POLYMER ATTACHED COBALT-PHTHALOCYANINES AS CATALYSTS IN THE AUTOXIDATION OF THIOLS

PROEFSCHRIFT

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CHAPTER 1

INTRODUCTION

1.1 Multifunctional catalysts and the application of polymers in catalysis

In recent years an increasing effort has been devoted to the design of multifunctional catalysts. Apparently, this interest has been stimulated by the fact that multifunctionality is one of the most important characteristics of enzymes, the catalysts in biological systems. Synthetic model systems are investigated to elucidate the factors governing the efficient cooperation between different catalytic groups in enzymatic catalysis. Polymers may be advantageously applied for the development of model systems for enzymes and of new multifunctional catalysts for complex reactions. The physical and chemical properties of polymers may be varied to a large extent and, therefore, tailormade polymers may be designed to hold a desired combination of catalytic sites.

This thesis deals with an investigation on multifunctional polymeric catalysts for the autoxidation of thiols. It is well established, that an efficient catalyst for this autoxidation should possess oxidation sites and basic sites in cooperative interaction. Such a bifunctional catalytic system can be obtained by attachment of an oxidation catalyst (in our case a cobaltphthalocyanine) to a polymer with incorporated basic groups (see [1]).

The development of specifically functionalized polymers recieves currently the attention of chemists in a variety of fields [2-11]. Biologically active molecules, such as drugs [11], hormones [12] and enzymes [4, 6, 7] have been attached to polymers for a number of uses. Functionalized resins have found applications, for example as insolubilized chelating resins [10, 13], supports for
Fig. 1. Various applications of polymers in catalysis (a) solid polymeric support, (b) weakly crosslinked polymer, (c) non-crosslinked polymer, and (d) non-crosslinked polymer fixed on a solid support (* = catalytic site).

organic syntheses [2, 8], ion exchangers [14] and as beads for various chromatography purposes [5, 6, 9, 14]. Solid highly crosslinked polymers may also act as carriers of catalytically active species (see Fig. 1a). Several investigations have indicated that just as in case of catalysts supported on inorganic oxides the behavior of the catalytically active sites is often influenced by the polymeric support [3, 4]. Swellable weakly crosslinked polymers have also been applied as carriers for catalytically active species (Fig. 1b). This approach is characterized by the possibility for large diffusional limitations of the reaction rate and the small influence of the macromolecule on the rate due to limited chain mobility [15].

More interesting from a mechanistic point of view is the application of soluble (non-crosslinked) polymers in catalysis [16, 17] (Fig. 1c). Several soluble (co)polymers have shown remarkable high activities due to specific effects of the macromolecular chain itself. Overberger and his coworkers, who investigated the hydrolytic activity of vinyl (co)polymers containing imidazole have been responsible for a large number of contributions in this field [17, 18]. It is often claimed that the study of this type of polymeric catalysts offers the opportunity for better understanding of the unique role of enzymes [4, 16, 17].
However, it must be stressed that enzymes always seem to have a single active site per subunit, whereas in contrast the synthetic polymers often possess very large numbers of active sites per chain. Furthermore, the models mostly have statistically defined active sites, while the enzyme active site is accurately defined by nature.

Particularly interesting is the homogeneous catalysis by metal ions and metal complexes which are attached to macromolecules [16]. In this case the polymer does not serve solely as an inert carrier but the polymer chain influences the behaviour of the catalytic sites. Owing to the ligand being macromolecular, the local volume in the vicinity of the metal species may possess physical-chemical properties differing from the solvent. The study of the catalytic behaviour of polymer/metal complexes is therefore of interest for developing new types of catalysts, and furthermore it may give the opportunity for elucidating the role of metal ions in the active centres of metallo-proteins.

For example, heme (Fe-protoporphyrin IX) modified with short peptide chains and coupled to poly(oxoethylene) was proven to be a fairly acceptable model system for the naturally occurring oxygen carriers myoglobin and hemoglobin [19]. In this model system the shielding effect exerted by the polymer prevents the dimerization and thus irreversible oxidation of the iron (II)-porphyrin. In recent years, new efficient homogeneous polymeric catalysts have been obtained for instance for hydroformylation [20], hydrogenation [21, 22], thiol oxidation [23], peroxide decomposition [24], polymerization [25] and oxidative coupling of phenols [26]. Evidently, the cited papers reveal that increase of activity by binding of active sites to polymers is not only a privilege of proteins, but may also be achieved with many synthetic polymers.

The solubility in the reaction medium seriously reduces the practical applicability of the catalytic systems consisting of linear (non-crosslinked) polymers with attached catalytic sites (Fig. 1c). In order to avoid this problem it was proposed [15, 27] to immobilize the soluble
polymeric catalyst onto a solid polymeric or other support. This new approach (see Fig. 1d) is still practically unexplored, but it is evident that this fixation of soluble polymeric catalysts shows many similarities with the immobilization of enzymes. In both cases the attachment of the macromolecular chain to the carrier should not cause any changes in the micro-environment of the active site(s). It may be expected that immobilization of a polymeric catalyst via terminal monomeric units will offer the best results and such a system may for instance be obtained by graft copolymerization onto or from the support.

1.2 Catalytic oxidation of thiols: nerox sweetening

Contamination of hydrocarbons with thiols (formerly called mercaptans) is a prevailing problem in the industry [28-32]. Thiols are frequently present in LPG and natural gases, such as methane and ethane. They are invariably present in hydrocarbon distillates including kerosene and fuel oil. The presence of thiols is objectionable because of their unpleasant odour, corrosive properties, deleterious effect on stability of oil products and their poisoning of metal catalysts (i.e. especially for hydroformylation). Furthermore, when oil products containing thiols are combusted undesirable atmospheric contaminants in the form of sulphur-oxides are generated. There are several treating methods available in the refining industry for rendering thiols harmless; a very effective one is the UOP Nerox process [28, 31]. This process uses a catalyst, preferably a cobalt chelate supported on an activated carbon, to oxidize thiols to disulphides, at ambient temperature or slightly above, in the presence of oxygen and caustic (eq. (1)). Disulphides are lower in volatility than thiols and are inert.

\[ 4 \text{RSH} + O_2 \xrightarrow{\text{catalyst}} 2 \text{RSSR} + 2 \text{H}_2\text{O} \quad (1) \]
Scheme I. UOP Merox Process. Extraction and sweetening of a sour gasoline is used here as a non-limiting example of a commercially operating unit.

The Merox process (see scheme I, [29]) can perform the dual function of extracting easily removable mercaptans and thereafter converting the remaining part to disulphides. Either of these functions can also be carried out independently when desired (section 1 and 2 in scheme I). Desulphurization is accomplished by extraction of thiols with aqueous NaOH solution, however, desulphurization by the Merox process is limited to light hydrocarbon fractions containing soluble thiols (i.e. predominantly C_1–C_3 thiols). Merox catalyst does not improve thiol extraction, but rather is applied to regenerate the NaOH solution for reuse. For higher boiling fractions (for instance: heavy naphtha and kerosine) with low thiol content, Merox treatment is effected without desulphurization; that is, thiols are simply oxidized to disulphides which remain in the final product.
It is estimated that more than 1000 Marox units in the world are in operation treating a total amount exceeding 9 million barrels per standard day [29]. Because of the worldwide interest which was shown in this process there are continuing attempts to improve and simplify the treatment. Interest in the oxidation of thiols is also implemented by the biological importance of sulphhydryl-groups and the role of disulphide-linkages in enzymes [33]. A further reason for studying the behaviour of thiols is inspired by the protective action against radiation damage of some low molecular weight thiols [34].

1.3 Aim and outline of this thesis

It was our aim to prepare an active and stable catalyst for the autoxidation of thiols to disulphides (eq. (1)). It is evident (see [22]) that efficient oxidation needs operation in the presence of base, because the thiolate anion is the species sensitive to oxidation. The present thesis mainly deals with an investigation of the most promising bifunctional catalytic system (see [1]) consisting of poly(vinylamine) -instead of the conventionally applied alkaline base - and a cobaltphthalocyanine (CoPc). The polymeric base may function both as carrier of the oxidation sites and as supplier of basic groups. Furthermore, in aqueous solution the (soluble) polymer may counteract the inherent tendency to dimerize of water-soluble CoPc (i.e. deactivation) by shielding the cobalt moieties from each other (see also [35]).

In chapter 2 the preparation and characterization of this bifunctional catalyst is described and two different methods for coupling CoPc to the polymer are presented. It is demonstrated that addition of small amounts of NaOH markedly reduces the loss of activity in successive runs while the high activity of the catalytic system is not substantially affected. Apparently, the addition of NaOH prohibits the accumulation of the intermediate oxidation
product $H_2O_2$.

In chapter 3 it is shown that in case accumulation of $H_2O_2$ does occur, sulphur-containing oxo-acids are formed due to non-selective oxidation of thiol by $H_2O_2$. It is proven that these acidic by-products are responsible for the observed deactivation by poisoning the essential basic sites of the catalyst. Since peroxide-induced deactivation can only be avoided by instantaneously removal of the produced $H_2O_2$ from the reaction system, it was investigated whether catalysts for the decomposition of $H_2O_2$ could be applied in combination with the bifunctional thiol oxidation catalyst (see chapter 4).

Chapter 5 deals with medium effects on the catalytic oxidation of thiols. It will be shown that although the presence of some $H_2O$ appears to be essential, the bifunctional catalyst can also be applied in predominantly polar media. The remarkable results of activity measurements in alkaline (polymer-free) CoFc solution containing varying amounts of electrolytes and alcohols are presented and discussed.

In chapter 6 it will be shown that the isolation of cobalt centres in the bifunctional catalyst (i.e. prevention of inactivation due to dimerization reactions) and the catalytic activity are related. A statistical calculation of the distribution of cobalt sites over the PVAm coils is presented and this calculation will be used to explain the observed influence of the number average degree of polymerization ($P_n$) of the applied polymer sample on the catalytic activity.

Because its solubility in the mostly applied reaction medium (i.e. water) seriously reduces the applicability of the PVAm/CoFc catalyst, an investigation was started to immobilize the polymeric catalyst on a solid support (see Fig. 1d). In chapter 7 the preparation and testing of PVAm/CoFc attached to (especially prepared) macroporous styrene-dimethylbenzene copolymers is described and discussed.

In chapter 8 a short final discussion concerning some important results of this investigation is given.
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CHAPTER 2

AUTOXIDATION OF THIOLS PROMOTED BY A BIFUNCTIONAL CATALYST
PREPARED BY POLYMER ATTACHMENT OF A COBALTPHTHALOCYANINE

2.1 Introduction

It is well established [1], that the catalytic autoxidation of thiols (RSH) is appreciably accelerated by addition of a base, the generated thiolate anion (RS⁻) being the species susceptible to reaction with oxygen.

\[
\begin{align*}
2\text{RSH} + 2\text{OH}^- & \xrightarrow{\text{catalyst}} 2\text{RS}^- + 2\text{H}_2\text{O} \\
2\text{RS}^- + 2\text{H}_2\text{O} + \text{O}_2 & \xrightarrow{\text{catalyst}} \text{RSSR} + 2\text{H}_2\text{O}_2 + 2\text{OH}^- 
\end{align*}
\]  

(1) (2)

Metal ions [2, 3] and metal complexes [4, 5] can be used as catalysts in this oxidation. A class of highly active catalysts is formed by transition metal phthalocyanine compounds [6]. Because of this high activity, metallophthalocyanines have also industrial application as catalysts in sweetening processes [7, 8].

Recently it was shown [9], that a particularly active catalytic system could be obtained using a polymeric base - instead of alkaline hydroxide - in combination with cobalt(II)-tetrasulphophthalocyanine (CoPc(\text{SO}_3\text{Na})_4) as oxidation catalyst. This bifunctional catalytic system was found to consist of a complex between the polymeric carrier and the cobaltphthalocyanine (CoPc).

While the activity of this bifunctional catalyst in aqueous media was appreciably higher than the activity of the conventional CoPc/NaOH system (a factor of about 50), a disadvantage of the polymeric system was the loss of activity observed in successive runs. This deactivation was ascribed to strong sulphur-containing oxo-acids, generated in traces during the reaction, which poison the basic groups
of the polymer. It was expected, that the formation of these strong acids could be avoided by employment of small amounts of alkaline hydroxide. However, when adding NaOH to the polymeric catalyst a dramatic deactivation was found, due to rupture of the polymer/CoPc(SO₃Na)₄ complex.

Based on these observations we started an attempt to prepare a catalyst with enhanced stability in the presence of small amounts of NaOH. Improvement of the catalyst was attempted along two routes. Firstly, poly(vinylamine) was used as the polymeric amine carrier, having stronger complexing abilities than the polymer previously used, i.e. poly(arylamide) with incorporated amine groups. A further improvement was aimed at linking the CoPc to the polymer via a covalent bond between the phthalocyanine ring substituents and the amine groups of the polymeric carrier. For instance a peptide linkage can be formed by using the tetracarboxy substituted cobaltphthalocyanine (CoPc(COOH)₄).

The effect of these modifications on the stability of the resulting catalysts in aqueous media is reported in this chapter.

2.2 Experimental

Poly(vinylamine-hydrochloride) (PVAm-HCl)

PVAm-HCl was obtained from poly(N-vinyl-tert-butyl-carbamate), PVCa, by hydrolysis in 10N hydrochloric acid/ethanol solution (1:1, v/v) [10]. PVCa was prepared from the corresponding monomer under nitrogen in benzene with 2,2'-Azobisisobutyronitrile, AIBN, as initiator (reaction time: 48 h, T = 60°C). PVCa with different average molecular weights were obtained by varying the amount of AIBN. Number average molecular weights - from viscosity measurements in toluene at 25°C, calculated with data of Bloys van Treslong [10] - were in the range 3.8·10⁴ ≤ Mₙ ≤ 14.4·10⁴. Anal. PVAm-HCl·xH₂O (24 hrs. dried at 30°C and 1 mm Hg). Found: C 28.14, H 7.71, N 16.40; C/N (atomic ratio) 2.00. Calcd. for PVAm-HCl·0.3H₂O: C 28.28, H 7.83,
N 16.50 %; C/N (atomic ratio) 2.00. Hughes et al. [11] report PVAm-HCl·0.5H₂O as product. The IR-spectrum of PVAm-HCl is in accordance with the data in the literature [11, 12].

**Polyvinylamine (PVAm)**

An aqueous solution (2-3 %) of PVAm-HCl was passed through an ion-exchange column (Amberlite IRA 410 in OH⁻ form), thereafter the column was rinsed with water. The effluent collected from the column was concentrated to about 5 % under reduced pressure; PVAm could be obtained by precipitation of the resultant solution in acetone p.a. [12]. All PVAm-solutions were kept continuously under nitrogen to prevent absorption of carbon dioxide. Calculated molecular weights (see [10]) from viscosity measurements in water with 0.01 N NaOH and 0.1 N NaCl at 25°C were in the range 1.5·10⁴ < Mn < 6·10⁴. The IR-spectrum of PVAm is in accordance with the data in the literature [12].

**Cobalt(II)-tetraacarboxyphthalocyanine (CoPe(COOH)₄)**

Prepared with trimellitic acid (1, 2, 4-tricarboxy-benzene) as starting-material by analogy with the method given by Weber and Bush [13]. The crude reaction product was purified by dissolving it in 0.1 N NaOH and subsequent precipitation in ethanol p.a. The precipitate was isolated with the aid of a centrifuge and washed four times with ethanol p.a. The obtained product is (somewhat impure) cobalt(II)-tetraamidophthalocyanine (CoPe(CNH₂)₄). Anal. Found: C 55.56, N 20.73, Co 7.4; atomic ratios: C/N = 3.13, N/Co = 11.8. Calcd. for CoPe(CNH₂)₄: C 58.14, N 22.61, Co 7.9 %; atomic ratios: C/N = 3.00, N/Co = 12.0.

Characterisation by IR, see Fig. 1a.

Conversion into the desired tetracarboxy-compound was carried out by boiling in 50 % KOH (8-10 h) and subsequent precipitation with concentrated HCl according to the method given by Boston and Bilal [14]. After purification by washing twice with 0.1 N HCl and once with, successively, acetone and ether, the product was dried during 24 h (100°C,
Fig. 1. IR absorption spectra of substituted cobalt(II)-phthalocyanines: (a) CoPc(COONa)$_4$, (b) CoPc(COOH)$_4$, and (c) CoPc(COONa)$_4$. 
1 mm Hg). Anal. Found: C 52.62, H 2.67, N 13.75, Co 6.74;
C/N (atomic ratio) 4.47. Calcd. for CoPc(COOH)$_4$·4H$_2$O: C
52.76, H 2.95, N 13.68, Co 6.79 %; C/N (atomic ratio) 4.50.
IR-spectrum (Fig. 1b): 3400 cm$^{-1}$ (b) (H$_2$O); 3000-2500 cm$^{-1}$
(b) (COOH); 1720 (sh), 1705 (s), and 1685 cm$^{-1}$ (s) (COOH);
1330 (s), 1085 (s), 910 (w), 775 (m) and 735 cm$^{-1}$ (s)
(characteristic CoPc-peaks). UV-spectrum: 671 nm (log ε =
4.88), 620 nm (sh) and 328 nm (log ε = 4.77). CoPc(COOH)$_4$
is insoluble in water, soluble in DMF and THF.

Tetrasodiumsalt of Cobalt(II)-tetracarboxyphtalocyanine
(CoPc(COONa)$_4$)

CoPc(COOH)$_4$ was dissolved in 0.1 N NaOH and the resulting
tetrasodiumsalt precipitated with ethanol p.a. The precipi-
tate was collected with the aid of a centrifuge and washed
with ethanol and aceton and finally dried during 24 h (100°C,
1 mm Hg). Anal. Found: C 43.83, H 2.96, N 11.43, Co 5.74;
C/N (atomic ratio) 4.47. Calcd. for CoPc(COONa)$_4$·4H$_2$O: C
44.13, H 2.88, N 11.44, Co 6.02 %; C/N (atomic ratio:
4.50). IR-spectrum (Fig. 1c): 3400 cm$^{-1}$ (b) (H$_2$O); 1610 (s),
1560 (s), and 1375 cm$^{-1}$ (s) (COO$^-$); 1325 (s), 1085 (m),
785 (m) and 735 cm$^{-1}$ (s) (characteristic CoPc-peaks).

