Textile-fixed catalysts - a new tool for heterogeneous catalysis

Klaus Opwis[1*], Thomas Mayer-Gall[1,2], Jochen S. Gutmann[1,2]
[1]*Deutsches Textilforschungszentrum Nord-West gGmbH, Krefeld, Germany*
[2]*Institute of Physical Chemistry, University Duisburg-Essen, Essen, Germany*
**corresponding author: opwis@dtnw.de*

Introduction

The efficiency of many chemical processes is based on the use of catalysts. The acceleration of the respective reaction relies on the decreased activation energy compared to the non-catalyzed conversion. For many applications the catalysts are embedded in a solid matrix, which allows the recycling of the catalysts and the separation of the products. Such immobilizations offer the multiple or even permanent use. Common carrier materials are from polymeric or mineral nature. But their production and the charging with the catalysts are often complex and high-prized. In contrast, textile carrier materials made of cotton, polyamide or polyester are considerably inexpensive. The flexible construction of fabrics enables reactor constructions of arbitrary geometry and a quick removal of the catalyst without any residues after the reaction. Moreover, their open structure guarantees an optimal substrate turn-over and the active surface is easily adjustable by the fiber diameter.

Here, we report some simple but efficient methods for the permanent fixation of various catalysts such as enzymes (1-3), organo-metallic (4) and organic (5) species on fiber forming polymers such as photo-induced grafting, the use of bifunctional anchor molecules, monomeric and polymeric cross-linking agents or specific catalyst modifications for a direct immobilization.

Materials and Methods

Various catalysts were dissolved in adequate solvents. Afterwards, different fabrics made of fiber-forming polymers were wetted with the catalyst solution. The immobilization of the catalysts on the textile carrier material was conducted by various wet chemical or photo-chemical processes using, e.g., cross-linking agents or excimer UV lamp technology. The textiles were characterized by means of surface sensitive analyses such as UV-Vis or FT-IR(ATR) spectroscopy, scanning electron microscopy and EDX. In addition, in some cases ICP-OES measurements were carried out (metal-containing enzymes and organo-metallic catalysts). Finally, the catalytic activity and the reusability of the textile-fixed catalysts were measured on the base of suitable model reactions.

Results and Discussion

We have started our investigations with the immobilization of enzymes representing the class of biocatalysts resp. white biotechnology. The successful immobilization procedures have been proven via scanning electron microscopy and other spectroscopic methods. We succeed in enzyme loads from 20 - 70 mg/g textile carrier. Exemplarily, **Figure 1** shows SEM pictures of polyamide fibers before and after the photo-induced immobilization of catalase. In nature, this iron-containing protein catalyzes the decomposition of hydrogen peroxide to water and molecular oxygen as a detoxifying mechanism. In addition to its crucial biological relevance, this enzyme has many industrial applications, including the elimination of hydrogen peroxide after milk sterilization in the dairy industry or the prevention of inactivation of other oxidases in the presence of high peroxide concentrations. All immobilization products show a distinct bio-catalytic activity even after 20 reuses. Depending on the used procedure the integral activity over 20 reuses reaches up to 350 % (1-3).

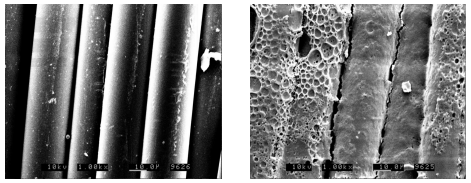

Figure 1. SEM of polyamide 6.6 fibers before (left) and after the immobilization of catalase.

Afterwards, we have transferred our photo-chemical approach successfully to the immobilization of metal porphyrins and bispidines representing the class of organo-metallic catalysts (4). The textile-fixed catalysts are useful for, e.g., various oxidation reactions and "click chemistry" in organic synthesis.

In collaboration with the Max-Planck-Institut fuer Kohlenforschung (Germany) we have recently widen our concept successfully to organic catalysts (5). These textile-fixed catalysts can be used for various enantioselective chemical syntheses of industrial relevance. Especially a textile-fixed chinchona alkaloid shows an amazing performance with regard to catalytic activity, enantioselectivity and recyclability. For example, the enantioselective desymmetrization of cyclic anhydrides runs for more than 250 cycles without a significant loss of its catalytic activity and an impressive enantiomeric ratio of 96.5:3.5.

Significance

Low-cost textile fabrics made of cotton, polyamide or polyester were identified as alternative carrier materials for catalysts. With a low preparative and economic expense fabrics with a high load, a high catalytic activity and excellent permanence against desorption can be produced. Therefore, our *Textile-fixed Catalysts* represent a totally new tool for heterogeneous catalysis with widespread potential applications in pharmaceutics, chemistry and eco-friendly white biotechnology. In addition, the dry and light textiles loaded with catalysts can be easily transported to places where it is practically impossible to set up sophisticated chemical systems. For example, textile-fixed catalysts could help in the water treatment in regions where people are cut off from fresh water supply.

References

1. Opwis, K.; Knittel, D.; Schollmeyer, E. *AATCC Review.* **2004**, *4*, 11, 25-28.
2. Opwis, K.; Knittel, D.; Bahners, T.; Schollmeyer, E. *Eng. Life Sci.* **2005**, *5*, 1, 63–67.
3. Opwis, K.; Knittel, D.; Schollmeyer, E. *Biotechnol. J.* **2007**, *2*, 347–352.
4. Opwis, K.; Mayer-Gall, T.; Textor, T.; Schollmeyer, E. Mittal, K. L., Ed. 2009; Polymer Surface Modification: Relevance to Adhesion Vol. 5, pp. 177-185.
5. Lee, J.-W.; Mayer-Gall, T.; Opwis, K.; Song, C. E.; Gutmann, J. S.; List, B. *Science* **2013**, *341*, 1225–1229.