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Catalases as biocatalysts in technical applications: current state and perspectives

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Abstract Catalases represent a class of enzymes which has found its place among industrially relevant biocatalysts due to their exceptional catalytic rate and high stability. Textile bleaching prior to the dyeing process is the main application and has been performed on a large scale for the past few decades. Their limited substrate scope has not prevented the development of various other catalase-based applications. Newly developed approaches continue to exploit their excellent catalytic potential to degrade hydrogen peroxide while (per)oxidase activity of catalases is opening a new range of possibilities as well. This review provides an overview of applications that involve heme-containing catalases that have been demonstrated in recent years.

Keywords Catalase · Bleaching · Peroxidase · Oxidation · Hydrogen peroxide

Introduction

The class of catalases encompasses three different types of enzymes: monofunctional heme-containing catalases, heme-containing catalases-peroxidases and non-heme catalases (Fig. 1). Monofunctional heme-containing catalases are designated as such due to the long-accepted opinion that their sole role is hydrogen peroxide removal. This rather restricted catalytic role has been questioned in recent years (vide infra). The

catalase-peroxidases represent bifunctional enzymes which display both catalase and peroxidase activities. Non-heme catalases contain manganese as cofactor and typically display lower specific activities when compared with heme-containing catalases. This may explain why they are not as widespread among all kingdoms of life but limited to bacteria (Chelikani et al. 2004). There are several well-described members of non-heme catalases, and research on these enzymes has mainly focused on elucidating their biological significance.

The dismutation of hydrogen peroxide is considered as the primary role of catalases (Nicholls 2012). For the heme-containing catalases, catalysis involves the oxidation of the heme cofactor by hydrogen peroxide to an oxyferryl species that leads to the formation of a porphyrination radical (reaction (1)). This radical is subsequently reduced by a second molecule of hydrogen peroxide, and thus, the resting enzyme state is regenerated (reaction (2)):

Except for catalyzing the dismutation of hydrogen peroxide, catalases have also shown to be able to catalyze other types of redox reactions. Reaction mechanisms have been suggested for oxidase and peroxidase activities of heme-containing catalases, but these are yet to be confirmed experimentally (Vetrano et al. 2005). While mechanistic studies are ongoing to establish the catalytic mechanisms for catalase-catalyzed reactions, catalases are explored and exploited for a variety of applications. Readers are referred to excellent recent reviews on structural and functional properties of catalases (Chelikani et al. 2004; Diaz et al. 2012; Nicholls 2012; Njuma et al. 2014; Switala and Loewen 2002).

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Fig. 1 Structures of representatives of three types of catalases: **a** monofunctional heme-containing catalase from bovine liver (pdb code 3J7B), **b** heme-containing catalase-peroxidase from *Mycobacterium tuberculosis* (pdb code 1SJ2), and **c** manganese-containing catalase from

Thermus thermophilus (pdb code 2V8U). Monofunctional heme-containing catalases have a tetrameric structure, heme-containing catalase-peroxidases occur as dimers and tetramers, and manganese-containing catalases are mostly dimeric

New catalase-based applications exploit catalase or (per)oxidase activities of these enzymes. Catalase has found its place in a number of industrial applications as an effective tool to scavenge hydrogen peroxide. Most catalases are robust enzymes with unusually high catalytic rates, among the highest of known enzymatic rates and hence the name *catalase*. New applications are emerging, and promising ones from recent years are pointed out in this article. This review is not intended to be an exhaustive review of all newly envisioned applications of heme-containing catalases but rather to give a flavor of the wide spectrum of their possible use and to shed light on particularly interesting ideas.