Tetrasodiumsalt of Cobalt(II)-tetrathionolphthaloxyanine
(CoPc(SO$_4$Na)$_4$)

The preparation of this compound was as described in
a previous paper [9].

Coupling of CoPc and PVAm

a. Coupling by complexation. Prior to the addition of
thiol, aqueous solutions of PVAm and CoPc were brought
together in the reaction vessel in which the catalytic
activity measurements were performed. Generally, a complexing
time of 40 min was applied before the substrate 2-mercapto-
ethanol was added.

b. Covalent coupling. Covalent polymer attachment was
achieved by a carbodiimide-promoted condensation reaction
[15, 16]. A typical coupling experiment was performed in
the following way: 0.9 mg (1.1 µmol) CoPc(COOH)$_4$ and 6.5 mg (32 µmol) dicyclohexyl-carbodiimide (DCCI) were, successively, added to 300 mg PVAm-HCl suspended in 15 ml THF (p.m., dried before use on CaH$_2$). After stirring the reaction mixture for about 48 h at ambient temperature, the coupling product was collected by means of centrifugation. The solid product was extracted extensively with DMF until a colourless wash liquid resulted, whereupon three extractions with THF were carried out. In this way 295 mg of a blue coloured product could be obtained.

HCl was removed from the product as described previously for unmodified PVAm-HCl. The amount of HCl-free coupling product so obtained was 140 mg. Cobalt-content was 0.0129 %, i.e. 28 % of the introduced CoPc has been attached to the polymer. The IR-spectrum of the coupling product is identical with that of unmodified PVAm [12]. The same experiment in THF without DCCI resulted in a colourless product (after extraction with DMF and THF); no coupling was achieved under these conditions.

Activity measurements

Activity measurements were carried out in an all-glass, thermostated (T = 23°C), double-walled Warburg apparatus provided with a mechanical (glass-)stirrer. The rate of oxidation was determined by measuring the rate of consumption of the first 20 ml of oxygen at constant oxygen pressure ($p(O_2) = 1$ atm) and a constant stirring speed ($v = 3000$ r.p.m.). Because of this high stirring speed, no oxygen transport limitations were observed. Water was used as the solvent; total reaction volume was 75 ml. The amount of catalyst was chosen in such a way that an appropriate rate of oxygen consumption resulted (0.5 - 10.0 ml/min). The substrate, 2-mercaptoethanol (Merck) was distilled before use and kept under nitrogen. Accumulated H$_2$O$_2$ was analyzed spectrophotometrically using TiCl$_3$-H$_2$O$_2$ as reagent [17]. The data reported in this chapter were obtained using a PVAm sample with a number average molecular weight, $M_n = 21000$.  

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**Instrumentation**

IR-spectra were recorded on Hitachi EPI G and Grubbs-Parson IR-spectrophotometers using KBr-pellets. Optical spectra were measured with a Unicam SP 800 spectrophotometer. ESR-spectra were recorded on a Varian E-15 ESR-spectrometer with E-101 microwave bridge (X-band) and a V-4540 variable temperature controller. A Hewlett Packard (Model 185) apparatus has been used for C, H, N analysis (in duplo). Co-contents were determined in duplo by means of neutron activation analysis using a Ge(Li)-semiconductor detector. Viscosity measurements were carried out with a Hewlett Packard automatic solution viscometer of the Ubbelohde type.

### 2.3 Results

#### 2.3.1 Characterization of the catalysts

Geaard et al. [18] suggest that the ammonium salt of the tetracarboxyphthalocyanine can be obtained using trimesitic acid as the starting material. Our findings are at variance with this suggestion, as the product composition could not be modified by treatment with strong acid. In addition the IR-spectrum of the product (see Fig. 1a) shows specific amide-bands (1660, 1620 and 1580 cm\(^{-1}\)) and lacks bands in the 1675-1750 cm\(^{-1}\) region characteristic of aromatic carboxy-groups [14]. These results and the elemental analysis of the product (see Experimental) give strong indication that in fact the obtained product is cobalt(II)-tetaamidophthalocyanine (CoPc(CONH\(_2\))\(_4\)).

The desired CoPc(COOH)\(_4\) could be obtained by hydrolysis of CoPc(CONH\(_2\))\(_4\) in 50 % KOH [14]. The IR-spectrum of CoPc(COOH)\(_4\) (see Fig. 1b) reveals bands characteristic of aromatic carboxy-groups (1720, 1705 and 1685 cm\(^{-1}\)). CoPc(COOH)\(_4\) was prepared in a simple way by dissolving the CoPc(COOH)\(_4\) in 0.1 N NaOH followed by precipitation in ethanol. The IR-spectrum of the tetrasodiumsalt is shown in
Fig. 2. Polymer attachment of tetracarboxy cobaltphthalocyanine: (a) by complexation (catalyst I), (b) by formation of a peptide linkage (catalyst II).
Fig. 1c.

As reported in the experimental part two different types of catalysts were prepared. In the following it will be demonstrated that although of similar composition, these two are indeed structurally different. When a solution of CoPc(COOH)$_4$ is added to PVAm (in solution or in the solid state) complex formation is observed. Besides dipolar interactions between COOH-substituents of the phthalocyanine and polymeric amine groups, an important contribution to the binding should be ascribed to a coordinative interaction between polymeric amine groups and the central metal atom of the phthalocyanine (Fig. 2a, catalyst I). Conclusive evidence of this so-called axial coordination was obtained from ESR-measurements on CoPc(COOH)$_4$/PVAm complexes suspended in DMF. After extensive evacuation to eliminate oxygen adducts, a well-resolved ESR signal could be observed exhibiting a distinct $^{14}$N superhyperfine triplet-splitting on one of the central parallel Co hyperfine absorptions (Fig. 3a). In addition the overall picture of the signal is quite typical of 5-coordinate cobalt complexes [19] and differs appreciably from the signal of CoPc(COONa)$_4$ dissolved in DMF in the absence of PVAm (Fig. 3b). These results reveal the existence of a bonding interaction between one polymeric amine group and the cobalt centre of the phthalocyanine. Similar interactions between low molecular N-bases and planar Co-compounds are well known in the literature [19] and have been fairly thoroughly studied because of their biological relevance [20].

It should be stressed that complexation does not occur when the amine carrier is in the salt form, as could be shown experimentally. On the other hand the formation of a peptide linkage in the presence of dicyclohexyl-carbodiimide (DCCI) will be favoured, when the hydrogen chloride salt of PVAm (PVAm-HCl) is used [15]. Hence, in this case application of DCCI necessarily results in formation of a peptide-linkage between an amine group of the polymer and one or more carboxy-group(s) of CoPc(COOH)$_4$ (see Fig. 2b, catalyst II). It should be noted, that this catalyst has to be
Fig. 3. ESR-spectra (recorded at -140 °C) of (a) CoFe(COONa)_4/
PVAm complex suspended in DMF, and (b) CoFe(COONa)_4
dissolved in DMF.
desalted prior to its use in a catalytic experiment. It will be obvious that after this removal of bonded HCl, apart from the peptide linkage, also a coordinative cobalt-amine bond may be expected.

2.3.2 Catalytic activity measurements

Activities without polymer base

In Tab. 1 some results are presented which allow comparison to be made between the catalytic activities of CoPc(SO$_3$Na)$_4$ and CoPc(COONa)$_4$ using NaOH as the base. It appears that the activities of both catalysts are almost equal and that the actual rate is strongly dependent on the amount of base applied, completely consistent with the idea that the thiolate anion (RS$^-$) is the species involved in the oxidation reaction. However, excess of base - e.g. 15 mmol NaOH per 14.25 mmol thiol - causes a loss of activity. Furthermore during any catalytic experiment such a loss of activity is observed due to a sharp rise of the pH, as soon as the amount of base exceeds the amount of unconverted thiol.

Introduction of a fresh portion of thiol after completion of the first run did not restore the original activity. Relative initial activities of CoPc(COONa)$_4$ in successive runs are presented in Tab. 2. Obviously, the reduction of reaction rate in successive runs is less pronounced as lower amounts of base are used. By contrast, for CoPc(SO$_3$Na)$_4$ the loss of activity in successive runs was appreciably less and did not vary with the amount of NaOH present. A combination of the results shown in Tabs. 1 and 2 leads to the conclusion, that relatively stable CoPc(COONa)$_4$/NaOH systems can only be obtained, when using low amounts of NaOH. However, under these conditions only low initial rates can be reached.
Tab. 1. Catalytic activities of substituted cobaltphthalocyanines in aqueous media.

| NaOH (mmol) | \(\frac{[RS^-]}{([RSH] + [RS^-])}\) | \(\bar{v}\) (ml min\(^{-1}\) mmol\(^{-1}\))
|-------------|---------------------------------|----------------
| 0           | 0.00                            | 4.1            | 3.6            |
| 1           | 0.07                            | 11.3           | 8.8            |
| 2           | 0.14                            | 15.1           | 15.6           |
| 6           | 0.42                            | 48.4           | 48.8           |
| 10          | 0.70                            | 60.6           | 58.9           |
| 15          | 1.00                            | 16.1           | 15.2           |

reaction conditions: see Experimental, 2 · 10\(^{-7}\) mol CoPc, substrate: 2-mercaptethanol (1 ml, 14.25 mmol).

\(\bar{v}\) = average specific rate (ml of O\(_2\) and mmol of Co).

Tab. 2. Relative activities in successive runs of CoPc(COONa)\(_{4}\) in aqueous media.

<table>
<thead>
<tr>
<th>NaOH (mmol)</th>
<th>run 1</th>
<th>run 2*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.78</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.36</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.40</td>
</tr>
</tbody>
</table>

reaction conditions: see Experimental, 2 · 10\(^{-7}\) mol CoPc, substrate: 2-mercaptethanol (1 ml, 14.25 mmol).

* this run was carried out after completion of the previous run by adding 1 ml 2-mercaptethanol.

Activities of bifunctional catalysts in water

The catalytic activities of catalyst I (i.e. CoPc(COONa)\(_{4}\) attached by complexation to PVAm, see Fig. 2a) and catalyst II (i.e. CoPc(COONH)\(_{4}\) covalently attached to PVAm, see Fig. 2b) have been investigated (see Tab. 3). Both polymeric systems show remarkably high activities as compared with their polymer-free analogues. Even in the
Tab. 3. Activities of the polymeric catalysts in aqueous media.

<table>
<thead>
<tr>
<th>NaOH (mmol)</th>
<th>$\tilde{\nu}$ (ml min$^{-1} \cdot$ umol$^{-1}$)$^{**}$</th>
<th>H$_2$O$_2$ accumulation</th>
<th>catalyst I$^{*}$</th>
<th>catalyst II$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>526</td>
<td>444</td>
<td>yes, high conc.</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>506</td>
<td>478</td>
<td>yes, low conc.</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>482</td>
<td>552</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>506</td>
<td>696</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>154</td>
<td>453</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>63</td>
<td>233</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td>15.0</td>
<td>26</td>
<td>36</td>
<td>no</td>
<td></td>
</tr>
</tbody>
</table>

reaction conditions: see Experimental, substrate: 2-mercaptoethanol (1 ml, 14.75 mmol).
$^*$ added 10 min before start of the experiment.
$^{**}$ $\tilde{\nu}$ = specific rate (ml of O$_2$ and umol of Co).
$^+$ CoFe(CO)$_3$(NH)$_4$ (10$^{-4}$ mol) coupled by complexation to PVA (10$^{-4}$ mol amine) with stirring; time of complexation 40 min.
$^{**}$ CoFe(CO)$_3$ (covalently coupled to PVA (Co-content: 0.0129 %, always 5 mg was used).

Absence of alkaline base extremely high activities are attained, due to the bifunctional character of the polymeric catalysts. It appears, that the activities observed are not appreciably affected by the presence of low amounts of alkaline base, in strong contrast with polymer-free systems (cf. Tab. 1).

A disadvantage of previous polymeric systems in the absence of alkaline base was their loss of activity observed in subsequent runs [9]. The same behaviour is observed for the bifunctional catalysts presently under investigation (see Tab. 4). This loss of activity has been ascribed to a poisoning of the basic groups of the polymer by acidic by-products (see chapter 3). For both polymeric catalysts the loss of activity can be diminished by addition of NaOH. This effect is more distinct with addition of higher amounts of base. Relative activities in the presence of amounts of base...
Tab. 4. Relative activities in successive runs of the polymeric catalysts in aqueous media.

<table>
<thead>
<tr>
<th>NaOH (mmol)*</th>
<th>catalyst I</th>
<th>catalyst II</th>
<th>catalyst II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>run 1</td>
<td>run 2</td>
<td>run 1</td>
</tr>
<tr>
<td>0.0</td>
<td>1</td>
<td>0.19</td>
<td>1</td>
</tr>
<tr>
<td>0.1</td>
<td>1</td>
<td>0.46</td>
<td>1</td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>0.58</td>
<td>1</td>
</tr>
<tr>
<td>2.0</td>
<td>1</td>
<td>0.80</td>
<td>1</td>
</tr>
<tr>
<td>6.0</td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Reaction conditions: see Experimental. Substrate: 2-mercaptoethanol (1 ml, 14.25 mmol).

* Specifications as in Tab. 3.
** This run carried out after completion of the previous run by adding 1 ml 2-mercaptoethanol.
† Not determined, see text.
** Relative activities in run 4, 5 and 6, respectively, are 0.42, 0.46 and 0.42.
*** Flattered result, see text.

NaOH larger than 6 mmol were not determined as this would not be meaningful, considering the reduced activity values observed in the first runs (cf. Tab. 3, starting with 10.0 and 15.0 mmol NaOH).

2.4 Discussion

Activities of the catalysts

Whereas the promoting role of alkaline hydroxide in the systems without polymeric base is very significant, in catalytic systems with a polymeric base it is of minor importance. Only a tendency towards increased activity can be noted for the covalently bonded catalyst (II), when small amounts of NaOH are applied. This may be explained by taking into account that addition of alkaline base
Indeed increases the overall concentration of thiolate anions (RS⁻), but it does not appreciably contribute to the relative high local Rs⁻ concentration at the oxidation site. The non-homogeneous distribution of amine groups, inherent to the coil structure of PVAm in the dilute aqueous solution is responsible for this high local concentration of Rs⁻ [9].

It is remarkable, that catalyst I (CoPc(COO)₄ attached by complexation to PVAm) retains its activity level in the presence of low amounts of NaOH. This is in strong contrast with the behaviour reported for the systems in which poly(acrylamide) modified with amine groups was used as the polymeric base [9]. In that particular case, a substantial loss of activity was observed on addition of 6 mmol NaOH due to decomposition of the polymer/CoPc complex. These phenomena are ascribed to the better complexing properties of PVAm towards CoPc resulting from the much higher density of amine groups in PVAm. Nevertheless, there are indications that also for catalyst I decomposition by NaOH is not completely avoided. Firstly, the promoting effect of low amounts of NaOH as observed for catalyst II, is not detected here. Secondly, while the use of 6 mmol NaOH gives no significant deactivation of the covalently attached catalyst (II), in the case of catalyst (I) a distinct fall in activity occurs. Both phenomena are explained by a partial rupture of the polymer/CoPc interaction.

The activity loss observed for both catalysts with use of more than 6 mmol NaOH (see Tab. 3) requires a further explanation. In the case of catalyst II (covalently bonded) a rupture of the CoPc/PVAm linkage by alkaline base seems improbable, as excessively high pH values cannot occur due to the buffering action of the weak acid (RSH) present. A more probable explanation can be found by taking eq. (3) into consideration:

\[ \text{Pol- NH}_2^- + \text{RSH} \rightleftharpoons \text{Pol- NH}_3^+ \text{SR} \] (3)
Pol- NH$_3$ represents the PVAm base. One can calculate (taking for PVAm $pK_a = 10$) with RSH representing 2-mercaptoethanol:

$$\log \frac{[\text{Pol-} \text{NH}_3^{+}\text{SR}]}{[\text{Pol-} \text{NH}_3]} = 10 - pH$$

Hence, under reaction conditions (1 mL RSH) using 10 mmol NaOH (initial pH $\approx$ 10) the ratio $[\text{Pol-} \text{NH}_3^{+}\text{SR}]/[\text{Pol-} \text{NH}_3]$ will be 1.0 and using 15 mmol NaOH (initial pH $\approx$ 12) this ratio will be only 0.01. From this calculation we can learn that when using higher amounts of base, the thiolate anions (RS$^-$) will be expelled from the polymeric base. Consequently, the oxidation rate will decline because of the reduced local RS$^-$ concentrations. Other possible effects, as for instance inhibition of the catalyst by the action of OH$^-$ cannot be excluded at this moment. In the case of catalyst I, a rupture of the polymer/CoPc complex will certainly contribute to the sharp fall of the activity observed for higher amounts of NaOH.

**Stability of the catalysts**

The deactivation of the CoPc(COONa)$_4$/NaOH systems and of the CoPc(COONa)$_4$/PVA systems as observed in successive runs is affected by NaOH (see Tabs. 2 and 4). However, the effect of added alkaline base on the deactivation is quite different in the two cases. In the conventional polymer-free system the deactivation is more pronounced with increasing amounts of alkaline base. On the other hand, for the polymeric systems, increasing amounts of alkaline base cause improvement of the stability of the catalysts. Such an improvement could be expected assuming that the loss of activity is caused by strong sulphur-containing acids poisoning the basic groups of the polymer.

Presumably, alkaline base can reduce the loss of activity of the polymeric catalysts because it prevents the formation of these acids. It seems probable that the acids are formed in trace amounts by the reaction of H$_2$O$_2$ with RSH while disulphide (RSSR) is the main product of this particular
reaction. It is interesting to know, that the disulphide formation is accelerated at higher pH [21]. As a consequence at higher pH-values H$_2$O$_2$ accumulation has not been detected during the reaction (see Tab. 3). On the other hand at low pH-values (i.e. in the absence of NaOH or in the presence of very low amounts of NaOH) H$_2$O$_2$ accumulation was observed. It seems probable that only in the latter case sulphur-containing acids are formed [21]. In the next chapter this problem will be discussed in more detail.

