase and 1 mL of phosphate buffer with a pH of 7.2 via vacuum infiltration (Figure S1, Supporting Information). Based on the hydrolysis assay of 4-nitrophenyl palmitate (*p*NPP), the amount of lipase immobilized in a single stainless steel support amounts to ≈2.14 U (where, U = µmol min^{-1}). Therefore, the amount of lipase in the attached pair of stainless steel discs was ≈4.28 U. The leaching of the enzyme was monitored for five consecutive runs at a pH of 7.2 as described in the Supporting Information. **Figure 2** shows the amount of lipase detected in solution after every run from the attached noncoated and attached zeolite Beta-coated stainless steel porous supports having a zeolite layer thickness of ≈1 µm. A significant amount of lipase was leached (≈0.57 U = 13.8%) in the first run of the attached, noncoated stainless steel supports. In contrast, only a very low amount of lipase (≈0.1 U) was leached in the attached, one-time zeolite Beta-coated stainless steel supports having a zeolite layer thickness of ≈1 µm. In the second run, a very low amount of lipase (<0.05 U) was extracted in both cases. In the following runs, no lipase leaching from the attached stainless steel porous supports was observed. The higher leaching in the first run of noncoated stainless steel supports was attributed to the absence of protective zeolite layer. In contrast, leaching of lipase was suppressed in the attached one-time zeolite Beta-coated stainless steel supports due to the presence of the zeolite layer (≈1 µm).

2.2. Lipase-Catalyzed Transesterification on Zeolite-Coated Stainless Steel Supports

Motivated by the results described above, the thickness of the zeolite layer on the stainless steel porous supports was further increased by repeating zeolite crystallization for three times. This led to the formation of zeolite layers with a thickness of ≈2–3 µm on the stainless steel supports. The X-ray diffraction patterns of the single and threefold zeolite Beta-coated stainless steel discs showed two reflections at $2\theta = 7.7°$ and 22.5°, which are indicative for the BEA* crystalline phase (Figure S4, Supporting Information). The corresponding cross-sectional scanning electron microscopy (SEM) images are shown in **Figure 3**a,b, respectively. The presence and thickness of the zeolite Beta layer for the single and threefold zeolite Beta-coated

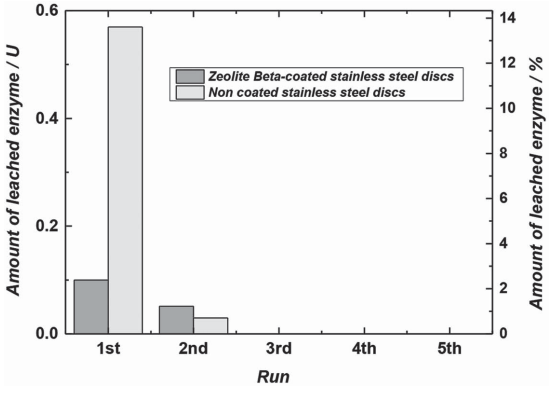

Figure 2. Leaching of lipase from the attached, coated stainless steel porous discs with a zeolite Beta layer thickness of ≈1 µm and the attached, stainless steel porous discs without a zeolite layer, respectively.