Exploitation of catalase activity

Strict environmental laws regulate disposal of hydrogen peroxide containing effluents into open streams. This creates need for its efficient removal. Conventional chemical methods require extensive washing with alkaline solutions, taking advantage of the relative poor stability of hydrogen peroxide at higher pH values. However, extensive water consumption is obviously undesired. Another approach for degrading hydrogen peroxide is the use of reducing agents such as sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) which in turn generates large amounts of salt. Compared to average reaction rates for enzymatic catalysis ($1\text{--}100\text{ s}^{-1}$), catalases are among the enzymes that are extremely potent biocatalysts with rates of catalysis of up to 10^6 s^{-1} (Switala and Loewen 2002). These high catalytic rates render catalases attractive eco-friendly alternatives for hydrogen peroxide removal. Another important property for industrial use of enzymes is thermostability. Most monofunctional heme-containing catalases display a relatively high thermostability which makes them suitable for use under harsh conditions. Even bovine liver catalase shows a T_m of $57\text{ }^\circ\text{C}$ (Loncar and Fraaije 2014; Switala and Loewen 2002) which is a

surprisingly high value considering its mammalian origin. As it is commercially available and robust, bovine catalase is a widely used catalase for research purposes (Table 1). For bulk industrial processes, catalases are used that are of fungal and bacterial origin. These microbial enzymes are relatively easy to produce by large-scale fermentations.

Textile bleaching

Textile is usually bleached with hydrogen peroxide before the dyeing process. Since the 1980s, enzymatic bleach cleanup with catalases is used on industrial scale. Knitted fabrics and yarns used for production of textile with light colors have to be bleached, whereas this is not necessary for production of textiles with dark shades (Blackburn 2009). However, in practice, all textiles undergo scouring and bleaching to ensure maximal hydrophilicity so that the dyer can choose the dyes depending on the demands of the end user. Removal of bleaching agents has to be done due to their interference with the dyeing process. Traditionally, this is done by extensive washing with hot water, but the use of enzymes reduces water consumption significantly. Using catalase has the advantage of eliminating a rinsing step in between bleaching and dyeing of textile because the peroxide is decomposed without side products and the residual enzyme has no effect on the textile fibers or dye-stuff. A life cycle analysis study of textile manufacturing aimed at replacing traditional washing steps with an industrially produced catalase suggested water savings of $20\text{ m}^3/\text{t}$ of yarn when using 1 kg of Novozymes' Terminox Ultra® 50-L catalase preparation (Blackburn 2009). This product contains catalase originating from the thermophilic fungus *Scytalidium thermophilum*, while other commercial preparations may contain catalases from *Aspergillus niger*, *Aspergillus oryzae*, *Micrococcus luteus*, *Streptomyces coelicolor*, *Thermomyces lanuginosus*, and *Bacillus subtilis* (Kaasgaard 2008). Enzymatic bleach removal was first launched in the 1980s

Table 1 Examples of application of catalases

Enzyme	Organism	Application	Reference
rhCat	Human	Immunomodulatory effect	(Shi et al. 2013a)
PEG-rhCat	Human	Quenching infection-induced reactive oxygen species caused by H1N1 infection	(Shi et al. 2013b)
Cat	Bovine liver	Wound healing	(Abdel-Mageed et al. 2012)
HPI	<i>Escherichia coli</i>	Enzymatic polymerization	(Di Gennaro et al. 2014)
CATPO	<i>Scytalidium thermophilum</i>	Altering antioxidant properties	(Koclar Avci et al. 2013)
KatG	<i>Bacillus pumilis</i>	Oxidation of beta-lactams to their sulfoxides	(Sangar et al. 2012)
KatG	<i>Bacillus</i> SF	Hydrogen peroxide removal from textile-bleaching effluents	(Fruhwrth et al. 2002)
Cat	Bovine liver	Hydrogen peroxide determination	(Shamsipur et al. 2012)
Cat	Bovine liver	Ca ²⁺ ions for application in milk and dairy products	(Akyilmaz and Kozgus 2009)
Cat	Bovine liver	Forchlorfenuron (CPPU) detection	(Xu et al. 2015)
Cat	N/A	Construction of micromotors	(Simmchen et al. 2014).
Cat	Bovine liver	Immobilization on Eupergit C	(Alptekin et al. 2010)
Cat	<i>Aspergillus niger</i>	Immobilization on new supports	(Bayramoglu et al. 2011)
Cat	N/A	Artificial enzyme-powered microfish	(Orozco et al. 2012)
Cat	Bovine liver	Infected milk detection	(Fütő et al. 2012)
Cat	<i>Escherichia coli</i>	Biocorrosion prevention	(Baeza et al. 2013)
TfuCat	<i>Thermobifida fusca</i>	Textile bleaching/catechol oxidation	(Loncar and Fraaije 2014)