The results presented in Tab. 4 indicate that the use of NaOH cannot afford a complete protection against the deactivation of the bifunctional catalysts. This remaining loss of activity is not entirely understood, but presumably product inhibition (by RSSR) may play a role here. The maintenance of activity observed for catalyst II, when using 6 mmol NaOH, seems remarkable. However, in this case no complete conversion was attained during the first run. Consequently, the amount of chiol present in the initial stage of the second run was higher than usual, resulting in more favourable starting-conditions for this particular run.

The relative activities in successive runs (stabilities) of the CoPc/NaOH system and of the CoPc/PVAm systems seem to be comparable (see Tabs. 2 and 4). However, a better understanding of the stability of the catalytic system is provided by considering, at the same time, the number of turnovers (average total number of RSH molecules converted per cobalt site) involved per run. For a typical experiment with the polymeric catalysts ($10^{-8}$ mol CoPc and $14.25.10^{-3}$ mol RSH) this number amounts to $1.4.10^6$, while for the polymer-free catalyst ($2.10^{-7}$ mol CoPc and $14.25.10^{-3}$ mol RSH) it amounts to $7.10^4$. Observing for both catalytic systems a similar activity loss per run, these conversion values imply that the polymeric catalyst has a much higher total conversion capacity per cobalt site. Hence, the polymeric catalysts allow a more profitable use during their lifetime than their conventional counterpart.
References

18.
CHAPTER 3

THE ROLE OF HYDROGEN PEROXIDE DURING THE AUTOXIDATION OF THIOLS PROMOTED BY BIFUNCTIONAL POLYMER-BONDED COBALT-PHTHALOCYANINE CATALYSTS

3.1. Introduction

The reaction of thiols with metal complexes has been known for over 50 years. Interest in the interaction of thiols with metals focuses on the biological importance of the sulphhydryl groups and the possible relationship of model systems to cytochrome P-450 [1, 2]. Furthermore, studies on the reaction of thiols with metals have also been performed with the aim of understanding the catalytic behaviour of metals in the oxidation of thiols. The knowledge concerning the catalytic oxidation of thiols is applied in industrial processes for the purification of oil products [3, 4]. In the petroleum industry the thiol contamination is a prevailing problem because thiols possess an obnoxious odour and corrosive properties.

It is now well established that thiols (RSH) can be readily oxidized to disulphides (RSSR) in basic media using metal ions [5, 6] or metal complexes [7, 8] as catalysts. Recently [9-11], we have shown that a particularly active catalytic system is obtained when using a polymeric base—instead of the commonly applied alkaline hydroxide—in combination with a cobaltphthalocyanine (CoPc) as oxidation site. The reaction pathway for the oxidation of thiols in our system may be represented by a set of consecutive reactions (eqs. 1-3).

\[
Poli-NH_2 + RSH \rightarrow Poli-NH_3^{+}SR \quad (1)
\]

\[
2Poli-NH_3^{+}SR + O_2 \rightarrow 2Poli-NH_2 + RSSR + H_2O_2 \quad (2)
\]
\[ 2\text{Pol-NH}_3^+\text{SR} + \text{H}_2\text{O}_2 \rightarrow 2\text{Pol-NH}_2 + \text{RSSR} + 2\text{H}_2\text{O} \quad (3) \]

While the activity of the bifunctional polymeric catalyst in aqueous media is appreciably higher than the activity of the traditional CoPc/NaOH system, a serious drawback limiting the practical applicability of the polymeric system is the loss of activity observed in successive runs [9, 10]. Rollmann [12] applied similar bifunctional catalysts composed of polymer-bonded porphyrins to the oxidation of thiols and noticed also a rather rapid ageing of his catalyst. He ascribed this deactivation to decomposition of the porphyrins by free radical processes. We however, have assumed [9, 10] that the deactivation of our polymeric catalytic system is caused by traces of sulphur-containing oxo-acids. A strong acid may occupy the basic groups of the polymer, thus hindering the thiolate groups from coordinating to the polymeric base (i.e. inhibition of reaction (1)). Presumably, these sulphur-containing oxo-acids (RSO\(_x\)H) are formed in traces by the reaction of H\(_2\)O\(_2\) with RSH, while disulphide (RSSR) is the main product of this particular reaction (see eq. (3a)).

\[ (2+b)\text{RSH} + (1+b)x\text{H}_2\text{O}_2 \rightarrow \text{RSSR} + b\text{RSO}_x\text{H} + (2+b)x\text{H}_2\text{O} \quad (3a) \]

\( (b << 1, x \ll 3) \)

This hypothesis is supported by literature data [13] revealing that in industrial processes for the removal of mercaptans also problems might occur (i.e. consumption of base and formation of coloured products) due to overoxidation by H\(_2\)O\(_2\).

It is the scope of this chapter to describe the role of H\(_2\)O\(_2\) in the reaction system and to clarify the way of deactivation of the bifunctional catalysts. Obviously, a sound explanation of the behaviour of H\(_2\)O\(_2\) during the catalytic oxidation can only be obtained when taking into consideration all possible reactions of H\(_2\)O\(_2\). Therefore, in this investigation we have studied not only the various
reactions of $\text{H}_2\text{O}_2$ with RSH, but also the reaction of $\text{H}_2\text{O}_2$ with the amine groups of the polymeric carrier, the decomposition of CoPc by $\text{H}_2\text{O}_2$ and the disproportionation of $\text{H}_2\text{O}_2$ catalyzed by CoPc.

3.2 Experimental

Reagents and methods

The applied thiol, 2-mercaptoethanol (Merck), was distilled before use and carefully kept under nitrogen. $\text{H}_2\text{O}_2$ (30%) was obtained from Broacel B.V. and used as purchased. Distilled and deionized water was applied in the experiments. The measurements on the activity of the catalysts for the oxidation of 2-mercaptoethanol were carried out as described in chapter 2. The concentrations of $\text{H}_2\text{O}_2$ were determined spectrophotometrically using $\text{TiCl}_3$-$\text{H}_2\text{O}_2$ as reagent [14]. In solutions containing thiol these latter measurements have to be carried out immediately after sampling. In this way a possible error due to the oxidation of RSH with $\text{Ti(III)}$-$\text{H}_2\text{O}_2$ [1] can be avoided.

Optical spectra were recorded with a Unicam SP 800 spectrophotometer. IR-spectra were measured on Hitachi EPI L and Grubb-Parsons IR-spectrophotometers. The pH-measurements were carried out using a Radiometer type TTT 10 apparatus.

Preparation of the catalysts

Details of the preparation of the tetrasodium salt of cobalt(II)-tetrathionatecobalycyanine (CoPc(SO$_3$Na)$_4$), cobalt (II)-tetracarboxyphthalocyanine (CoPc(COOH)$_4$), cobalt(II)-tetraminothiacyanine (CoPc(NH$_2$)$_4$), poly(vinylamine) (PVAm) and of the coupling of cobaltphthalocyanines to PVAm have been described previously ([10, 15] and references therein). CoPc(NH$_2$)$_4$ was coupled by means of 2, 4, 6-trichloro-s-triazine [16] to the amine groups of Enzacyl AA (i.e. a porous crosslinked poly(acrylamide) with aniline-substituted acrylamide groups supplied by Koch-Light Laboratories Ltd.). CoPc(NH$_2$)$_4$ was also coupled (using the same
method) to a Enzacryl AA sample which was modified by amine
groups (i.e. with Bis(3-aminopropyl)-amine) according to the
method given by Inman and Dintzis [17]. The amine-modified
Enzacryl AA sample contained 2.1 umol amine per mg (measured
by titration with 0.1 N HCl).

3.3 Results and discussion

3.3.1 The concentration of $H_{2}O_{2}$ during the catalyzed
oxidation of thiol

In chapter 6 we will show that the activity of cata-
lysts consisting of cobalt(II)-tetrasulphophthalocyanine
(CoPc(SO$_3$Na)$_4$) and poly(vinylamine) (PVAm) for the autoxi-
dation of 2-mercaptoethanol (RSH) increases with increasing
amine content at constant CoPc(SO$_3$Na)$_4$ concentration. Our
present measurements of the concentration of hydrogen per-
oxide formed during reaction reveal that also the level of
$H_{2}O_{2}$ accumulation depends strongly on the content of poly-
meric amine in the reaction mixture. From the results
presented in Fig. 1, it is obvious that the amount of $H_{2}O_{2}$
present diminishes with increasing amine concentration.
Evidently, the amount of polymeric base in the bifunctional
catalyst is of considerable importance for both the cata-
lytic activity and the level of $H_{2}O_{2}$ accumulation. A rela-
tively high excess of polymeric amine groups as compared to
CoPc molecules favours the rate of oxygen uptake and di-
minishes the accumulation of $H_{2}O_{2}$.

The amount of $H_{2}O_{2}$ in the reaction system decreases
not only with increasing PVAm content (cf. Fig. 1), but de-
creases also substantially on addition of small amounts of
NaOH. This is demonstrated by experiments performed with
cobalt(II)-tetracarboxyphthalocyanine (CoPc(COH)$_4$) cova-
rently bonded to PVAm (see Fig. 2). Comparable results have
also been obtained using CoPc(SO$_3$Na)$_4$: the structural
differences between CoPc(COH)$_4$ and CoPc(SO$_3$Na)$_4$ are at
least in this case of minor importance.

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Fig. 1. The accumulation of $H_2O_2$ as a function of the amount of poly(vinylamine) during the oxidation of 2-mercaptoethanol using $10^{-8}$ mol CoPc(SO$_3$Na)$_2$ (conditions: 14.25 mmol thiol, $T = 24^\circ$C, $p(O_2) = 1$ atm, reaction volume: 75 ml). (a) $10^{-5}$, (b) $10^{-4}$, and (c) $5.10^{-4}$ mol amino.

Fig. 2. The influence of the addition of NaOH on the concentration profile of $H_2O_2$ during oxidation of 2-mercaptoethanol using PVAm with covalently attached CoPc(COOH)$_4$ ($9.10^{-5}$ mol amine/3.10$^{-8}$ mol Co) as catalyst (conditions: see Fig. 1). (a) no NaOH, and (b) 0.1 mmol NaOH added.
Obviously, the concentration-time dependence of \( \text{H}_2\text{O}_2 \) (cf. Figs. 1 and 2) can only be explained when taking into consideration production as well as conversion of \( \text{H}_2\text{O}_2 \).

3.3.2 Production of \( \text{H}_2\text{O}_2 \)

The overall stoichiometry of the oxidation of RSH by \( \text{O}_2 \) in an alkaline solution with transition metal compounds as catalysts is represented by \( 4\text{RSH} + \text{O}_2 \rightarrow 2\text{RSSR} + 2\text{H}_2\text{O} \). In such conventional systems no \( \text{H}_2\text{O}_2 \) was detected \cite{10} and so a direct 4-electron reduction of \( \text{O}_2 \) to \( \text{H}_2\text{O} \) by means of the catalysts cannot be excluded. On the other hand, we have found that with CoPc bonded on polymers with amine groups, \( \text{H}_2\text{O}_2 \) was present as an intermediate and the amount of \( \text{H}_2\text{O}_2 \) depended strongly on the amount of CoPc in the reaction mixture (see Fig. 3). From measurements at low [amine]/[CoPc] ratios (Fig. 4), it can even be concluded that all \( \text{O}_2 \) consumed by the thiol oxidation is converted to \( \text{H}_2\text{O}_2 \) before it is reduced to \( \text{H}_2\text{O} \). Our results strongly indicate that the production of \( \text{H}_2\text{O}_2 \) is catalyzed by CoPc and in analogy with a mechanism suggested previously \cite{9}, we present in Scheme I a mechanistic interpretation of the production of \( \text{H}_2\text{O}_2 \) during thiol oxidation with cobalt-phthalocyanines.

![Scheme I](image)

3.3.3 Conversion of \( \text{H}_2\text{O}_2 \)

In order to establish the precise role of \( \text{H}_2\text{O}_2 \) during
Fig. 3. The accumulation of $\text{H}_2\text{O}_2$ as a function of the amount of $\text{CoPc(SO}_3\text{Na)}_4$ during the oxidation of 2-mercaptoethanol using $10^{-6}$ mol amine (as FVAm; conditions: see Fig. 1). (a) $10^{-5}$, and (b) $10^{-9}$ mol $\text{CoPc(SO}_3\text{Na)}_4$.

Fig. 4. The influence of the amount of amine on the ratio of the amount of $\text{H}_2\text{O}_2$ and the amount of consumed $\text{O}_2$ during the oxidation of 2-mercaptoethanol catalyzed by $\text{CoPc(SO}_3\text{Na)}_4$ ($10^{-8}$ mol)/FVAm complexes (conditions: see Fig. 1). (a) $10^{-5}$, (b) $10^{-4}$, and (c) $5\cdot10^{-4}$ mol amine.
the catalytic oxidation of thiols, the various possibilities for the conversion of H$_2$O$_2$ have been investigated separately.

We have found that the uncatalyzed decomposition of H$_2$O$_2$ according to eq. (4) does not contribute considerably to the conversion of produced H$_2$O$_2$; the rate of reaction (4) is some orders of magnitude lower than the rate of H$_2$O$_2$ conversion during thiol oxidation with bifunctional catalysts. Our results are in agreement with literature data [18] demonstrating that the decomposition of H$_2$O$_2$ is a very slow reaction in the absence of transition metal ions.

$$2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O}$$ (4)

The decomposition of H$_2$O$_2$ according to eq. (4) is catalyzed by various metal ions and metal ion complexes [19, 20]. In biological systems peroxide decomposition is carried out by the enzyme catalase, which is a heme iron protein containing four heme groups per molecule, each heme moiety consisting of high-spin iron (III) in a protoporphyrin IX ring [20]. The catalase-like activity of various metallophthalocyanines was investigated in recent years because of the structural similarity of phthalocyanines with the naturally occurring porphyrins. Also CoPc(SO$_3$Na)$_4$ has shown catalytic activity for the H$_2$O$_2$ disproportionation reaction, although it is proven by several authors [21, 22] that Fe-phthalocyanines are considerable more active catalysts. However, the available turnover numbers for the decomposition of H$_2$O$_2$ catalyzed by CoPc(SO$_3$Na)$_4$ are much lower than the turnover numbers usually encountered in the production of H$_2$O$_2$ during RSW oxidation with polymer-bonded phthalocyanines. A typical value for the turnover number of the decomposition of H$_2$O$_2$ in a polymer-free CoPc(SO$_3$Na)$_4$ solution (at pH = 6 and T = 25°C) is 1 min$^{-1}$ [23], whereas with our bifunctional system the turnover number for the production of H$_2$O$_2$ is in the order of magnitude of 10$^4$ min$^{-1}$. Evidently, it is very unlikely that the CoPc is able to provide a significant contri-
bution to the conversion of $H_2O_2$ during thiol oxidation experiments. Moreover, in the presence of an excess of PVM (i.e., $[amine]/[CoPc] > 200$ as usual in catalytic experiments) $CoPc(SO_3Na)_4$ has virtually lost its catalytic activity for decomposition of $H_2O_2$. This is confirmed by visible light spectroscopy on solutions containing for example $10^{-3}$ mol/l $H_2O_2$, $10^{-2}$ mol/l amine and $2\cdot10^{-6}$ mol/l $CoPc(SO_3Na)_4$ (see [11]); even after 2 hours no perceptible change occurred in the spectra. Nevertheless, bubbling of oxygen through these solutions immediately caused the formation of binuclear cobalt dioxygen adducts, while on the other hand in a polymer free solution both the addition of $H_2O_2$ as well as the bubbling through of oxygen immediately produced these binuclear dioxygen adducts.

Evidently, the presence of PVM inhibits the interaction of $H_2O_2$ with $CoPc(SO_3Na)_4$. The above observations strongly suggest that amine groups of PVM compete with $H_2O_2$ for the "free" coordination positions at the cobalt nucleus. Waldmeier et al. [23] have reported a fall in the catalase-like activity of $CoPc(SO_3Na)_4$ on addition of imidazole. They explained this phenomenon by taking into account an obstruction of the two "free" ligand positions at the catalyst by imidazole. Unfortunately, their explanation is not applicable to our system, because ESR-measurements have shown that the formation of complexes of PVM and a CoPc includes the coordinative interaction of amine groups of the polymer with only one apical site of the cobalt complex [10]. In such a case still one apical site of the cobalt complex is left available for an entering peroxide molecule. However, Sigel et al. [24] and Barteri et al. [25] have shown recently a drastic loss of catalase-like activity of trans-Co and $Fe$ complexes when only one of the two available coordination positions is blocked by a ligand not displaceable by $H_2O_2$ molecules. Our present experiments reveal that the addition of PVM to $CoPc(SO_3Na)_4$ results in a dramatic fall in catalase-like activity, and confirm the idea [24, 25] that an intramolecular dual-site mechanism for the catalytic decomposition of $H_2O_2$ is far more efficient than a single-
site mechanism.

A third possibility for the conversion of $\text{H}_2\text{O}_2$ is formed by its reaction with the primary amine groups of the carrier resulting in the formation of hydroxylamines, which in turn are susceptible to further oxidation into primary nitro compounds [26].

\[ \text{R-NH}_2 + \text{H}_2\text{O}_2 \rightarrow \text{R-NH}_2\text{O}_2 \rightarrow \text{R-N}_{\text{OH}} \rightarrow \text{R-NO}_2 \]  \( \text{(5)} \)

Experimental work has not given any indication that reaction (5) occurs with poly(vinylamine) under our catalytic conditions: IR-measurements have demonstrated that PVAm is not affected in aqueous solutions containing peroxide in a concentration comparable to that usually encountered during oxidation experiments with bifunctional catalysts. Furthermore, we found that pretreatment of a bifunctional PVAm/CoPc(SO$_3$Na)$_4$ catalyst with $\text{H}_2\text{O}_2$ during 1 h before the start of a catalytic run results in the same high reaction rate as in the case that the catalyst is treated with $\text{H}_2\text{O}_2$ immediately before the start of the RSH oxidation reaction.