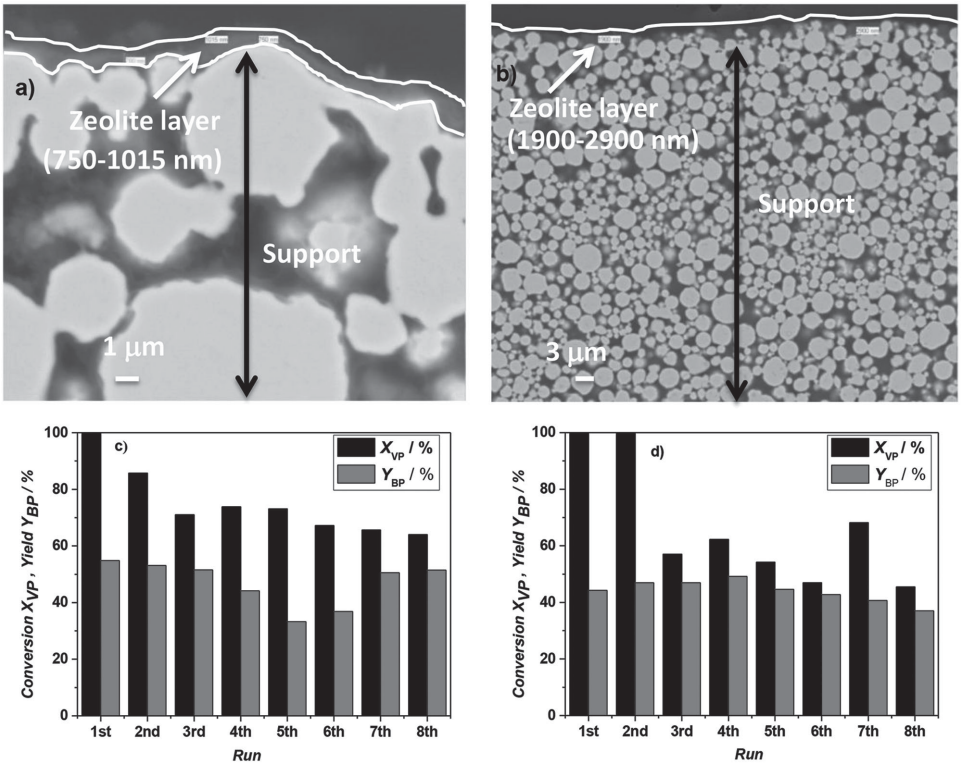

Figure 3. a,b) SEM cross-sectional images of single zeolite Beta-coated and threefold zeolite Beta-coated stainless steel porous discs, respectively, c,d) results of the recycling experiments obtained for the transesterification of vinyl propionate on the attached, single zeolite Beta-coated and threefold zeolite Beta-coated stainless steel porous discs, respectively. The reaction time of each run was 24 h.

stainless steel discs was determined by elemental mapping during the SEM analysis. For the clear visibility, the thickness of the zeolite layer was marked by the lines in Figure 3. Spherical nanocrystals with a size of ≈100 nm were observed in the SEM image of excess zeolite Beta powder as shown in Figure S4d, Supporting Information. Using the hydrolysis of *p*NPP as the activity assay, the activity ratio of the lipase-immobilized on attached, one-time (0.7–1 µm) and threefold (2–3 µm) zeolite Beta-coated stainless steel porous discs was determined to 1.8:1, respectively, through in situ UV–vis spectroscopy (see Supporting Information). Thus, the hydrolytic activity of the zeolite Beta-coated supports depends on the thickness of the zeolite layer. This indicates the presence of lower diffusion limitations for the substrate in the hydrolysis test performed on the attached, one-time zeolite Beta-coated stainless steel porous discs compared to the attached, threefold zeolite Beta-coated stainless steel porous discs. This was further confirmed by performing a model biocatalytic reaction, i.e., the enzymatic transesterification of vinyl propionate (VP) and 1-butanol to butyl propionate (BP) in a nonaqueous medium, viz., *n*-hexane, using both, single and threefold zeolite Beta-coated stainless steel supports. In Figure 3, results of recycling tests of transesterification were compared for the attached, lipase-immobilized stainless steel supports containing single zeolite Beta-coated and threefold zeolite Beta-coated stainless steel supports. The reaction temperature (40 °C) and the amount of enzyme in the pair of stainless steel discs (4.28 U) were the same in both cases. In the first run, the conversion of vinyl propionate (X_{VP}) and yield of butyl propionate (Y_{BP}) on the attached, lipase-immobilized zeolite Beta-coated supports having a zeolite layer thickness of ≈1 µm amounted to 100% and 50%, respectively. Even in the subsequent runs, significant conversion of vinyl propionate (≈70%–80%) was maintained in the transesterification. This indicates that the lipase encapsulated in the gradient pores of stainless steel supports having ≈1 µm zeolite layer thickness was stable up to eight runs. In comparison with the conversion of vinyl propionate (X_{VP}), lower yields of butyl propionate (Y_{BP}) were observed in all runs. The low yield of butyl propionate probably is a consequence of the acid-catalyzed hydrolysis of the vinyl propionate on the acidic beta zeolite.[14] Another reason for lower product yields is the difficult desorption of the butyl propionate from the biocatalytic stainless steel supports through the pores of zeolite Beta. In the case of lipase encapsulated in stainless steel supports having zeolite layer with a thickness of ≈2–3 µm, the conversion (X_{VP}) and yield (Y_{BP}) in the first two runs amounted to 100% and ≈40%, respectively. However, in the following runs, lower conversion and lower yields were observed in comparison with the lipase-encapsulated stainless steel supports possessing a ≈1 µm thick zeolite layer. This could be due to the larger diffusion limitations of the reactant and product molecules as confirmed by the lower activity of the attached threefold zeolite Beta-coated stainless steel supports in the activity tests. This result indicates that a zeolite layer thickness below 1 µm is beneficial in the transesterification reaction in order to overcome diffusion limitations.