(Blackburn 2009). Use of catalase reduces the water consumption and waste of energy by half, and costs of chemicals up to 83 %, and saves 33 % of time required for completion of process (Blackburn 2009).

It is worth noting that, while catalases are robust and catalytically potent, each catalase has its specific enzymatic properties. Therefore, careful selection of a proper catalase for a particular application is important. For example, catalase from *Micrococcus* displays a relatively low K_m (150 mM) which is good for removal of low levels of hydrogen peroxide. Yet, it suffers from quick inactivation by high levels of substrate (Switala and Loewen 2002). Catalases from *Aspergillus* species typically exhibit relatively high K_m values (~500 mM) that can be used for treatment of solutions with high levels of hydrogen peroxide while having a higher tolerance to inactivation by high levels of hydrogen peroxide (Switala and Loewen 2002). As textile and wood bleaching is taking place at pH 5 to 10, with a working temperature range from 30 to 80 °C and peroxide concentrations from 0.002 to 0.1 %, it may be necessary to use different catalase preparations in several steps if complete removal of peroxide is to be achieved.

Different approaches are still being investigated for bleach cleanup. Enzyme immobilization is one of the first methods to be employed for reducing cost of enzymes as it allows its reuse. An additional advantages achieved by enzyme immobilization is stabilization of enzymes toward inhibitors, organic solvents, and/or thermal damage. An often observed disadvantage of immobilization is an increase in the K_m value due to diffusion limitations. Standard ways of immobilization are

adsorption, entrapment, or covalent attachment to a solid support. Immobilized catalase-peroxidase from *Bacillus* SF has been produced on a large scale and used for treatment of textile-bleaching effluents, where removal of hydrogen peroxide is a prerequisite for the reuse of process water in the dyeing process (Fruhwrth et al. 2002). Recent examples includes microbeads modified with poly(styrene-*d*-glycidylmethacrylate) and tetraethyldiethylenetriamine (Bayramoglu et al. 2011) and immobilization on Eupergit C (Alptekin et al. 2010).

Catalases in medical applications: H1N1 influenza treatment and wound healing

Reactive oxygen species (ROS) are considered to be responsible for induction of lung damage upon pneumonia. Reduction of acute oxidative injury in lung tissue has been demonstrated after administration of recombinant human catalase (Shi et al. 2010). After showing the immunomodulatory effect of recombinant human catalase on H1N1 virus infection (Shi et al. 2013a), it was also demonstrated that by PEGylation of human recombinant catalase, the stability and effectiveness of the catalase-based new agent for fighting H1N1 pneumonia were improved (Shi et al. 2013b).

Non-ionic sugar ester nanovesicles are used as a biocompatible material for encapsulation of catalase (Abdel-Mageed et al. 2012). This approach of encapsulation makes catalase more stable at acidic pH and protects catalase from trypsin digestion. Such formulation of catalase is important for topical administration aiming at faster wound healing and has been

demonstrated by an *in vivo* study which was carried out on rats (Abdel-Mageed et al. 2012).