Finally, the reaction of $\text{H}_2\text{O}_2$ with RSH has been investigated. In chapter 2 we have already proposed this reaction to be the main reason for the consumption of $\text{H}_2\text{O}_2$ during thiol oxidation. The results of the reaction of RSH with $\text{H}_2\text{O}_2$ in the presence of NaOH and PVAm with exclusion of O$_2$ and CoPc are presented in Fig. 5. It appears that the reaction rate strongly depends on the amount of added base. Comparison of the measurements performed with equivalent amounts of NaOH and amine groups (see Fig. 5) reveals that the reaction rate is higher when using NaOH. Comparing both types of base one has to realize that use of polymeric base has advantages as well as disadvantages: in the catalytic conversion of RSH the high local concentration of both RS$^-$ and CoPc(SO$_3$Na)$_4$ at the polymer gives the polymeric system a strong advantage compared to the system with NaOH. On the other hand, in case of reaction of RSH with $\text{H}_2\text{O}_2$ the $\text{H}_2\text{O}_2$ will not become attached to the polymer and then the inhomogeneous distribution of basic sites in the
Fig. 5. The conversion of \( \text{H}_2\text{O}_2 \) in consequence of its reaction with 2-mercaptoethanol as a function of the added base (conditions: \( T = 23^\circ\text{C} \), \( p(\text{O}_2) = 1 \) atm, reaction volume: 75 ml, 14.25 mmol thiol, \( [\text{H}_2\text{O}_2] = 1.6 \times 10^{-2} \) mol/l). (a) no base, (b) \( 10^{-4} \) mol amine (as PVAm), (c) \( 10^{-4} \) mol NaOH, (d) \( 5 \times 10^{-5} \) mol amine (as PVAm), and (e) \( 5 \times 10^{-4} \) mol NaOH.

Solution is a disadvantage causing diffusional limitations. Addition of CoPc(SO_3Na)_4 (\( 10^{-7} \) mol) or bubbling of oxygen through the solutions had no noticeable influence on the observed rates of reaction of \( \text{H}_2\text{O}_2 \) with 2-mercaptoethanol.

Our results are in agreement with the literature data concerning the reaction of \( \text{H}_2\text{O}_2 \) with other thiols [27, 28]. Barton et al. [27] have investigated the reaction of \( \text{H}_2\text{O}_2 \) with cysteine and cysteamine in the pH range 6-11. These authors have demonstrated that their kinetic results can be explained by a mechanism in which the rate limiting step consists of a nucleophilic attack of the thiolate anion on an oxygen atom of \( \text{H}_2\text{O}_2 \). Most probable the reaction of the nucleophilic \( \text{RS}^- \) species with \( \text{H}_2\text{O}_2 \) occurs via simple \( \text{S}_2\text{H}_2 \) substitution reactions, as shown in eqs. 6 and 7.
\[ \text{RS}^- + \cdot\cdot\cdot + \cdot\cdot\cdot - \cdot\cdot\cdot + \cdot\cdot\cdot - \cdot\cdot\cdot + \cdot\cdot\cdot \quad (6) \]

\[ \text{RS}^- + \cdot\cdot\cdot \rightarrow \cdot\cdot\cdot + \cdot\cdot\cdot - \cdot\cdot\cdot + \cdot\cdot\cdot \quad (7) \]

The rate of reaction of \( \text{H}_2\text{O}_2 \) with RSH that is derived from Fig. 5 agrees with the rate of the consumption of \( \text{H}_2\text{O}_2 \) during oxidation of RSH with the bifunctional catalysts. This demonstrates that this reaction is the main path for conversion of the \( \text{H}_2\text{O}_2 \) formed.

3.3.4 Deactivation of the catalysts

Although the reaction between RSH and \( \text{H}_2\text{O}_2 \) results in a highly selective formation of disulphides, literature data [28] show that small amounts of higher oxidation products may be formed. Scheme II displays some interconversions which are possible between the sulphur functional groups starting from thiols [1]. Some of the steps shown in this scheme may be bypassed and alternative hydrolytic products may be possible. The main end product to be expected is sulphonic acid due to the instability of most of the other oxidation products [26].

\[
\begin{array}{cccc}
\text{RSH} & \rightarrow & \text{RSOH} & \rightarrow \\
\text{thiol} & \text{sulphenic acid} & \text{sulphinic acid} & \text{sulphonic acid} \\
\downarrow & & \downarrow & \\
\text{RSSR} & \rightarrow & \text{RSOSR} & \rightarrow \\
\text{disulphide} & \text{thiosulphinate} & \text{thiosulphonate} & \\
\downarrow & \leftarrow & \leftarrow & \\
\text{RSO}_2\text{SO}_2\text{R} & \text{\( \alpha \)-sulphonylsulphone} & \\
\end{array}
\]

Scheme II.

In order to check the formation of sulphur-acids in our catalytic system we have carried out the following set
of experiments. Firstly, an oxidation experiment has been performed with cobalt(II)-tetraaminophthalocyanine (CoPc(NH$_2$)$_4$) coupled with the aid of 2,4,6-trichloro-s-triazine to Enzacyrl AA (20 mg of this heterogeneous catalyst containing 0.25 wt.% of Co was applied) as a catalyst using 6 mmol of NaOH and 1 ml (14.25 mmol) 2-mercaptoethanol (RSH). As expected, during this experiment no H$_2$O$_2$ accumulation could be detected and we assume to produce the disulphide (RSSR) with high selectivity. Having the conversion of RSSR completed, the catalyst was separated and the reaction mixture was neutralized with 0.1 M HCl. A small part of this solution was poured into a beaker and carefully concentrated by flushing with oxygen-free nitrogen. Application of this concentration method during one night resulted in a highly viscous product. The IR-spectrum of one drop of this material between CaI discs is given in Fig. 6a.

When 25 ml of an aqueous 0.1 M H$_2$O$_2$ solution is added to 25 ml of the neutralized solution (containing 1.4 mmol RSSR) and the resulting mixture is concentrated at ambient temperature as just described, the obtained material shows an IR-spectrum as depicted in Fig. 6b. In the latter spectrum absorption peaks show up that are absent in Fig. 6a and which can be assigned to sulphur-containing oxo-compounds (see for instance [29]), i.e. 1312 (O=S=O, asymm.), 1118 (O=S=S, asymm.), 612 (S=O$_2$), 560 and 525 cm$^{-1}$ (S=O$_3$).

Subsequently, we have performed a RSH oxidation experiment using a bifunctional catalyst in the absence of additional alkaline base (i.e. Enzacyrl AA modified by amine groups and CoPc(NH$_2$)$_4$ coupled to this carrier using 2,4,6-trichloro-s-triazine as coupling agent, see Experimental). Using 10.7 mg of this heterogeneous catalyst (containing 0.66 wt.% of Co) for the conversion of 1 ml (14.25 mmol) RSH under standard conditions we observe - as expected - the accumulation of H$_2$O$_2$ in the reaction mixture. When after complete conversion of the thiol the reaction mixture is subjected to the same concentration
Fig. 6. IR-analysis of the reaction products after oxidation of 2-mercaptoethanol under various conditions: (a) in the presence of catalyst and NaOH, (b) the product of (a) after treatment with $\text{H}_2\text{O}_2$, and (c) in the presence of bifunctional catalyst without additional NaOH.
procedure as described above, we obtain a product which gives the IR-spectrum shown in Fig. 6c. Comparison of the latter spectrum with Fig. 6a and 6b reveals that the characteristic peaks of sulphur-containing oxo-acids are also present in spectrum 6c. In conclusion, we have shown the possibility that small amounts of sulphur-acids may be produced during the autoxidation of thiols with bifunctional catalysts.

In [9] the essential role of the basic groups in our bifunctional catalysts was demonstrated. It was found that addition of a stoichiometric amount of HCl was sufficient for a dramatic decrease of the catalytic activity. Poisoning of the basic sites of the polymeric catalysts will also occur when strong sulphur-containing oxo-acids are formed during the catalytic oxidation of thiols. Due to the excess of RSH in relation to the amount of catalyst in our oxidation experiments, stoichiometric amounts of basic groups and strong sulphur-acids are already obtained when a low percentage (< 1 %) of the amount of RSH is converted to sulphur-acids.

The known sensitivity of metallophthalocyanines to oxidative destruction prompted us to consider also deactivation of our bifunctional catalyst by means of decomposition of CoPc by H_2O_2. The instability of metallophthalocyanines and related chelates is thought to be caused by direct demetallation and by hydroxylation of the mesoposition followed by ring cleavage and demetallation [30, 31].

We have investigated the decomposition of CoPc(SO_3Na)_4 as a function of the pH. It has appeared that in polymer-free solutions the instability of CoPc(SO_3Na)_4 is decreased at higher pH-values (see Fig. 7). However, in the presence of excess of PVAm, as usual in our catalytic experiments, the degradation of the phthalocyanine did not show up. This shows once again that the presence of PVAm inhibits the interaction of H_2O_2 with CoPc(SO_3Na)_4. When the bonding interaction between the amine groups of PVAm and the CoPc is hindered, for instance by addition of acid, the interaction of H_2O_2 with CoPc is not prohibited anymore. In the
Fig. 7. The destruction of CoPc(SO$_3$Na)$_4$ ($2.5 \times 10^{-6}$ mol/l) by H$_2$O$_2$ ($1.3 \times 10^{-2}$ mol/l) according to visible light spectral measurements at 15000 cm$^{-1}$ determined as a function of pH (at ambient temperature). (a) pH = 10.2, (b) pH = 9.1, and (c) pH = 5.8.

The decomposition of CoPc does occur. Such a situation may arise when during RSH oxidation with the bifunctional catalyst a low pH (pH < 6) is generated as a consequence of the formation of strong sulphur-containing oxo-acids. An oxidation experiment with CoPc(SO$_3$Na)$_4$ ($10^{-7}$ mol) / PVAm ($10^{-4}$ mol amine) as catalyst has revealed that after 5 runs (each run carried out with 14.25 mmol 2-mercaptoethanol as substrate) 30% of the original amount of CoPc(SO$_3$Na)$_4$ is decomposed, according to visible light spectral measurements at 15000 cm$^{-1}$. However, the catalytic activity in the fifth run is only 2% of the original activity, so it is safe to conclude that deactivation of the catalyst is not primarily caused by decomposition of CoPc(SO$_3$Na)$_4$. 

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3.4 Conclusions

During the catalytic oxidation of thiol (RSH) to disulphide (RSSR) the presence of \( H_2O_2 \) can be accounted for by the reactions (8) and (9):

\[
2\text{RSH} + O_2 \xrightarrow{\text{CoPc/base}} \text{RSSR} + H_2O_2 \quad (8)
\]

\[
2\text{RSH} + H_2O_2 \xrightarrow{\text{base}} \text{RSSR} + 2H_2O \quad (9)
\]

The relative rates of these reactions determine the amount of accumulated \( H_2O_2 \) in the reaction system and these rates can be varied with respect to each other as is proven by the results given in Figs. 1-3. A crucial aspect of this coupled oxidation system is that only the production of \( H_2O_2 \) (eq. (8)) is catalyzed by CoPc, whereas the influence of CoPc on the conversion of \( H_2O_2 \) is of negligible importance. On the other hand, the role of base in the catalytic oxidation of thiols is a more complicated one. In addition to the conversion of RSH into reactive RS\(^-\) species, which is necessary for reaction (8) as well as for reaction (9), the base also takes care for the neutralization of the small quantities of sulphur-oxides formed according to scheme II.

The deactivation of the bifunctional catalysts in the absence of additional alkaline base is mainly the result of the poisoning of the basic sites by these sulphur-oxides. Although decomposition of the CoPc in the bifunctional catalysts has been observed, this is not the primary cause of the deactivation. Furthermore, the contribution of the conversion of the amines groups by \( H_2O_2 \) to the poisoning can be neglected.

In reaction systems containing a surplus of NaOH a fair stability of the catalytic activity was observed under our conditions and in such systems also no perceivable \( H_2O_2 \) accumulation occurred (see also [10]). However, the absence of a detectable amount of \( H_2O_2 \) does not preclude its intermediate production, since our present measurements
have demonstrated that the base-catalyzed reaction of $\text{H}_2\text{O}_2$ with $\text{RSN}$ (eq. (9)) can account for a rapid conversion of $\text{H}_2\text{O}_2$.

Since the deactivation of the bifunctional catalyst is apparently connected with the accumulation of $\text{H}_2\text{O}_2$, in the next chapter the in situ decomposition of the produced $\text{H}_2\text{O}_2$ by means of compounds with a high catalase-like activity will be discussed.

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CHAPTER 4

CATALYSIS OF THE DECOMPOSITION OF HYDROGEN PEROXIDE

4.1 Introduction and literature survey

We have shown before [1] that the peroxide produced during the oxidation of thiols with poly(vinylamine) (PVAm) / cobaltphthalocyanine (CoPc) catalysts must be decomposed quickly in order to ensure catalyst stability over long times. Among the possible remedies for peroxide-induced deactivation are decomposition by radiation (by photochemical or radiochemical processes), electrolytic decomposition and catalytic decomposition [2]. Since the first two of these approaches involve substantial inputs of energy and may themselves affect the activity of the bifunctional thiol oxidation catalysts, we confined ourselves to an investigation of catalytic methods for the decomposition of $\text{H}_2\text{O}_2$. It was our aim to search for a substance which could decompose $\text{H}_2\text{O}_2$ and which could be incorporated in the bifunctional catalytic systems. Such an incorporation might be accomplished by methods such as:

(a) application of the active substance as a carrier for the bifunctional catalyst or fixation of both the active substance and the bifunctional catalyst to the same inert support (heterogeneous catalytic system, see scheme I-a)

(b) attachment of an active substance to the soluble polymeric base containing already the CoPc (homogeneous catalytic system, see scheme I-b).

Since many research groups have already investigated the disproportionation of peroxide into water and oxygen (eq. (1)), we will start with a short review of the relevant literature.

$$2 \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}_2\text{O} \quad (1)$$
Scheme 1. Examples of the incorporation of catalytic sites for $\text{H}_2\text{O}_2$ decomposition (•) in the bifunctional thiol oxidation catalyst: (a) heterogeneous catalytic system, and (b) homogeneous catalytic system (Ca = cobalt phthalocyanine).

Despite more than hundred years of extensive research the catalytic decomposition of $\text{H}_2\text{O}_2$ still provides matter for further investigations [3]. Nowadays the decomposition of $\text{H}_2\text{O}_2$ attracts for instance considerable attention in electrochemical research [4, 5]. In this field it is generally agreed that the formation and decomposition of peroxide plays a central role in the cathodic reduction of $\text{O}_2$ at metal electrodes [6, 7]. For this reason potential cathode materials for fuel cells and batteries are often tested for their ability to catalyze $\text{H}_2\text{O}_2$ decomposition [4, 8, 9]. The catalytic decomposition is also of interest in many areas of food processing [10]. One application of $\text{H}_2\text{O}_2$ is the sterilization of food products, for it is suitable to destroy harmful organisms at low temperatures. Furthermore, $\text{H}_2\text{O}_2$ occurs as a by-product which must be removed following for instance the enzymatic production of gluconic acid. The various types of catalysts which have been investigated in the course of the years will now be described briefly.

Metals and metal ions. It is well established that many metals and metal ions catalyze the decomposition of $\text{H}_2\text{O}_2$ [11]. Metal species have been used both unsupported and supported on carriers and appear to vary widely in their ability to catalyze this decomposition reaction. Perhaps
the best known homogeneous catalyst is Fe$^{2+}$, because the combination of Fe$^{2+}$ and H$_2$O$_2$ (Fenton's reagent) can be applied for the mild oxidation of a great variety of hydrocarbons [12]. The activities of metal ions attached to a Y molecular sieve [11] were in order of Pd(II) < Fe(III) < Ni(II) < Ag(I) > Mn(II) > Co(II) > Co(III) > Hg(II) > Cu(II) > Ti(I) > Cr(III) > Zn(II). In an investigation of metals supported on alumina [13] the order Ag > Pt > Pd > Au has been established. For unsupported noble metals it was determined, that in some cases alloying resulted in considerable synergistic effects [4]. Alloys of platinum–iridium, containing 10–20 % Ir were for instance much more active in a neutral H$_2$O$_2$ solution than platinum black. From the literature it appears that Ag or Ag$^+$ is the most versatile compound in this class of H$_2$O$_2$ decomposition catalysts. However, the dissolution of silver generally occurs as a side-reaction and furthermore in 2-5 M H$_2$O$_2$ solution poisoning occurs due to the formation of oxide layers by the partly irreversible sorption of the reaction product oxygen [14].

Metallic oxides. In several papers studies of the decomposition of H$_2$O$_2$ on metallic oxides and mixed metallic oxides have been reported [15, 16]. It was shown by vapour-phase decomposition of H$_2$O$_2$ in a flow system that the order of catalytic efficiency of a wide range of unsupported metallic oxides [15] could be given as follows: Mn$_2$O$_3$ > PbO > Ag$_2$O > CuO > SnO > Cu$_2$O > CdO > ZnO > MgO > Al$_2$O$_3$ > glass (pyrex). Taking into consideration this reactivity order it is not surprising, that a superior commercial inorganic catalyst for the decomposition of H$_2$O$_2$ is manganese dioxide on activated alumina (Hareshaw Mn 0201) [10]. Measurements on various active manganese oxides (MnO$_2$, Mn$_2$O$_3$, Mn$_3$O$_4$ and MnO) have shown, that these compounds when exposed to H$_2$O$_2$ gradually achieve the same specific catalytic activity [17], which indicates that the active species on these different oxides are ultimately identical. Because of its H$_2$O$_2$ decomposition activity manganese oxides have been applied as support for the enzyme glucose oxidase [18], and it was indeed found that the rate of deactivation of the enzyme
immobilized on MnO₂ is much lower than that of the free enzyme.

Metal complexes. The numerous studies on metal complexes have revealed that a suitable catalyst for the disproportionation of H₂O₂ must have the following three properties [19]:

1. The metal ion has to be redox active.
2. Free coordination positions must be available, so that H₂O₂ or derivatives thereof (OOH⁻ for instance) can coordinate to the metal ion.
3. Ligands bound in the first coordination sphere of the metal ion must be labile, i.e. they must exchange with high rates.