2.3. Numbering-Up of the TLL-Encapsulated Stainless Steel Supports in the Reactor

Another important feature of using the attached, lipase-encapsulated zeolite-coated stainless steel porous discs in biocatalysis is the easy numbering-up of the stainless steel supports in the process. Thus, the transesterification of vinyl propionate was performed on the attached lipase-encapsulated one pair, two pairs, and three pairs of zeolite Beta-coated stainless steel porous supports. The amount of TLL immobilized in each zeolite Beta-coated stainless steel porous disc amounted to ≈2.14 U. Therefore, the total amount of TLL immobilized in one pair, two pairs, and three pairs of zeolite Beta-coated stainless steel porous discs was 4.28, 8.56, and 12.84 U, respectively. **Figure 4** shows the conversion (X_{VP}) and yield (Y_{BP}) during the transesterification of vinyl propionate with 1-butanol performed at 40 °C. The conversions and yields are compared in the transesterification reaction up to a reaction time of 8 h. The conversion of vinyl propionate and yield of butyl propionate increased with increasing reaction time. When the transesterification reaction was carried out on one pair of the attached lipase-encapsulated zeolite Beta-coated stainless steel supports, the X_{VP} and Y_{BP} after 8 h of reaction time amounted to only ≈30% and 18%, respectively. Upon reactor numbering-up with two pairs of the attached lipase-immobilized zeolite-coated stainless steel supports (i.e., 8.56 U), conversion and yield increased to ≈40% and 30%, respectively. With the use of three pairs of lipase-immobilized zeolite Beta-coated stainless steel porous discs (i.e., 12.84 U), a conversion of vinyl propionate of 65% was achieved within 8 h, while the yield of butyl propionate amounted to 45%. Although a comparison of the performance of the novel immobilization strategy with conventional catalysts prepared by immobilization (by physical adsorption, covalent anchoring, or cross-linking) of lipase on silica or polymer supports is not straightforward, we observed that in particular the recycle stability is improved under similar experimental conditions while activity and selectivity of the catalysts are comparable.[5,15]

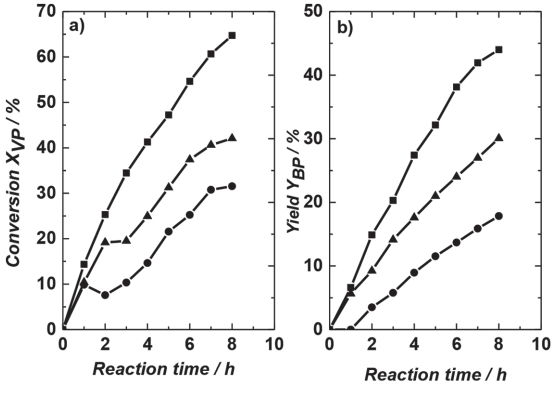

Figure 4. a) Conversion (X_{VP}) of vinyl propionate and b) yield (Y_{BP}) of butyl propionate obtained during the transesterification of vinyl propionate and 1-butanol to butyl propionate at 40 °C using one (●), two (▲), and three (■) pairs of zeolite Beta-coated stainless steel porous discs loaded with lipase via vacuum infiltration (i.e., physical adsorption).