Catalases in biosensors

The biosensor field is one of the most advanced areas of enzyme application where the choice of enzyme and a vast array of synthetic semiconducting materials provide endless possibilities. The common principle of enzyme-based biosensors is the use of a redox enzyme and the transformation of the respective substrate(s) to generate a signal. Numerous examples are presented in literature regarding catalase-based biosensors (Shamsipur et al. 2012). Several catalase-based biosensors for detection of hydrogen peroxide have been described in the literature, often with catalase immobilized and in contact with a Clark-type oxygen electrode. Depending on the construction and choice of the used enzyme, different sensitivities have been demonstrated. As an example, spoiled milk can be detected via an increased hydrogen peroxide content. Such increased level of hydrogen peroxide can be measured using biosensors in which catalase is immobilized on the surface of a thin-layer enzyme cell and used with flow injection analysis technique (Fűtő et al. 2012).

Another approach for the use of catalases in biosensors is to monitor the effect of inhibitors or activators on catalase activity and to determine their concentration indirectly. Two illustrative examples concern the determination of calcium ions in milk and the quantification of a plant growth hormone in fruits. The effect of calcium ions on catalase was exploited in such a biosensor construction that resulted in a linear response in the range of 1–10 mM Ca^{2+} ions. Such biosensor can find application in milk and dairy product control (Akyilmaz and Kozgus 2009). 1-(2-Chloropyridin-4-yl)-3-phenylurea (forchlorfenuron or CPPU) is a plant growth hormone used widely for fruit production. CPPU is a non-competitive inhibitor for catalase which makes it possible to be detected by yet another type of biosensor (Xu et al. 2015). In this case, catalase was immobilized on boron nitride sheets dispersed in chitosan. The presence of CPPU in a hydrogen peroxide solution reduces catalase activity giving a reduced current response which makes it possible to determine CPPU in the range of 0.5–10.0 μM with a detection limit of 0.07 μM . The CPPU-detecting biosensor is stable and has been successfully used for CPPU determination in fruit samples (Xu et al. 2015).

Corrosion and micromotors

Microbiologically triggered corrosion is responsible for a large portion of the corrosion on engineering machines as biofilm formation alters the electrochemical conditions on the metal/solution interphase (Little and Lee 2014). Stainless steel is used for a wide range of industries ranging from food

industry to sewage tanks, all due to its strengths and resistance to corrosion. However, it is prone to microbial corrosion. The mechanism of *Escherichia coli* mediated corrosion is explained by catalase activity which generates oxygen upon degradation of hydrogen peroxide. The *in situ* generated dioxygen is reduced on the stainless steel surface giving as a product another hydrogen peroxide molecule causing an overall increase in cathodic current (Busalmen et al. 2002). In a recent study, bacterial cultures of *E. coli* and a catalase-deficient *E. coli* strain were used for immersion of stainless steel (Baeza et al. 2013). This demonstrated the inability of the latter cells to cause corrosion and indicates that catalases are an interesting target for corrosion prevention strategies.

A novel use of catalase is the construction of artificial enzyme-powered microfishes which are solely based on catalase activity and used for toxicity testing of water samples by visual inspection (Orozco et al. 2012). Propulsion of these artificial biocatalytic microswimmers is dependent on the presence of pollutants which affect catalase activity. Inspecting this device allows quantitative measurements in terms of common ecotoxicological parameters like EC_{50} (Orozco et al. 2012). Artificial microfishes as detecting devices may avoid the use of live fish. Enzyme-based micropulsion is being further investigated for construction of more robust micromotors (Simmchen et al. 2014). Most of the enzyme-based micromotors use catalase, and the main limitation so far has been the sensitivity to high peroxide concentrations causing inactivation. Current efforts are put into solving this issue by immobilizing the enzyme before grafting it on motor particles (Simmchen et al. 2014).

Exploitation of (per)oxidase activity of heme-containing catalases

Additional functions of catalases have been explored including oxidase and peroxidase activities (Koclar Avci et al. 2013; Loncar and Fraaije 2014; Vetrano et al. 2005). It is suggested that these reaction types catalyzed by these hemoproteins are dependent on whether a substrate can reach the active site, but the exact mechanisms are yet to be elucidated. It is tempting to consider exploitation of the peroxidase activity of catalases. Peroxidases are in focus of research aiming at their application in a wide range of applications, and the drawbacks of their typical low pH optimum and poor stability are yet to be overcome. Problematic recombinant peroxidase production is an additional drawback in the large-scale application of these enzymes.