Condition (1) is mainly determined by the choice of the metal ion, whereas condition (2) is fulfilled by selecting suitable ligands. Considering, for example Fe³⁺ and Cu²⁺, it must be realized that in aqueous solution Cu²⁺ usually has a coordination number of 4 and Fe²⁺ one of 6 [20]. Thus, it could be predicted that application of a tetradeinate ligand (for instance hematoporphyrin or tetrasulphophthalocyanine) results in catalytic active complexes in the case of Fe³⁺, but not in the case of Cu²⁺. Recently, we [1] and others [21, 22] have shown that a drastic loss of catalytic activity of Co- and Fe-complexes with tetradeinate ligands (trans-complexes) occurs when one of the two available apical coordination positions is blocked by a ligand not displaceable by H₂O₂ molecules. These results prove that two free coordination positions must be available and that an intramolecular dual-site mechanism for the catalytic H₂O₂ decomposition is far more efficient than a single-site mechanism. In other experiments it has been observed that a trans-Fe complex is more active than its cis-isomer (Scheme II) [23]. Condition (3) is determined both by the metal ion and the ligand [19]. The influence of the ligand on the exchange rates is illustrated by the work of Fleischer et al. [24, 25]. These authors show that cobalt-hematoporphyrins are rather labile with respect to substitution reactions, whereas classical Werner-type Cobalt(III)-compounds are
Scheme II. (a) cis-Fe(N,N'-bis(2-methylpyridyl)ethylenediamine)X₂, and (b) trans-Fe(2, 2':6', 2'' :6'')-tetrapyridyl)X₂; X = "free" coordination position, for example occupied by H₂O or OH⁻.

rather inert.

In biological systems the decomposition of H₂O₂ (eq. (1)) is very efficiently catalyzed by the enzyme catalase which consists of a protein molecule with four iron(III)-porphyrin groups per molecule [3]. Much work has been devoted to synthetic metalloporphyrins and -phthalocyanines because these compounds are good models for the active sites of catalase. Various metalloporphyrins and -phthalocyanines have been found active catalysts for the peroxide decomposition [8, 9, 19, 20, 26], the Fe-complexes being the most active compounds. However, even the activity of these Fe-complexes does not distinctly reach the high activity of catalase. On the other hand, Wagnerova et al. [27] attributed the activity of some metallophthalocyanines to trace impurities. However, these authors performed their experiments in the presence of EDTA and in our opinion they overlooked the inhibiting action of EDTA (i.e., occupation of the essential coordination sites) on the activity of the phthalocyanines [29].

Although several groups published that Mn-phthalocyanines possess a low activity for the disproportionation of H₂O₂ [8, 9, 26, 29], in a UOP patent [30] it has been
claimed that Mn-phthalocyanines can be advantageously applied for decomposition of redundant \( \text{H}_2\text{O}_2 \) during thiol oxidation. Because of the conflicting data a detailed study on the true activity of Mn-phthalocyanine seems appropriate. A disadvantage limiting the practical applicability of metalloporphyrins and phthalocyanines is their lability towards oxidative destruction [1, 9, 31, 32] and although suggestions have been made to overcome this problem [31, 32] a definitive solution seems not to be available at the moment.

Activated Carbon. As early as 1907 Lemoine [33] reported that activated carbon has a strong catalytic action for the decomposition of \( \text{H}_2\text{O}_2 \). Nowadays there is general agreement that the basicity of the surface is the most important factor determining the catalytic activity, and that chemical and thermal treatments therefore have a distinct influence [34, 35]. However, it must be realized that the peroxide decomposition rates are composite reflections of a variety of factors including surface chemistry of the material, density and accessibility of the micropores, and possible concealed diffusional limitations of the true intrinsic activity [36]. Activity measurements in conjunction with trace-metal assays of the various carbon preparations suggest that trace metals play an insignificant role relative to functional groups on the activated carbon surface [36]. As in the case of MnO\(_2\) the activity of carbon can be combined with covalent enzyme immobilization in order to minimize the damaging effect of \( \text{H}_2\text{O}_2 \) on immobilized enzyme activity [2, 36, 37]. This concept is especially significant for enzymatic oxidation catalysts, as for instance glucose oxidase, which generate \( \text{H}_2\text{O}_2 \) during the oxidation reaction.

Polyquinones. Several purely organic polymers like pyrolyzed polycrylonitril, polyaminoquinones, vulcanized aniline black or ordinary aniline black and pyrolyzed chlorinated polyvinylchloride were shown to be active for \( \text{H}_2\text{O}_2 \) decomposition [38]. Since all the organic polymers tried for this reaction may be assumed to contain quinone groups, the most probable explanation for their activity is the capability
of groups of this kind to undergo reversible oxidation/reduction.

From the above literature survey we conclude that some metallic oxides, activated carbons and several metal complexes might be suitable for our purposes. Metallic oxides and activated carbons may serve as carriers for bifunctional catalysts and prevent the deactivation of the immobilized polymeric catalysts (see scheme 1-a). Using such solids as carriers offers the additional advantage of creating a heterogeneous catalytic system [39]. Examples of this approach are the immobilizations of glucose oxidase on \( \text{MnO}_2 \) [18] and activated carbon [2], where decomposition of \( \text{H}_2\text{O}_2 \) produced by the enzymatic oxidation is required too. Guided by these results we decided to study the use of the most promising metal oxides (\( \text{MnO}_2 \), \( \text{PbO}_2 \) and \( \text{Ag}_2\text{O} \)) and of activated carbons in the decomposition of \( \text{H}_2\text{O}_2 \).

Another possibility may be to incorporate water-soluble metal complexes into the bifunctional catalysts by simple complexation with the polymeric amine groups or by covalent attachment to the amine groups via functional groups of the ligand [40]. In case water is applied as reaction medium this results in a homogeneous polymeric catalyst (see scheme 1-b). We have tried this approach by studying water-soluble metallophthalocyanines as catalysts in the decomposition of \( \text{H}_2\text{O}_2 \). Various metal ions may readily be incorporated in the phthalocyanine molecule [8, 41], and it may be expected that the phthalocyanine ligand greatly increases the substitution rates of the central metal ion [24, 25, 42], which may result in a high catalytic activity.

4.2 Experimental

\( \text{MnO}_2 \) was electrochemically prepared with a platinized Pt-electrode at 110°C from \( \text{Mn(NO}_3)_2 \) (Kiedel-De Haën AG, p.a.). \( \text{PbO}_2 \) (Merck p.a.) was used as recrystallized, whereas \( \text{Ag}_2\text{O} \) was prepared from \( \text{AgNO}_3 \) (Merck p.a.) by adding \( \text{NaOH} \), washing the precipitate extensively with water and subsequently
drying in a desiccator. VO−, Mn−, Fe−, Co−, and Cu-tetra-
sulphophthalocyanine were prepared on the analogy of the
method given by Weber and Busch [43].

The various types of carbons, i.e. Merck activated
carbon p.a., Meckog C (soot produced in an oil-gasification
process), Norit R1 and R3 extra, Norit RO3 and Norit MRK,
were dried before use and applied without any further pre-
treatment.

The preparation of PVAm and of the bifunctional PVAs/
CoPC catalyst and the measurements on the activity of the
catalysts for the oxidation of 2-mercaptoethanol (Merck)
were carried out as described in chapter 2. The applied
thiol was distilled before use and carefully kept under
nitrogen. The concentrations of H₂O₂ were determined
spectrophotometrically using ZnCl₂·H₂O₂ as reagent [44].

The measurements on the catalytic decomposition of
H₂O₂ were carried out in the same modified Warburg apparatus
as used for the testing of thiol oxidation catalysts. The
rate of H₂O₂ decomposition was determined by measuring the
initial rate of oxygen production, at constant oxygen
pressure (p(O₂) = 1 atm) and a high stirring speed (3000
r.p.m.). H₂O₂ (30 %) was obtained from Brocacef B.V. and
used as purchased. For thiol oxidation experiments as well
as for H₂O₂ decomposition measurements the total reaction
volume amounted to 75 ml (solvent: water). Aqueous NaOH
solutions were used to bring the reaction mixtures to the
desired pH-values and a Radiometer TTI 1c apparatus was
applied for the pH-measurements.

The rates of oxidative destruction of the metallophtha-
locyanines during H₂O₂ decomposition were determined with
visible light spectral measurements on a Unicam SP 800
spectrophotometer by circulating the reaction mixture
through an optical flow cell. In these experiments the
total volume of the reaction solution amounted to 150 ml.
Circulation of the solution was effected by means of a
teflon coated Saturn pump type SPM-100 (Fluorocarbon,
Anaheim (Cal.)—USA) operated at the maximum attainable flow
rate (i.e. about 300 ml/min in the applied recirculation
system. Distilled and deionized water was used throughout this investigation.

4.3 Results and discussion

4.3.1 Metallic oxides

The catalytic activity of MnO₂ for the decomposition of H₂O₂ as a function of the pH of the reaction mixture is given in Fig. 1. A maximum activity is found in the pH range 10-12, which is in qualitative agreement with literature data. Unfortunately, measurements in neutral solution have shown that the initial high activity of MnO₂ declined markedly in subsequent runs (see Fig. 2). The addition of an amount of MnO₂ (calculated to be amply sufficient to decompose all H₂O₂ produced quickly) to the bifunctional PVAm/CoPc thiol oxidation catalyst does not reduce the loss of activity in the second and third run (see Tab. 1). However, in the presence of MnO₂ the thiol oxidation activity diminishes to a constant level, whereas in the absence of MnO₂ it is almost completely vanished in the fourth run. For the explanation of this apparent stabilizing effect it is necessary to take into account the thiol oxidation capacity of MnO₂ itself. Actually, it has been shown that MnO₂ possesses a fairly high and stable catalytic activity for thiol oxidation in a PVAm solution without CoPc (see [45] and Tab. 1). Moreover, in the third run the activity of MnO₂ with PVAm is even somewhat higher than in the case of the PVAm/CoPc catalyst with MnO₂. Only with the latter catalyst system accumulation of H₂O₂ was found to occur and poisoning of the amine groups of PVAm by acidic by-products is then expected to take place (see [1]). So the lower activity from the third run of PVAm/CoPc with MnO₂ might be caused by the poisoning of the polymer base. The apparent stabilization of the PVAm/CoPc catalyst in the presence of MnO₂ is caused by the stable oxidation capacity of MnO₂ and is not the result of decomposition by MnO₂ of the H₂O₂.
Fig. 1. Initial rate of oxygen production as a function of the pH during decomposition of $\text{H}_2\text{O}_2$ with suspended MnO$_2$ powder (10.0 mg) as catalyst (conditions: see Experimental, $[\text{H}_2\text{O}_2]_{t=0} = 2.4 \cdot 10^{-2}$ mol/l, T = 22°C).

Fig. 2. Relative activity in subsequent runs for peroxide decomposition of suspended MnO$_2$ powder (conditions: see Experimental, T = 21°C, pH = 6). (a) 29.0 mg MnO$_2$ and $[\text{H}_2\text{O}_2]_{t=0} = 1.2 \cdot 10^{-2}$ mol/l in each run, and (b) 36.0 mg MnO$_2$ and $[\text{H}_2\text{O}_2]_{t=0} = 5.9 \cdot 10^{-2}$ mol/l in each run.
Tab. 1. Influence of the addition of MnO₂ on the activity and the stability of the PVAm/CoPc(SO₄Na)₄ catalyst \(^a\)

<table>
<thead>
<tr>
<th>Runs (n)</th>
<th>PVAm/CoPc</th>
<th>PVAm/CoPc with MnO₂</th>
<th>PVAm with MnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>v (v_{rel})</td>
<td>v (v_{rel})</td>
<td>v (v_{rel})</td>
<td>v (v_{rel})</td>
</tr>
<tr>
<td>1</td>
<td>9.2 1.00</td>
<td>13.3 1.00</td>
<td>3.6 1.00</td>
</tr>
<tr>
<td>2</td>
<td>3.3 0.36</td>
<td>4.9 0.37</td>
<td>3.6 1.00</td>
</tr>
<tr>
<td>3</td>
<td>1.9 0.21</td>
<td>2.7 0.20</td>
<td>3.6 1.00</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.05</td>
<td>2.6 0.20</td>
<td>3.6 1.00</td>
</tr>
<tr>
<td>5</td>
<td>&lt;0.05</td>
<td>2.6 0.20</td>
<td>3.6 1.00</td>
</tr>
</tbody>
</table>

\(^a\)Conditions: see Experimental, 10⁻⁴ mol amine (PVAm), 10⁻³ mol CoPc(SO₄Na)₄, 10.0 mg MnO₂, substrate: 2-mercaptoethanol (1ml, 14.25 mmol), T = 23°C.

\(^b\)v = rate of oxygen uptake \(\text{mol O}_{2} \cdot \text{min}^{-1}\).

\(^c\)\(v_{rel}\) = ratio of v in the nth run and v in the first run.

produced by the bifunctional catalyst. Presumably, the ability of MnO₂ to destroy the redundant peroxide is severely reduced by the presence of thiol. It can be concluded that our aim, i.e. avoiding of the accumulation of \(\text{H}_2\text{O}_2\) during thiol oxidation with bifunctional catalysts, can not be achieved by adding MnO₂.

The activity of lead dioxide \(\text{PbO}_2\) for peroxide decomposition was about 5 % of the activity of MnO₂, but \(\text{PbO}_2\) was found to be a stable catalyst. In contrast with MnO₂, no catalytic activity could be measured in the oxidation of thiols. This is not totally unexpected, since in an aqueous solution of thiol \(\text{PbO}_2\) is immediately converted to a yellow-green solid (presumably lead mercaptide) and similar reactions occur during Doctor sweetening [46]. In view of this reaction it is to be expected that \(\text{PbO}_2\) is unsuitable for \(\text{H}_2\text{O}_2\) decomposition during thiol oxidation. Indeed, our experiments have shown that even the employment of a large excess of \(\text{PbO}_2\) (i.e., 200 mg \(\text{PbO}_2\) with 10⁻⁴ mol amine and 2·10⁻⁶ mol CoPc) gave no improvement of the stability of the
bifunctional catalyst.

H₂O₂ decomposition measurements with Ag₂O have revealed that Ag₂O is very active but also very unstable: using a neutral aqueous suspension of 24.0 mg Ag₂O and 4.4 mmol H₂O₂ per run the activity in the third run decreased to 5 % of its original value. Therefore it is not surprising that Ag₂O did not improve the deactivation of the PVAm/CoFc catalyst.

4.3.2 Metal complexes

The activities of the Co, Fe and Mn-tetrasulphophthalocyanines as a function of pH are presented in Fig. 3. Vo-phthalocyanine which has only one axial coordination place available for the substrate H₂O₂ and Cu-phthalocyanine, in which all four available coordination sites are occupied by the phthalocyanine ligand, were almost inactive (see also [8, 27]). This confirms the idea that two free coordination positions must be available in order to get an active catalytic substance [1, 21, 22]. From the results obtained with Fe-, Mn-, and Co-phthalocyanine it is evident that optimum activities are obtained in the pH-range 10–12. The Fe-compound was found to be much more active than the Co-complex as was already expected from the literature data [8, 9, 19, 20, 27]. Unfortunately, Fe-, Mn-, and Co-phthalocyanine are found to be very labile in the presence of H₂O₂. This oxidative destruction of the phthalocyanine molecule is dependent on the pH of the solution and on the applied metal ion. In chapter 3 the destruction of CoFc as a function of the pH was described, and it was found that generally the stability towards oxidative destruction increases with increasing basicity. In Fig. 4 the production of O₂ from H₂O₂ and the simultaneously occurring decomposition of the Fe-complex is shown. Obviously, the rate of oxygen production decreases rapidly due to the degradation of the catalyst. It is remarkable that Fe-tetrasulphophthalocyanine is not completely destroyed by H₂O₂ (i.e. about 20 % remains intact, see Fig. 4); there seems to be no obvious explanation of this phenome-
Fig. 3. Amount of oxygen produced in 5 min as a function of pH during decomposition of H₂O₂ with water-soluble metallo-tetrasulphophthalocyanines (0.7·10⁻⁴ mol/l) as catalyst (conditions: see Experimental, [H₂O₂]t-o = 2.4·10⁻² mol/l, T = 22°C). (o) Fe, (•) Mn, (△) Co, and (••••••••) blank.

In the case of Mn-phthalocyanine the production of oxygen does not diminish simultaneously with the destruction of the Mn-complex (see Fig. 5); the presence of intact Mn-phthalocyanine and the occurrence of H₂O₂ disproportionation are not related. It must be concluded that MnPc itself is not an active catalyst for the reaction studied. In view of the known instability of Mn-phthalocyanine [47], one might suggest that Mn-oxide(s) is formed which provides for the measured catalytic activity. Indeed, the pH-dependence found for the apparent activity of Mn-phthalocyanine (Fig. 3) and for the activity of MnO₂ (Fig. 1) are in very good agreement with each other. The apparent activity of Mn-phthalocyanine is somewhat higher than the activity of MnO₂ (with the same amount of Mn), which is presumably caused by a lower dispersion when starting with MnO₂.

The turnover number for peroxide decomposition of the
Fig. 4. Oxygen production and the percentage of intact Fe-tetrasulphophthalocyanine (determined by following the absorbance at 15000 cm\(^{-1}\)) as a function of time during decomposition of H\(_2\)O\(_2\) (conditions: see Experimental, starting with 3 \(\cdot\) 10\(^{-6}\) mol of catalyst, [H\(_2\)O\(_2\)]\(_{t=0}\) = 2.4 \(\cdot\) 10\(^{-2}\) mol/l, pH = 10.7, T = 22\(^\circ\)C).

Fig. 5. Oxygen production and the percentage of intact Mn-tetrasulphophthalocyanine (determined by following the absorbance at 16000 cm\(^{-1}\)) as a function of time during decomposition of H\(_2\)O\(_2\) (conditions: see Experimental and Fig. 4).
most active phthalocyanine, Fe-phthalocyanine, is approximately 200 times lower than the turnover number of CoPc in bifunctional thiol oxidation catalysts. This means that a large excess of the Fe-complex with respect to the Co-complex must be used in the thiol oxidation experiment. However, even when we employed such large excessive amounts of Fe-complex no improvement of the stability of CoPc/FVAm catalysts was observed. Presumably, thiol molecules hinder the H₂O₂ molecules in coordinating to the Fe-nucleus of the phthalocyanine and prohibit the decomposition of the H₂O₂ produced. It is not surprising that Fe-phthalocyanines form complexes with RSH since these compounds possess some catalytic activity (i.e., more than 35 times less active than CoPc [28]) for thiol oxidation.