3. Conclusions

In conclusion, a novel method with the benefit of negligible enzyme leaching was developed to prepare the enzyme-encapsulated structured biocatalyst. For this purpose, zeolite Beta-coated porous asymmetric stainless steel supports having gradient porosity were used as filter-panels for lipase immobilization. The large void volume of the porous support allows encapsulation of the enzyme in its native state (in contrast to physical adsorption, covalent anchoring, or cross-linking), while leaching is hindered by the zeolite layer. The latter advantage is clearly evident from the performed leaching tests. The results revealed that the presence of zeolite Beta layer with thickness below 1 μm prevents enzyme leaching from the supports. The lipase-encapsulated zeolite Beta-coated stainless steel porous discs prepared via this novel approach were also tested in the enzymatic transesterification of vinyl propionate with 1-butanol. It was observed that the thickness of the zeolite layer plays a crucial role on the performance of the biocatalyst in the transesterification reaction. An optimum zeolite layer thickness of below 1 μm yielded better conversions and yields. Recycling experiments in the transesterification reaction showed that a stable performance up to eight runs was achieved. We expect this novel approach of enzyme encapsulation to foster further applications in enzyme immobilization and biocatalysis. Nevertheless, several factors such as enzyme loading, compatibility of the zeolite-coated stainless steel discs with different enzymes, membrane pore size, and material, the influence of the physicochemical properties of zeolite layer in the biocatalytic reactions still require better understanding and further improvement. In particular, the selection of a different zeolite or mesoporous silica layer is important in order to suppress diffusion limitations and tailor the chemical catalytic functionality is important on the way to bifunctional chemical and biocatalytic systems. These studies are currently under way and will be reported in the near future.

4. Experimental Section

*Crystallization of Zeolite Beta (*BEA) on Stainless Steel Porous Supports*: Porous asymmetric 316L grade stainless steel disc supports with ≈18 mm diameter were purchased from GKN Sinter Metals Filter GmbH. The stainless steel porous discs have a fine layer on one side (i.e., top) and a coarse layer on the other side (i.e., bottom). The average pore size in the top layer of the stainless steel disc was <0.2 μm. Crystallization of zeolite Beta was performed on the fine layer side of the stainless steel support. A uniform layer of zeolite Beta on a stainless steel support was achieved by MISC technique.[16] A typical synthesis batch procedure was as follows: Initially, 13.0 g of Ludox AS 40 and 20.4 g of tetraethylammonium hydroxide (TEAOH, 35%) were mixed and stirred for 1 h at room temperature. Thereafter, 1.3 g of aluminum nitrate nonahydrate was dissolved in 1.3 g of distilled water in a separate beaker. Subsequently, this mixture was added to the above-mentioned mixture and stirred for another hour at room temperature. Finally, the synthesis mixture together with the stainless steel porous discs were loaded into a stainless steel autoclave (45 mL) containing a Teflon inner cylinder. The stainless steel porous disc was placed in a slanted position inside the autoclave with the help of a polymer tube holder. Crystallization of zeolite Beta was performed single or threefold at 150 °C for 72 h. After each crystallization step, the membranes were washed thoroughly with distilled water, while the excess powder samples were recovered by centrifugation. At the end of three crystallization

steps, the zeolite membranes were washed with distilled water, dried at 100 °C, and calcined at 400 °C in a flow of synthetic air for 16 h.

Encapsulation of Lipase on Zeolite Beta-Coated Stainless Steel Supports: TLL was encapsulated onto zeolite Beta-coated stainless steel membranes via vacuum infiltration. In a typical immobilization experiment, 50 µL of lipase and 1 mL of sodium phosphate buffer (pH = 7.2) were mixed in a small glass bottle. This mixture was filtered in a drop wise manner through the coarse layer (i.e., bottom) of the calcined zeolite Beta-coated stainless steel support under vacuum. In this approach, the lipase and buffer mixture was physically adsorbed in the inner pores of the stainless steel membrane. On the other side of the stainless steel porous support (i.e., top), the zeolite layer acts as filter-panel for the enzyme solution. The filtrate solution was readsorbed into the stainless steel porous disc by repeating the filtration procedure until the enzyme mixture was completely adsorbed in the pores of stainless steel disc. Afterward, two lipase-encapsulated zeolite Beta-coated stainless steel supports were attached using an adhesive composite, which was prepared by mixing aluminum oxide and acetic acid as peptizing agent.

Lipase-Catalyzed Transesterification: The transesterification reaction on the attached, lipase-encapsulated zeolite Beta-coated stainless steel porous supports was performed in a batch reactor shown in Figure S2, Supporting Information. The reactor was designed with a possibility to hold several biocatalytic stainless steel porous discs. In a typical transesterification reaction, an equimolar mixture (1:1) of vinyl propionate (217.8 µL, 2 mmol) and 1-butanol (183.06 µL, 2 mmol) was used. Afterward, excess amount of hexane (≈30 mL) was used in order to completely immerse the biocatalytic supports in the batch reactor. At regular time intervals, small aliquots were withdrawn and analyzed by a Varian gas chromatograph equipped with a CP-sil5 fused silica column using decane as the internal standard.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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