The recently uncovered peroxidase activity of a thermostable catalase from the bacterium *Thermobifida fusca* (*TfuCat*) may open new avenues for catalase-based applications (Loncar and Fraaije 2014). *Thermobifida fusca* is a mesothermophilic organism able to use plant cell wall and

other organics as carbon source, and it represents a useful resource of genes coding for promising industrial enzymes (van Bloois et al. 2010). It was found that *TfuCat* exhibits significant peroxidase activity toward small phenols at alkaline pH. Its narrow substrate scope is in contrast to what is observed for peroxidases, and enzyme redesign is needed if one is to pursue the idea of expanding its substrate scope. What may make worth putting efforts in this is the ease of expressing *TfuCat*. Using *E. coli* as heterologous expression host, 400 mg of enzyme could be easily obtained from 1 L of culture broth. *TfuCat* was also shown to be a highly robust biocatalyst as evidenced by its tolerance toward solvents and high temperatures. While recent research has revealed that catalases may also be exploited as (per)oxidase, the full potential of catalases as peroxidase biocatalysts has still to be established.

Synthetic applications of catalases: polymers and pharmaceuticals

Chemical synthesis nowadays is also considering the use of enzymes as catalytic tools. These so-called biocatalysts can often replace time-consuming and laborious steps in synthesis. Enzymes can circumvent problematic reaction steps under mild conditions while they are often highly chemo-, regio-, or enantio-selective. Since enantio-pure building blocks are often required for synthesis of pharmaceuticals, the use of enzymatic catalysts is increasing. Also, the use of catalases in polymer production is an area of interest.

The catalase-peroxidase HPI from *E. coli* is one of the most known members of the group of catalase-peroxidases and has also been well characterized (Kudalkar et al. 2012; Njuma et al. 2014). The crystal structure of this tetrameric enzyme has been published (Carpena et al. 2004). Compound I formed upon interaction of enzyme with hydrogen peroxide can react with phenols or anilines to facilitate one-electron reduction releasing phenolic or anilic radicals. Such radicals can initiate polymerization reactions. HPI has been successfully used for the enzymatic polymerization of simple phenols to produce oligomers (Di Gennaro et al. 2014). Phenol, methoxyphenol, catechol, and aniline have been tested for oligomer synthesis. Size-exclusion chromatography confirmed the oligomeric nature of the formed products and revealed that the oligomer length depends on the type of aromatic substrate. For phenol and 3-methoxycatechol, up to 27- and 23-monomeric unit oligomers were formed, while for catechol, mainly the 7-unit oligomer was formed. In case of aniline, two populations of products were detected, 4- and 10-unit polymers (Di Gennaro et al. 2014). Several of the products were the same as when the reaction was performed with horseradish peroxidase (HRP). HRP is known as a very active peroxidase, but significant efforts have been put into its replacement due to the high cost of the enzyme. Horseradish is a seasonal plant and HRP

isolation involves a complicated purification procedure. Furthermore, recombinant production of HRP has been proven to be very difficult. HPI can, at least in this application, serve as a valid substitute.

Catalase can also serve as catalyst to dismutate residual hydrogen peroxide after a peroxide-triggered polymerization reaction. For example, the typical polymerization reaction that leads to polyacrylates involves the use of hydrogen peroxide. Residual hydrogen peroxide after the polymerization has to be destroyed as it can compromise long-term storage of polyacrylate preparations or interfere with formulations in which polyacrylates are used. As these reactions are carried out at low pH, catalase is needed that can work efficiently under acidic conditions.