4.3.3 Activated carbon

The results in Tab. 2 show that the catalytic activities of the various activated carbons differ widely. In accordance with literature data [34, 35] the basicity of the surface is a very important factor determining the activity, but the basicity of the surface alone allows no satisfying explanation of the results. Other factors, like the pore size distribution and the pore structure, will also influence the activity of the activated carbons. In Fig. 6 the activity of Norit MRX for decomposition of H₂O₂ as a function of the number of subsequent runs is depicted and it is seen that the catalyst deactivates fairly rapidly. Besides the decomposition of H₂O₂, activated carbon catalyzes a great variety of reactions [48] including the oxidation of H₂S and thiols [49, 50]. Obviously, the basicity of the surface is also important for the thiol oxidation activity (cf. Tab. 2). Measurements of the thiol oxidation activity of Norit MRX as a function of the number of subsequent runs (Fig. 7) reveal that this catalyst suffers from rather rapid deactivation. It has been investigated whether the addition of activated carbon resulted in any improvement of the stability of the bifunctional
Tab. 2. The catalytic activity of various types of activated carbons for \( \text{H}_2\text{O}_2 \) decomposition and thiol oxidation

<table>
<thead>
<tr>
<th>type of carbon</th>
<th>pH-value</th>
<th>thiol oxidation ( \text{v (mlO}_2\text{-min}^{-1}) )</th>
<th>( \text{H}_2\text{O}_2 ) decomposition ( \text{v (mlO}_2\text{-min}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Merck p.a.</td>
<td>6.7</td>
<td>1.14</td>
<td>0.12</td>
</tr>
<tr>
<td>Mekog C</td>
<td>6.7</td>
<td>1.72</td>
<td>0.18</td>
</tr>
<tr>
<td>Norit R1 extra</td>
<td>9.3</td>
<td>5.48</td>
<td>5.00</td>
</tr>
<tr>
<td>Norit R2 extra</td>
<td>9.3</td>
<td>5.56</td>
<td>5.33</td>
</tr>
<tr>
<td>Norit MQ</td>
<td>9.8</td>
<td>9.76</td>
<td>16.00</td>
</tr>
<tr>
<td>Norit MBX</td>
<td>10.3</td>
<td>8.70</td>
<td>5.80</td>
</tr>
</tbody>
</table>

a) Determination of the pH-value according to the method described in Norit Testing Methods (publication: Norit NV, Amsersfoort-Holland).
b) Conditions: see Experimental, 1.0 g carbon (pulverized) was used, substrate: 2-mercaptoethanol (1 ml, 14.25 mmol), T = 23°C.
c) Conditions: see Experimental, 0.5 g carbon (pulverized) was used, substrate: \( \text{H}_2\text{O}_2 \) (0.9 mmol), T = 21°C.

Tab. 3. Influence of the addition of activated carbon (Norit MBX) on the activity and stability of the PVAm/CoPc(\( \text{SO}_3\text{Na} \))\(_4\) catalyst

<table>
<thead>
<tr>
<th>Number of runs (n)</th>
<th>PVAm/CoPc ( \text{v (mlO}_2\text{-min}^{-1}) )</th>
<th>PVAm/CoPc ( \text{v (mlO}_2\text{-min}^{-1}) ) with carbon, ( \text{v} )</th>
<th>PVAm/CoPc ( \text{v (mlO}_2\text{-min}^{-1}) ) with carbon, ( \text{v} )</th>
<th>PVAm ( \text{v (mlO}_2\text{-min}^{-1}) )</th>
<th>PVAm ( \text{v (mlO}_2\text{-min}^{-1}) ) with carbon, ( \text{v} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.2</td>
<td>1.00</td>
<td>12.9</td>
<td>1.00</td>
<td>7.7</td>
</tr>
<tr>
<td>2</td>
<td>3.3</td>
<td>0.36</td>
<td>6.0</td>
<td>0.47</td>
<td>3.6</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
<td>0.21</td>
<td>4.1</td>
<td>0.32</td>
<td>2.7</td>
</tr>
<tr>
<td>4</td>
<td>&lt;0.05</td>
<td>2.9</td>
<td>0.22</td>
<td>1.8</td>
<td>0.23</td>
</tr>
</tbody>
</table>

a) Conditions: see Experimental, \( 10^{-4} \) mol amine (PVAm), \( 10^{-8} \) mol CoPc(\( \text{SO}_3\text{Na} \))\(_4\), 0.5 g Norit MBX (powdered), substrate: 2-mercaptoethanol (1 ml, 14.25 mmol), T = 23°C.
b) \( \text{v} \) = rate of oxygen uptake (mlO\(_2\)-min\(^{-1}\)).
c) \( \text{v}_{\text{rel}} \) = ratio of \( \text{v} \) in the \( n \)th run and \( \text{v} \) in the first run.
Fig. 6. Relative activity in subsequent runs for peroxide decomposition of suspended Norit MRX (0.5 g, powdered). (conditions: see Experimental, in each run $[\text{H}_2\text{O}_2]_0 = 5.9 \times 10^{-2}$ mol/l, no base added, $T = 24^\circ\text{C}$).

Fig. 7. Relative activity in subsequent runs for the autoxidation of 2-mercaptoethanol with suspended Norit MRX (1.0 g, powdered) as catalyst (conditions: see Experimental, 1 ml (14.25 mmol) RSH in each run, no base added, $T = 23^\circ\text{C}$).
thiol oxidation catalyst.

Tab. 3 gives the results of the measurements on the oxidation activity of the PVAm/CoPc catalyst, the PVAm/CoPc catalyst in the presence of Norit MRX, and of Norit MRX in the presence of PVAm without CoPc. Analyzing the obtained results learns that the activity of the bifunctional catalyst with Norit MRX is composed of contributions from Norit MRX and from the PVAm/CoPc catalyst. It must be concluded that the addition of Norit MRX does not result in a substantial improvement of the stability of the polymeric catalyst. Moreover, it has been found that peroxide accumulation resulting from the action of the PVAm/CoPc catalyst still occurs when carbons are present, although in the absence of thiol comparable amounts of peroxide are quickly decomposed by the applied amounts of carbon.

4.4 Conclusions

As stated in the Introduction we aimed at the catalytic decomposition of $\text{H}_2\text{O}_2$ produced during thiol oxidation with bifunctional catalysts and have therefore investigated the properties of some metallic oxides, metallo-phthalocyanines and activated carbons. The metallic oxides (MnO$_2$, Ag$_2$O and PbO$_2$) possess high activities for peroxide decomposition, but unfortunately this activity was dramatically reduced in the presence of thiol. Presumably, thiol molecules displace the H$_2$O$_2$ molecules from the active sites on these metallic oxides. Furthermore, the stability of MnO$_2$ (see Fig. 2) and Ag$_2$O for peroxide decomposition is rather low. Carbons which are active for peroxide decomposition are also active for thiol oxidation (cf. Tab. 2), but in the presence of thiols the activity for the decomposition of H$_2$O$_2$ is almost entirely suppressed. Apparently, also the active sites on the carbon surface strongly prefer the reaction with thiol molecules rather than with H$_2$O$_2$ molecules.

In this investigation we have simply suspended the metallic oxides and activated carbons in the reaction medium.
containing the PVAm/CoPc catalyst. In case the PVAm/CoPc catalyst would have been chemically coupled to such solid substances in principle a more efficient system might have been obtained, because a shorter distance between thiol oxidation sites and \( \text{H}_2\text{O}_2 \) decomposition sites would exist. However, because inhibition by thiols will occur in any case, the way in which the peroxide decomposition catalysts are applied will not substantially affect our conclusions. Therefore, further investigation on junction of metallic oxides and activated carbons with the PVAm/CoPc catalyst (as proposed in Scheme I-a) did not seem very fruitful and was not carried out.

The sensitivity for oxidative destruction of the metallophthalocyanines, which are active for peroxide decomposition, severely reduces the applicability of these substances. Since several authors have shown that the monomeric form of metallophthalocyanines is by far the most active species [20], a further disadvantage of these compounds is their tendency to dimerize. Despite the mentioned disadvantages it was found that especially Fe-tetrasulphophthaloxyanine is a fairly active catalyst for peroxide decomposition. However, also this compound is not able to destroy peroxide efficiently during thiol oxidation with bifunctional catalysts. Also here the thiol molecules compete with the \( \text{H}_2\text{O}_2 \) molecules for the coordination sites of the Fe-nucleus of the phthalocyanine. Although the problem of dimerization and oxidative destruction of the phthalocyanines may be obviated by polymer attachment of the phthalocyanine molecules at low concentration [32], the preference of the metal ion to react with thiol rather than with \( \text{H}_2\text{O}_2 \) seems to be unavoidable. Therefore, it is surprising that in a UOP patent [30] the employment of Mn-phthalocyanine for peroxide decomposition during thiol oxidation is recommended. Moreover, the instability of Mn-phthalocyanine noticed by us and others [47] raises still more doubt to the claim in the patent. We deduce from our measurements that Mn-phthalocyanine itself is not an active catalyst for peroxide decomposition, but an apparent high activity can readily be
observed due to the action of the degradation product(s) (i.e. manganese oxide(s)).

We conclude that the catalysts we have tested for the decomposition of $H_2O_2$, which are among the most powerful known in the literature, are unsuitable for our purposes because of the inhibition by thiols. Since no method for catalytic decomposition of peroxide during thiol oxidation has been found, the $H_2O_2$ accumulation must be kept at the lowest possible level by applying appropriate reaction conditions (see [1, 40]).

References

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33 G. Lemoine, Compt. rend., 144 (1907) 357.
38 J. Manassen, Fortschr. Chem. Forsch., 25 (1972) 1, and references therein.
CHAPTER 5

SALT AND MEDIUM EFFECTS
ON THE CATALYTIC OXIDATION OF THIOLS

5.1 Introduction

In our research on the catalytic oxidation of thiols we have used so far exclusively water as the reaction medium. However, in various fields of chemistry remarkable effects on reaction rates have been found by merely changing the solvent composition [1] and it may be interesting to examine if our thiol oxidation catalyst has a better performance in apolar media. Such an investigation will give the opportunity to elucidate the role of water in the overall reaction mechanism and would be of technological interest because it might result in a more simple method for the oxidation of thiol sulphur compounds in cracked gasolines (sweetening, see chapter 1). The industrial processes are usually carried out in a two-phase system, an oil phase containing the thiol and an aqueous phase containing the required base [2, 3]. The poly(vinylamine) (PVA)/cobaltphthalocyanine (CoPc) catalysts do not require additional base as a promoter and, therefore, they provide a possibility of avoiding the aqueous phase.

As described in chapter 1 the UOP Merox process can be used for autoxidation of thiols as well as for extraction of low molecular weight thiols from oil distillates. Extraction is accomplished with an aqueous alkaline solution and apparently it is common practice to enhance the solubility of the thiols by adding a water-soluble alcohol (i.e. usually from about 2 to about 100 vol.-% methanol) [2, 4]. Regeneration of the extraction liquid implies the conversion of thiols to disulphides and it may be expected that the presence of alcohols will have an effect on the rate of this oxidation. To our knowledge no literature data are
available on this catalytic oxidation of thiols in mixed water-alcohol solvents and, therefore, we decided to investigate the oxidation reaction in these mixtures.

Hitherto we have not investigated the influence of the addition of salts on the oxidation rate, though it is well established that the kinetics of homogeneous catalytic reactions are often complicated by salt effects [1, 5, 6]. Therefore, we will give in this chapter also a preliminary account of the pronounced effects of the ionic strength of the reaction mixture on the rate of the catalytic oxidation of thiols.

5.2 Results

5.2.1 Activities of the polymeric catalysts in toluene

Surprisingly, no activity of the bifunctional catalyst is observed in pure toluene as reaction medium. However, when a slight amount of water is added (i.e. about 0.15 vol.-%) a fairly high activity can be measured (see Fig. 1). Further addition of water gives rise to an increase of the catalytic activity up to a certain level. Evidently, the presence of water is essential for the activity of the bifunctional catalysts. It should be noted that the activity of the catalytic system in pure water is about half of the activity in a mixture of toluene with 2.8 vol.-% H₂O. The bifunctional catalyst not only is active in predominantly apolar toluene-water mixtures but even performs better than in pure water.

As described in chapter 2 polymer attachment of the cobalt-phthalocyanine may be achieved by complexation through polymeric amine groups (catalyst I) as well as by formation of a peptide linkage between the phthalocyanine ring system and the polymeric carrier (catalyst II). In order to compare the activities of catalyst I and II we carried out experiments in toluene (70 ml)/water (1 ml, i.e. 1.4 vol.-%) mix-

Experimental details are described in chapter 2.
Fig. 1. The average activity ($v$, ml of $O_2$ and mg of catalyst) of catalyst II (see chapter 2) in toluene (70 ml) as a function of the vol.-% of added water (conditions: see Experimental in chapter 2, always about 5 mg of catalyst was used, substrate: 1 ml (14.25 mmol) 2-mercaptoethanol, $T = 22^\circ C$).


tures. The specific rate observed for catalyst I ($10^{-8}$ mol $\text{CoPc(COONa)}_4/10^{-4}$ mol amine) is 67 m$\text{lO}_2$·$\text{mmolCO}^{-1}$·min$^{-1}$ and for catalyst II ($1.16 \cdot 10^{-8}$ mol $\text{CoPc(COONa)}_4/1.25 \cdot 10^{-4}$ mol amine) it is 442 m$\text{lO}_2$·$\text{mmolCO}^{-1}$·min$^{-1}$. The catalytic activity of catalyst II in this medium is comparable to that in pure water (see Tab. 3 in chapter 2) and so are the relative activities in successive runs (run 1: 1.00, run 2: 0.47, run 3: 0.07; cf. Tab. 4 in chapter 2).

5.2.2 Activities of the catalysts in the presence of alcohols

In Fig. 2 the activity of the bifunctional polymeric catalysts for the oxidation of 2-mercaptoethanol is presented as a function of the volume percentage of ethanol in the reaction medium. A severe decrease in activity occurs on increasing the organic component of the reaction mixture.
Fig. 2. Relative activity of catalyst I (●) \(10^{-9}\) mol Co/2 \(10^{-5}\) mol amine and catalyst II (○) \(3 \cdot 10^{-9}\) mol Co/9 \(10^{-5}\) amine) for the autoxidation of 2-mercapto-ethanol as a function of the vol.-% ethanol in the ethanol/water mixture (conditions: see Experimental in chapter 2, 1 ml (14.25 mmol) RSH, \(T = 23^\circ C\)).

up to 50 vol.-%, solvent systems with more than 50 vol.-% ethanol were not investigated. The decrease in activity is not dependent on the method of polymer attachment of the CoPc (see Fig. 2). Since the influence of alcohol on the catalytic activity of the bifunctional catalysts might be caused by changes of the conformation and the coil density of PVAm, also the effect in conventional CoPc/NaOH systems (without polymeric base) was investigated. The catalytic activity of CoPc(8O₂Na)₄ in the presence of NaOH as a function of solvent composition is given in Fig. 3. A decrease in reaction rate is also obtained in this case for solutions containing less than 50 vol.-% ethanol, but surprisingly above 50 vol.-% an increase is observed and a pronounced maximum is attained at about 92 vol.-%.

Evidently, there exists a dramatic dependence of the catalyst activity on the solvent composition: a gain in activity of a factor 10 may be acquired by using a medium with about
Fig. 3. The average activity of CoPc(SO$_3$Na)$_{4}$ ($\bar{\nu}$) (ml of O$_2$ and mmol of Co) for the autoxidation of 2-mercaptoethanol as a function of the vol.-% of ethanol in the ethanol/water mixture (measurements carried out in duplicate, conditions: see Experimental in chapter 2, 2·10$^{-3}$ mol CoPc, 1 ml (14.25 mmol) RS$_2$H, 2 mmol NaOH, $T = 23^\circ$C).

90 vol.-% alcohol instead of pure water.

The effect of changing the type of alcohol on the rate of thiol oxidation was determined in mixed solvents containing 10 vol.-% alcohol (see Fig. 4). For the water-soluble alcohols the inhibiting action becomes progressively larger with increasing length of the alkyl group of the alcohol. Thus methanol effects the rate of oxidation less than ethanol, propanol-1 and butanol-1. For the water-immiscible alcohols (i.e. pentanol-1 and hexanol-1) the inhibition is smaller and an even somewhat higher activity in 10 vol.-% hexanol-1 than in pure water was found.

Attempts to find an explanation for these results (cf. Figs. 2, 3 and 4) are made difficult by the complicated chemistry of the phthalocyanines in aqueous solution: they have a complex axial coordination chemistry [7] and aggre-
Fig. 4. The effect of the type of alcohol on the relative activity of CoPc(SO$_3$Na)$_4$ for the autoxidation of 2-mercaptoethanol in water/alcohol (9/1, v/v) mixtures (conditions; see Fig. 3).

gation of the phthalocyanine molecules may occur [8-12]. It is well established that the addition of polar organic solvents like alcohols may inhibit the formation of polymeric species [9-12]. We have measured the visible light spectra of CoPc(SO$_3$Na)$_4$ (under conditions comparable with activity measurements but without thiol) as a function of the composition of water/alcohol mixtures (Fig. 5). For a solution containing 50 vol.-% ethanol the aggregation is indeed considerably less than in pure water, but on further increasing the percentage of the organic component we obtain at 90 vol.-% the spectrum typical for highly aggregated CoPc species. Since the applied CoPc(SO$_3$Na)$_4$ is insoluble in pure ethanol, we conclude that the observed aggregation at 90 vol.-% is due to a decreased solubility. Judging from the low extinction some precipitation of CoPc(SO$_3$Na)$_4$ may even take place in the water/ethanol (10/90, v/v) mixture.
5.2.3 The influence of the addition of salt on the catalytic activity

The influence of the addition of NaCl on the rate of oxidation of 2-mercaptoethanol with a conventional catalytic system consisting of CoPc(903Na)₄ with NaOH (without polymeric base) is illustrated in Fig. 6. Surprisingly, the addition of NaCl dramatically promotes the rate of oxidation and in this conventional system even specific rates are obtained which are about equal to those encountered with polymeric catalysts [13, 14]. Moreover, in case of PVAm/CoPc catalysts normally a severe loss of activity in subsequent runs is observed, whereas with the conventional CoPc/NaOH system in the presence of NaCl the loss of activity is less prominent (see Fig. 7). On the other hand, it must
Fig. 6. The average activity of CoPc(SO$_3$Na)$_4$ (V) (ml of O$_2$ and μmol of Co) for the autoxidation of 2-mercapto-ethanol as a function of the ionic strength (μ) of the reaction medium (conditions: see Experimental in chapter 2, 2·10^{-8} mol CoPc, 6 mmol NaOH, 1 ml (14.25 mmol) RSH, μ was varied by using NaCl, T = 21°C).

It should be stressed that the bifunctional polymeric catalysts allow efficient operation in the absence of alkaline base [13] and offer also the possibility of designing heterogeneous bifunctional catalysts (as illustrated in chapter 1, Fig. 1d and chapter 7).

It is well-known that the aggregation of metallophthalocyanines (and -porphyrins) in aqueous solution may be enhanced by addition of salts [10, 12, 14]. Our visible light spectral measurements on CoPc(SO$_3$Na)$_4$ in alkaline solution (i.e. about the same conditions as during catalytic experiments, however without thiol) confirm that aggregation is
Fig. 7.
Relative activity in subsequent runs for the autoxidation of 2-mercaptoethanol (1 ml, 14.25 mmol): (a) CoPc(SO₃Na)₄ (2.10⁻⁸ mol)/NaOH (6 mmol) in the presence of NaCl (μ = 2.5 mol/l, T = 21°C), and (b) CoPc(COOH)₄ covalently attached to PVAm (catalyst II; data from Tab. 4 in chapter 2).

Fig. 8.
The influence of the addition of salt on the visible light absorption spectra of 2.5 μmol/l CoPc(SO₃Na)₄ solutions at ambient temperature (solvent: water, 0.1 mol/l NaOH, optical path length: 50 mm). (a) no salt added, and (b) 3.0 mol/l NaCl added.
favoured by addition of NaCl (see Fig. 8). The spectrum recorded with an ionic strength of \( \mu = 3.0 \) reveals strong polymerization of the CoPc molecules and comparison with the spectrum without NaCl leads to the conclusion that some precipitation occurs under these circumstances.

In order to determine the influence of the type of salt applied, we have performed experiments at \( \mu = 1.0 \) using various electrolytes. It was determined, that the promoting effect of alkali metal-chlorides may be represented as \( \text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ \). In case of potassium halides the activity was in the order \( \text{Cl}^- < \text{Br}^- < \text{I}^- \), whereas the promoting effect of NaClO₄ is lower than that of NaCl.

Surprisingly, CoPc(SO₃Na)₄ (10⁻⁸ mol) coupled by complexation to PVAm (10⁻⁴ mol amine) possessed no catalytic activity at all in the presence of 3.0 mol/l NaCl (i.e. under optimal conditions for the polymer-free catalytic system). In the presence of 3.0 mol/l NaCl the PVAm molecules will adopt a condensed conformation because the polyelectrolyte effect is totally suppressed. So presumably the absence of catalytic activity can be explained by poor accessibility of the active sites located in the polymeric coils.

5.3 Discussion

5.3.1 Polymeric catalysts in toluene

The results presented in Fig. 1 clearly indicate, that small amounts of water are required to obtain an active catalytic system. This phenomenon may be explained by considering an intermediate proposed to be formed during the catalytic oxidation of thiol [15]. At the stage depicted in scheme 1 protonation of the coordinated oxygen has to take place for the reaction to proceed. Protonation requires an effective proton transfer medium. Because of the hydrophility of the polymer used, added water will preferentially be in the environment of the polymer, therefore even
Scheme I. An intermediate situation at the PVAm/CoPc catalyst during the autooxidation of thiol.

small amounts of water are sufficient to provide the required proton transfer.

The non-ionie nature of the bonding of thiol to the amine carrier in an apolar medium may be another reason for the requirement of water, since it would inhibit the formation of a sufficiently reactive thiolate anion. In a dipolar aprotic solvent this inhibition might be avoided, but in DMP we found no catalytic activity. We therefore conclude that a proton transfer medium is essential for the catalytic reaction.

5.3.2 Catalytic activity in water/alcohol mixtures

In chapter 6 evidence will be presented to support our hypothesis that the catalytic activity of substituted cobalt-phthalocyanines for the oxidation of thiols is mainly due to monomeric species [14]. Since the formation of monomeric phthalocyanine in aqueous solution is favoured by the addition of an alcohol [9-12], a larger activity is expected for ethanol/water mixtures than for pure water. Surprisingly, for an alkaline CoPc solution a completely different result was obtained up to about 50 vol.-% ethanol. Although visible light spectral measurements demonstrated an increase of the monomer fraction (Fig. 5) a decreasing activity was observed (Fig. 3). Above 50 vol.-% the activity increases strongly, but the visible light spectral measurements indicate aggregation and possibly some precipitation at
90 vol.-% ethanol. Yet at this solvent composition a maximum activity is reached.

Apparently, an increase in monomeric species is not paralleled by an enhancement of the specific catalytic activity and it seems very likely that the observed activity pattern (Fig. 3) must be explained by other factors. This is supported by results presented in Fig. 2: for CoPc(COOH)$_4$ covalently attached to PVAm, no variation in the monomer/dimer equilibrium can occur but nevertheless a drastic decrease in activity is observed when using a medium with about 30 vol.-% ethanol instead of pure water.

The activity changes with varying solvent composition may perhaps be explained by solvation effects [1]. The regions of 10-30 and 80-90 wt.-% of organic component in a organic solvent-water system show in many instances drastic solvent effects. These are the regions in which the first, respectively the final hydration layers of any ion are replaced by the organic solvent. There exists a good similarity between our results (Fig. 3) and the activity patterns found for various chemical reactions in mixed solvent systems. For example, our results are in striking conformity with the data published for the reaction between $\text{UO}_{2}^{4+}$ and $\text{UO}_{2}^{6+}$ ions in water-ethylene glycol mixtures [16].

Although a gross understanding exists of how the presented kinetic effects can be based on solvation phenomena, many details about the molecularity of the effects remain to be elucidated. The maximum in the thiol oxidation activity found at about 90 vol.-% ethanol will now be discussed in some detail. It is generally accepted that substitution reactions of octahedral complexes in water go via aquo compounds rather than via direct ligand substitution [17]. Therefore, in pure water each step given in scheme II (that represents a possible mechanism of the catalytic oxidation of thiol) will consist of replacement of a particular ligand by a water molecule and subsequent replacement of this water molecule by a new ligand. In a solvent with poorer coordinating properties (i.e., for instance alcohols) a direct substitution without solvent intermediates may be possible [S$_{E}$]
Scheme II. Tentative mechanistic representation of the autoxidation of thiols catalyzed by CoPc/NaOH.

mechanism). In the case that also in alcohol the reaction proceeds via solvent intermediates (S₈₂ mechanism), these intermediates will be less stable and thus more reactive than their aquo counterparts [17]. Thus irrespective of which of the two substitution mechanisms is operative a higher substitution rate may be obtained in predominantly alcoholic solution and this may be the explanation of the maximum in the activity curve at about 92 vol.-% ethanol in Fig. 3. Furthermore, the high catalytic activity at about 90 vol.-% may be caused by the fact that not only the catalyst but also the reactants such as for instance RS⁻ will be dehydrated resulting in an enhancement of the reactivity of these species. The decrease of activity above about 92 vol.-% ethanol must be ascribed to the precipitation of the homogeneous catalyst.

The loss of activity as observed up to about 50 vol.-% ethanol (Fig. 3) is probably caused by some kind of cage effect [1]. In the region 0-50 vol.-% ethanol the inner hydration layer of the reactants and catalyst will be unaffected by alcohol molecules but with increasing organic component the outer solvation spheres will progressively be filled with alcohol molecules. Presumably, the organic
solvent layer forms a barrier hindering reaction of the
the reactants and/or the catalyst and the water molecules
can hardly escape from the solvent cage that surrounds them.
Thus at the average the water molecules will become more
firmly attached and the reaction rate will decrease. This
explanation is supported by the results obtained with
different types of alcohols (Fig. 4). For water-miscible
alcohols the inhibition of the catalytic system is less for
alcohols that resemble water most, since a water-like solvent
such as methanol does not shield as effectively the
reactants from the bulk of the solution as more apolar
alcohols like propanol-1 and butanol-1. In case of water-
immiscible alcohols (i.e. especially pentanol-1 and hexanol
-1) separate organic and aqueous phases are formed and the
oxidation rate is not appreciably influenced by the organic
part of the reaction mixture. Due to increased concentrations
of reactants and catalyst in the aqueous phase even
a somewhat higher activity can be observed in a water (90
vol.-%)/hexanol-1 (10 vol.-%) mixture than in pure water.

5.3.3 Catalytic activity in the presence of salts

It has often been observed that the aggregation of
metallophthalocyanines in aqueous solution increases with
the ionic strength [10, 12, 14]. Since we have shown that
monomeric species are the most active form in the catalytic
oxidation of thiols [14], we would expect a decrease in
catalytic activity with increasing electrolyte concentration.
However, the experimental results (cf. Fig. 6) show an
entirely different pattern, it is only in very concentrated
electrolyte solutions that a fall in activity occurs. This
decrease in activity is presumably caused by the precipita-
tion of CoPc(SO$_4$Na)$_4$ in the concentrated salt solution (see
[18]); limited solubility even in a 3.0 M solution is
indicated by the visible light spectral measurements (cf.
Fig. 8). Consequently, the increase of the activity on
addition of salt (up to 3.0 M) is not caused by a shift in
the monomer/dimer equilibrium.
Interpretation of effects of salts on the kinetics of reactions in water attracts continued interest [1, 6]. The now classical primary and secondary kinetic salt effects just as ion-pair formation [1, 5, 6] will certainly affect the reaction rate in our catalytic system, but the measured influence of the type of added electrolyte show that also specific salt effects are operative. For instance, the electrolyte may participate into the axial interactions which are thought to play an essential role in the catalytic process (see scheme II). In aqueous solutions the axial interaction of water with the metal is of fundamental importance to both redox and substitution reactions [17, 19-21]. In the preceding part of this Discussion it was already pointed out that aquo intermediates will occur in the catalytic cycle. In this respect it is noteworthy that it has been determined [17, 22] that anions, such as Cl⁻, will usually cause an increased rate of water exchange when coordinated to the same metal ion. Such an enhancement of the conversion rate of a solvent intermediate (i.e. a trans-effect) may of course increase the overall reaction rate.

Another comparable effect may be that the negative charge of the sulpho-groups on the Co-phthalocyanine molecule is compensated by ion-pair formation with alkali ions [23]. It is assumed that the charges at the periphery of porphyrins appreciably influence the size of the molecular orbitals containing the \( \pi \)-electrons and hence the delocalization of the electron density of the metal center [24]. Substantial effects of the peripheral charge on the ease of reduction and on the substitution rates of the metal center of substituted porphyrins have been described [25]; relative to positively charged peripheries, a negative periphery leads to a concentration of electron density near the porphyrin core and makes the metal ion more resistant to reduction. Thus, in our case it may be expected that the cobalt redox couple is favourable influenced by compensation of negatively charged sulpho-groups by added salt (i.e. a cis-effect).

In addition to the more classical ionic-strength
effects and the just now described (cis- and trans-) effects of salts on the reactivity of the CoPc, the kinetics of the catalyzed thiol oxidation can also be considered in the light of influences of added salt on the "water structure" [26]. In a salt-free reaction mixture we may expect, as already pointed out before, that the substitution reactions involved in the catalytic cycle (scheme II) proceed via aquo intermediates. An important reason for this phenomenon is that water has a much higher effective concentration than the reactant molecules. However, this may be different under conditions of optimal activity (i.e., with about 3.0 M NaCl, see Fig. 6). Under these conditions there are about 20 moles of H₂O available for each mole NaCl. Both Na⁺ and Cl⁻ will strongly attract solvent molecules and around each ion an inner-layer of polarized, immobilized water molecules will be formed. The effect of the ions will not be restricted to a first coordination sphere of H₂O molecules but will be extended to more layers [1, 26].

When assuming as a first approximation the same solvation number of the Na⁺ and Cl⁻ ion, about ten molecules H₂O are available per ion. Since in the first hydration layer 6 molecules may be located and hydration numbers for Na⁺ and Cl⁻ exceeding 10 are often encountered in the literature [1], it may be concluded that in an aqueous 3.0 M NaCl solution only a very limited amount of unrestricted H₂O molecules will be available. Obviously, the probability for aquo intermediates in the catalytic cycle will be seriously reduced and direct replacement of one ligand by another will be favoured which may enhance the overall thiol oxidation rate. Furthermore, on addition of NaCl the solvation of the reactant molecules will progressively diminish because of the relatively strong coordinating power of Na⁺ and Cl⁻ ions. Therefore, an enhancement of the reactivity of for instance RS⁻ may be expected when increasing the amount of NaCl; in case an thiolate ion is practically unsolvated (or "naked"), it will be very reactive.

Several explanations of the enhanced catalytic activity in the presence of added electrolytes have now been presented.
and it seems impossible to assess the importance of the various effects. Evidently, a further detailed kinetic study on these phenomena will be necessary to be able to obtain more definite conclusions. However, it seems appropriate to stress the similarity between the salt and solvent effects (cf. Figs. 3 and 6). In both cases optimal activity is obtained under such conditions that the amount of available $H_2O$ is limited. Therefore, it may be tentatively concluded that although a certain amount of $H_2O$ is necessary for the oxidation reaction to proceed, an optimal activity may be obtained when the amount of "free" water is kept to a minimum.

References

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CHAPTER 6

COBALT-PHTHALOCYANINE/POLY(VINYLAMINE) COMPLEXES AS BIFunctional CATALYSTS IN THE AUTOxIDATION OF THIOLS,
EFFECT OF THE DISTRIBUTION OF COBALT SITES OVER THE POLYMERIC COILS

6.1 Introduction

Metallophthalocyanines have attracted considerable interest because of their structural similarity with the naturally occurring porphyrins [1, 2]. Metalloporphyrins [2, 3] and phthalocyanines [4, 5] are well known oxidation catalysts, e.g. for thiols. An effective catalyst for the autoxidation of thiols should possess oxidation sites and basic sites in cooperative interaction [6-8]. In this chapter such bifunctional catalysts composed of a water-soluble cobaltphthalocyanine (CoPc) and a polymeric base are described. The prepared polymeric catalysts are being tested for the autoxidation of thiols (RSH) to disulphides (RSSR) in aqueous media:

\[
\text{......-NH}_2 + \text{RSH} \rightarrow \text{......-NH}_3^{\text{+}} \text{SR} \quad (1)
\]

\[
\text{......-NH}_3^{\text{+}} \text{SR} + \text{RSH} + \text{O}_2 \overset{\text{CoPc}}{\rightarrow} \text{......-NH}_2 + \text{RSSR} + \text{H}_2\text{O}_2 \quad (2)
\]

In previous papers [7, 8] it was shown that a particularly active catalytic system could be obtained using poly-(vinylamine) (PVAm) as the polymeric base. It was suggested [7, 8], that two phenomena, both inherently connected with the polymeric character of the base, account for the observed high activity of these bifunctional catalysts. Firstly, a more effective cooperation between oxidation sites and basic sites is achieved when using a polymeric base instead of a low molecular weight base. Taking into consideration the proposed mechanism of the reaction [7], an enhanced rate
of oxidation due to this effect may be expected. Secondly, the shielding effect exerted by the polymeric coils hinders undesirable dimerization reactions of CoPc molecules.

In case of conventional (i.e. polymer-free) CoPc/NaOH systems, in the presence of oxygen and substrate, dimerization reactions of CoPc molecules cannot be avoided and binuclear dioxygen adducts (A) are formed. These adducts are fairly stable, giving rise to a relatively low overall catalytic activity. On the other hand, in CoPc solutions in the presence of a sufficient excess of polymeric base, separation of cobalt centers may be achieved. In this case, the formation of the instable (i.e. reactive) mononuclear oxygen adduct (B) will be favoured during the oxidation reaction [7, 9], resulting in a relatively high overall reaction rate.

\[ \text{RS}^- + \text{Co}^2+ - \text{O} - \text{O} - \text{Co}^2+ - \text{SR} \]

A

\[ \text{RS}^- + \text{Co}^2+ - \text{O} - \text{O} \]

B

In this chapter we wish to present further supporting experimental evidence to this hypothesis. For this purpose the results of catalytic experiments on the antioxidation of thiols with CoPc/PVAm catalysts will be correlated with optical data on the CoPc/PVAm complexes. Because of the strongly complexing properties of PVAm towards CoPc, it might be expected that with increasing concentration of PVAm at a constant CoPc concentration, the formation of mononuclear CoPc species will be promoted. A statistical calculation on the distribution of CoPc over the PVAm chains confirms this presumption, and the results of this calculation are compared with the kinetic data obtained from catalytic experiments. Furthermore, from this statistical calculation a molecular weight dependence of the specific catalytic activity of the CoPc/PVAm systems might be
expected. The results of the measurements on the influence of the number average molecular weight of the PVAm on the catalytic activity are presented and discussed.

6.2 Experimental

Catalyst preparation

Poly(vinylamine) (PVAm): the preparation of this poly-
mer has been described in chapter 2. The prepolymer poly-
(N-vinyl-tert-butyl carbamate) (PVCa) was prepared from the
respective monomer under nitrogen in benzene with 2,2’-
azo-bis-isobutyronitrile, (AIBN) as initiator (reaction time:
10 h, T = 60°C) [10]. Products (PVCa) with different average
degrees of polymerization ($\bar{P}_n$) were obtained by varying the
amount of AIBN (see Tab. 1).

Tetrasodium salt of Cobalt (II)-tetracarboxy phosphalocyanine
(CoPc(SO$_3$Na)$_4$): this compound was prepared as described in a
previous paper [7].

Complexation of CoPc(SO$_3$Na)$_4$ and PVAm: for this purpose
aqueous solutions of PVAm and CoPc(SO$_3$Na)$_4$ were
simply mixed. The spontaneously formed complexes (see [7,
8]) were used in the various measurements. All solutions
were prepared with distilled and deionized water.