Preparation of (*R*)-sulfoxides of β -lactams is currently performed using a multi-step procedure that is quite laborious. These enantiopure chemicals are needed for testing biological activities of β -lactam derivatives where biological activity strongly correlates with the oxidation state of the sulfur in the lactam ring (Sangar et al. 2012). Another distinct catalase-peroxidase (KatG) originating from *B. pumilis* is an interesting representative of the catalase-peroxidases as it is monomeric in contrast to tetrameric HPI from *E. coli* and dimeric KatG from *Mycobacterium tuberculosis* (Kudalkar et al. 2012; Njuma et al. 2014). KatG from *B. pumilis* is able to convert β -lactams to their respective (*R*)-sulfoxides presenting the first report of the production of penicillin G (*R*)-sulfoxide (Sangar et al. 2012).

Food biotechnology: altering antioxidants by using catalases

The use of catalase in food has been approved by the FDA, and there are many patents that describe the use of catalase in food applications. A common application is the use of catalase in combination with an oxidase, e.g. glucose oxidase, which will scavenge molecular oxygen, thereby preventing oxidation and deterioration of food. Catalases may also have a future in food biotechnology due to their (per)oxidase activity.

Phenolic secondary metabolites serve various physiological roles, ranging from being antioxidants, pro-oxidants, and signal transduction molecules (Maqsood et al. 2014; Perron and Brumaghim 2009). Significant attention has focused on their exploitation in human consumption as part of diet or supplements. The catalase from *Scytalidium thermophilum* exhibits also phenol oxidase activity, and hence, it has been named catalase-phenol oxidase (CATPO) (Koclar Avci et al. 2013). CATPO shows activity toward phenolic compounds, and particularly (+)-catechin, catechol, caffeic acid, and chlorogenic acid are good substrates. Analysis of the formed products revealed the formation of dimers of both hydrophilic and hydrophobic dehydrocatechins, but also oligomers are formed including trimer and tetramer of (+)-catechin. Dimers and other oligomers of catechol, caffeicin-like dimers of

caffeic acid, and a dimer of chlorogenic acid could be produced using this fungal catalase as well. These results lead to the conclusion that CATPO prefers ortho-diphenolics and it also shows stereoselectivity in the oxidation of (+)-catechin. CATPO may be developed as a valuable biocatalytic tool for food and biotechnological applications aiming at altering the antioxidant potential of aromatic compounds or products that are rich in such compounds.

Enzyme improvement through rational redesign

Recent advances in enzyme engineering will facilitate effective redesign of catalases in order to tune their properties. One example of successful rational design of a catalase is the 5-fold improvement of catalytic efficiency of *B. subtilis* catalase by a single mutation (Cao et al. 2014). Improvement of 2.5-fold of the ratio in catalase/peroxidase activity has been achieved for *Thermobifida fusca* catalase by replacing a valine residue, resulting in a less constrained main substrate channel (Loncar and Fraaije 2014).

Future perspectives

Effort that has been put into research on the exploitation of catalases has shown that potential applications extend much further than just bleach removal in the textile industry. Depending on their specific use, different demands have to be fulfilled, and it is expected that more work will be put into stabilization of catalases either for longer shelf life or for enhanced process stability. Additives such as propan-1,2,3-triol and sucrose have stabilizing effects on catalases even at elevated temperatures (Cantemir et al. 2013). On the other hand, efficient improvement of process stability can also be achieved through immobilization, and similar to biosensor construction, a vast array of new materials is being investigated to broaden the applicability of catalases.

Monofunctional catalases are exploited in canonical catalase applications, the degradation of hydrogen peroxide. A novel approach to exploit the hallmark activity of catalases is the use of catalase in artificial microfishes. The limited substrate scope of catalases acting as peroxidases can still be used in synthetic chemistry if one is to explore domino reactions. Enzymatic oxidation of catechol to the corresponding o-benzoquinone and subsequent intermolecular 1,4-addition with a thiol as a nucleophile have been described recently (Abdel-Mohsen et al. 2014). Catalase-peroxidases allow a broader use in the sense of a larger number of chemical reactions where they can be used. In fact, catalase-peroxidases overlap significantly with classical peroxidases, and it is reasonable to expect that this class of catalases will receive more attention in the future as biocatalysts.

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