Tab. 1. Radical polymerization of N-vinyl-tert-butyl carbamate

<table>
<thead>
<tr>
<th>Monomer</th>
<th>AIBN</th>
<th>Benzene</th>
<th>$\bar{P}_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>weight in g</td>
<td>weight in g</td>
<td>volume in ml</td>
<td></td>
</tr>
<tr>
<td>5.01</td>
<td>0.8573</td>
<td>55</td>
<td>50 (b)</td>
</tr>
<tr>
<td>10.35</td>
<td>0.1155</td>
<td>55</td>
<td>570 (c)</td>
</tr>
<tr>
<td>4.95</td>
<td>0.0057</td>
<td>30</td>
<td>1600 (c)</td>
</tr>
</tbody>
</table>

a) reaction conditions: see text.
b) $\bar{P}_n$ determined by vapor pressure osmometry (solvent: benzene;
   $T = 45^\circ$C).
c) $\bar{P}_n$ determined by membrane osmometry (solvent: toluene; $T = 35^\circ$C).
Catalytic activity measurements and instrumentation

Activity measurements were carried out in an all-glass, thermostated (T = 23°C), double-walled, Warburg apparatus provided with a mechanical (glass) stirrer. Water was used as the solvent; unless otherwise stated the total reaction volume amounts to 75 ml. The substrate, 2-mercaptoethanol (Merck) was distilled before use and carefully kept under nitrogen. The reaction rate was determined by measuring the initial oxygen consumption rate at constant oxygen pressure (p(O2) = 1 atm) and a constant stirring speed (3000 r.p.m.).

Number average molecular weights were determined with a Hewlett-Packard High Speed Membrane Osmometer 502 and a Knauer Vapor Pressure Osmometer. Optical spectra were measured with quartz cuvettes by means of a Unicam SP 800 spectrophotometer.

6.3 Results

6.3.1 Visible light spectral measurements

It is well established, that the tetrasodium salt of cobalt(II)-tetrasulphophthalocyanine (CoPc(SO3Na)4) in aqueous solution may exist in at least three forms: the mononuclear form, binuclear form and binuclear dioxygen adduct [11, 12]. At neutral pH, low ionic strength and low CoPc(SO3Na)4 concentration an equilibrium between mononuclear and binuclear species prevails, whereas in alkaline medium the dioxygen adduct and the binuclear form of CoPc(SO3Na)4 predominate. Our results of visible light measurements on CoPc(SO3Na)4 in alkaline solutions of different basic strength (at constant CoPc concentration) are in accordance with data obtained from literature [11, 12] (see Fig. 1). With increasing NaOH concentration (under nitrogen) the concentration of binuclear species increases, as appears from the increasing peak at 16000 cm⁻¹.

When bubbling O2 through these alkaline solutions the peak at 15000 cm⁻¹ rapidly increases representing the
Fig. 1. Visible light absorption spectra of 2.5 μmol/l CoPc(SO₃Na)₄ solutions at ambient temperature (solvent: water; optical path length: 50 mm) in the presence of (a): no base, (b): 2.5 mmol/l NaOH, (c): 10.0 mmol/l, and (d): 25.0 mmol/l NaOH. Spectra after 0.5 h flushing with purified nitrogen (-----) and thereafter 1 h flushing with oxygen (----).

Formation of the binuclear dioxygen adduct. At higher NaOH concentrations, a faster formation of the latter adduct is observed.

Turning now to the CoPc(SO₃Na)₄/PVAm system it appears that the spectra in the presence of PVAm differ appreciably
Fig. 2. Visible light absorption spectra of 2.5 μmol/l \( \text{CoPc(NO}_2\text{Na)}_4 \) solutions at ambient temperature (solvent: water; optical path length: 50 mm) in the presence of PVAm \( (P_\text{m} = 570) \). (a): 2.5 mmol/l amine, (b): 5.0 mmol/l amine, (c): 10.0 mmol/l amine, and (d): 25.0 mmol/l amine. Spectra after 0.5 h flushing with purified nitrogen (-----) and thereafter 1 h flushing with oxygen (-----).

From the spectra recorded when using NaOH, the visible light spectra (see Fig. 2) recorded under nitrogen reveal that with increasing PVAm content at constant CoPc concentration, the peak at 16000 cm\(^{-1}\) diminishes and the peak at 14900 cm\(^{-1}\) increases. Evidently, with increasing
PVAm concentration at constant CoPc content, the equilibrium between mononuclear and binuclear form is shifted to the mononuclear form. When bubbling O₂ through the solutions of CoPc(SO₃Na)₄/PVAm complexes the peak at 14800 cm⁻¹ increases indicating the formation of dioxygen adducts (see Fig. 2).

Combining the results represented in Figs. 1 and 2, it can be concluded that binuclear adduct formation in the relevant CoPc(SO₃Na)₄ solutions (i.e. under nitrogen) is promoted by increasing the amount of alkaline base and is hindered by increasing the amount of polymeric base. On the other hand, it appears to be possible that for a given CoPc(SO₃Na)₄ concentration in a PVAm solution, more dimeric CoPc(SO₃Na)₄ species are present than in an alkaline solution containing the same amount of basic groups. This effect can be ascribed to the high local concentration of basic groups (i.e. coordinative sites) within the polymeric coil due to the specific non-homogeneous features of dilute polymer solutions [7, 8]. This phenomenon causes a relatively high concentration of CoPc molecules within the polymeric coils, which promotes the formation of binuclear CoPc(SO₃Na)₄ species. Evidently, the latter effect is most distinct when relatively low PVAm amounts are used. With increasing PVAm content this effect becomes less important due to the increasing shielding effect exerted by the polymer molecules.

6.3.2 Catalytic activity measurements

In Fig. 3 the results of the catalytic experiments carried out with PVAm samples of different average degrees of polymerization are shown. It appears that the specific catalytic activity of CoPc(SO₃Na)₄/PVAm complexes for the autoxidation of thiols as a function of the amine content (at constant CoPc(SO₃Na)₄ concentration) depends on the average molecular weight of the PVAm sample applied. To our knowledge this is the first time such a molecular weight dependence of the catalytic activity of polymeric catalysts has been found.

Furthermore, Fig. 3 reveals that the specific catalytic
Fig. 3. The average catalytic activity of CoPc(SO$_3$Na)$_4$/PVAm complexes (v; ml of O$_2$ and $\mu$mol of Co) as a function of the amine content (at constant CoPc content of 10$^{-8}$ mol) for PVAm samples with $P_a$ = 50 (•) and $P_a$ = 1680 (○). Measurements carried out in triplicate; substrate: 2-mercaptoethanol (1 ml, 14.25 mmol); time of complexation: 40 min.

activity of CoPc(SO$_3$Na)$_4$/PVAm complexes for the autoxidation of 2-mercaptoethanol increases with increasing amine content (at constant CoPc concentration). It has already been shown by visible light spectral measurements (see Fig. 2) that the formation of the binuclear adduct of the CoPc(SO$_3$Na)$_4$ is hindered by increasing the PVAm content (at constant CoPc content). Thus, it may be concluded that the enhanced catalytic activity (see Fig. 3) on increasing the PVAm concentration (at constant CoPc concentration) is effected by a reduced number of dimeric species.
Tab. 2. Catalytic activity of poly(vinylamine)/cobaltphthalocyanine complexes; [amine] = 4 mmol·l⁻¹ a)

<table>
<thead>
<tr>
<th>10⁻⁸ [CoPc] mol·l⁻¹</th>
<th>10⁻³ · v b) ml·μmol⁻¹·min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>2.37</td>
</tr>
<tr>
<td>0.4</td>
<td>1.05</td>
</tr>
<tr>
<td>0.9</td>
<td>0.89</td>
</tr>
<tr>
<td>4.0</td>
<td>0.29</td>
</tr>
<tr>
<td>8.0</td>
<td>0.21</td>
</tr>
</tbody>
</table>

a) reaction conditions: see Experimental, total reaction volume 11 ml; a PVA sample with $\bar{M}_n = 570$ was used; substrate: 2-mercaptoethanol (1 ml, 14.25 mmol); time of complexation 24 h.
b) $v$ = specific rate (ml of O₂ and 1 μmol of Co).

From Tab. 2 it becomes evident that the specific catalytic activity of the CoPc(SO₃Na)₄/PVAm catalyst decreases with increasing CoPc(SO₃Na)₄ concentration (at constant amine content). This result can be explained by taking into account the relatively decreasing amount of mononuclear species on increasing the CoPc concentration (at constant PVAm content).

6.4 Discussion

In recent years polymer-bonded metalloporphyrins have been studied as model systems for enzymes as for instance cytochrome P₄₅₀, myoglobin and hemoglobin [13]. Iron (II)-porphyrins in proteins can bind and activate molecular oxygen for oxidations of various substrates [13, 14]. However, in solution and in the presence of oxygen iron (II)-porphyrins are rapidly oxidized to the iron (III) state [15]. Up to now, three methods have been described in the literature [16] to avoid this irreversible dimeric oxidation of iron (II)-porphyrins: 1) steric restriction preventing dimerization of the metalloporphyrins, 2) low temperature
causing slower irreversible oxidation and 3) rigid surfaces preventing dimeric oxidation of anchored metalloporphyrins.

Steric protection against dimerization reactions can be achieved by the attachment of metalloporphyrins in low concentration to soluble polymers [13]; the porphyrin-complex then virtually behaves as in solution at infinite dilution. We have applied this method for analogous reasons using poly(vinylamine) (PVAm) as a polymeric ligand for cobalt(II)-tetrasulphophthalocyanine (CoPc(SO₃Na)₄). This polymeric base can give protection against the dimerisation reactions normally occurring in homogeneous polymer-free CoPc(SO₃Na)₄ solutions and can promote the formation of the highly reactive mononuclear oxygen adduct of CoPc(SO₃Na)₄ (R). It may be assumed that binuclear CoPc species cannot be formed when only one CoPc unit is present in each PVAm coil. Therefore, it can be expected that an optimal overall catalytic activity is obtained, when all CoPc molecules are found isolated in separate polymeric coils [7].

A simple statistical calculation with which it is possible to determine the distribution of CoPc(SO₃Na)₄ over the PVAm coils will now be presented. Because of the very dilute PVAm solutions (< 0.05 wt.-% of polymer) in which the catalytic experiments are performed, it can be assumed that each PVAm coil contains only one polymer molecule (i.e. no entanglements). In the following statistical treatment the polymer chains are considered as polyfunctional units in which every functional group (-NH₂) has the same reactivity, independent of its environment. When equilibrium is established there will be a binomial distribution of CoPc(SO₃Na)₄ over the amine groups. In case of PVAm with one functional group at each monomeric unit and with a molar ratio of CoPc(SO₃Na)₄ to amine groups q (q < 1), the fraction of the chains having a given degree of polymerization i with k CoPc molecules in each chain can be expressed as:
\[ x_{i,k} = \frac{1}{(i-k)!} q^{i-k} (1-q)^{k-1} \]  \hspace{1cm} (3)

PVAm has been prepared via a radical polymerization of N-vinyl-tert-butylcarbamate with AIBN as initiator (see Experimental). As under these conditions the termination step most probably occurs through disproportionation, a Flory-distribution of the degree of polymerization [17] of the instantaneously formed polymer molecules may be expected. The mole fraction of polymer chains with degree of polymerization \( i \) is then given by:

\[ x_i = p^{i-1} (1-p) \]  \hspace{1cm} (4)

where \( p = 1 - 1/\bar{F}_n \) (\( \bar{F}_n \) = the number average degree of polymerization). Combining Eqs. (3) and (4), the mole fraction of PVAm chains with \( k \) molecules CoPc can be described as:

\[ x_{pol,k} = \sum_{i=k}^{\infty} \frac{i!}{(i-k)!} q^{i-k} (1-q)^{i-1} p^{i-1} (1-p) \]  \hspace{1cm} (5)

For \( k \gg 1 \) and \( q < 1 \) Eq. (5) can be recast as:

\[ x_{pol,k} = \frac{(1-p)q^{k-1}k}{(1-p+pq)^{k+1}} \]  \hspace{1cm} (6)

The number of CoPc molecules on PVAm chains with \( k \) molecules CoPc is \( k \cdot x_{pol,k} \) times the total number of PVAm chains (\( N \)). The total number of CoPc molecules is \( q \cdot \bar{F}_n \) times the total number of PVAm chains (\( N \)). Based on these considerations one can calculate the mole fraction of CoPc on PVAm chains with \( k \) molecules CoPc (\( x_{Co,k} \)):

\[ x_{Co,k} = \frac{x_{pol,k} \cdot k \cdot N}{q \cdot \bar{F}_n \cdot N} \]  \hspace{1cm} (7)

Using Eq. (5) and \( \bar{F}_n = 1/(1-p) \) in Eq. (7), yields:

\[ x_{Co,k} = \frac{k(1-p)^2 (pq)^{k-1}}{(1-p+pq)^{k+1}} \]  \hspace{1cm} (8)

This Eq. (8) holds for \( k \gg 1 \) and \( q < 1 \).
In reality, each amine group of PVAm will not react independently of its environment. It should be expected that any CoPc(SO_3Na)_4 molecule will interact with more than one amine group of the polymer. This behavior can be accounted for by introducing a statistical chain element of N monomeric units as complexing moiety rather than a single monomeric unit. However, for small values of q the effects of this modification appear to be negligible.

The above statistical calculation supports the interpretation of the measured molecular weight dependence of the specific catalytic activity of CoPc/PVAm complexes for the autoxidation of thiols. It will be obvious from the calculated data presented in Tab. 3 that in the case of the lower average molecular weight PVAm sample ($\bar{M}_n = 50$) a rather high percentage of isolated CoPc molecules ($x_{Co,1}$) occurs, which decreases only slowly with increasing q ([CoPc(SO_3Na)_4]/[amine]) ratios. In contradistinction to this behavior, the higher average molecular weight sample ($\bar{M}_n = 1680$) contains a high percentage of polymeric coils with a single CoPc molecule only when the value of q is low. Under these conditions the number of isolated CoPc molecules decreases very rapidly as q increases. This implies that at relatively high CoPc contents the low molecular weight sample is expected to protect the CoPc(SO_3Na)_4 better from dimerization reactions than does the high molecular weight sample. Since, as stated before, the catalytic activity is predominately originating from the mononuclear CoPc(SO_3Na)_4 species, a relatively high CoPc content should lead to a higher specific activity when a comparatively low molecular weight PVAm sample is used. This hypothesis was confirmed by the experimental results presented in Fig. 3 and Tab. 3.

Since it has been found that non-polymeric amines were able to provide only a low catalytic activity [7], it can be inferred that there should exist a minimal $\bar{M}_n$ value necessary to protect the CoPc(SO_3Na)_4 efficiently against dimerization reactions. Up to now such a minimally required $\bar{M}_n$ value could not be determined.
Tab. 3. Calculated amount of isolated CoPc(SO₃Na)₄ molecules \((x_{\text{CoPc}})\) and the specific activity of CoPc(SO₃Na)₄/PVAm complexes \(\overline{\eta}\)

<table>
<thead>
<tr>
<th>(10^2)</th>
<th>(\overline{F}_n = 50)</th>
<th>(\overline{F}_n = 1680)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x_{\text{CoPc}})</td>
<td>(10^{-2})</td>
<td>(x_{\text{CoPc}})</td>
</tr>
<tr>
<td>in %</td>
<td>(\text{ml} \cdot \text{mol}^{-1} \cdot \text{min}^{-1})</td>
<td>in %</td>
</tr>
<tr>
<td>1.00</td>
<td>45.04</td>
<td>5.0</td>
</tr>
<tr>
<td>0.20</td>
<td>82.95</td>
<td>6.6</td>
</tr>
<tr>
<td>0.10</td>
<td>90.88</td>
<td>6.6</td>
</tr>
<tr>
<td>0.02</td>
<td>99.07</td>
<td>0.4</td>
</tr>
<tr>
<td>0.01</td>
<td>99.02</td>
<td>9.2</td>
</tr>
</tbody>
</table>

---

**Notes:**
- Reaction conditions: see Experimental; always \(10^{-2}\) mol CoPc was used; substrate: 2-mercaptoethanol (1 ml, 14.25 mmol); time of complexation 40 min.
- \(q = [\text{CoPc}(\text{SO}_3\text{Na})_4]/[\text{lamine}].\)
- \(x_{\text{CoPc}} =\) mole fraction of CoPc(SO₃Na)₄ in PVAm coils containing one CoPc molecule (calc. with Eq. (8)).
- \(\overline{\eta} =\) average specific rate; measurements carried out in triplicate (ml of \(O_2\) and \(\mu\)mol of Co).

It becomes evident that the above statistical calculation can be useful to a better understanding of the catalytic behaviour of CoPc/PVAm complexes. Moreover, this calculation can also be applied to related problems, for instance in the field of polymer attached metals and other metal complexes.

It may be expected that the concentration of basic groups \([N\text{Coil}]\) and consequently the concentration of substrate molecules in the polymeric coil \([R\text{Coil}]\) depend also on the \(F_n\) of the applied PVAm samples. When very dilute PVAm solutions are considered in the absence of CoPc, and all polyelectrolyte characteristics have been suppressed adequately, \([N\text{Coil}]\) is inversely proportional to the intrinsic viscosity of the polymer solution \([\eta]\) [18]. Furthermore, from the Mark-Houwink relation it is known that \([\eta]\) is related to the molecular weight of the polymer sample according to \([\eta] = K \cdot M^\alpha\) (0.7 < \(\alpha < 0.9\)). Thus, it
will be obvious that \([N]_{\text{coll}}\) is inversely proportional to \(n^{0.7}\) up to \(n^{0.9}\). It may be assumed that the polyelectrolyte behaviour is sufficiently suppressed in the presence of an excess of the substrate (2-mercaptoethanol). It can then be calculated using the above relationship that, in the absence of CoPc(SO\(_3\)Na)\(_4\), \([N]_{\text{coll}}\) and consequently \([RS^-]_{\text{coll}}\) is at least 10 times higher when using the sample with low \(\bar{M}_n\) (\(\bar{M}_n = 50\)) instead of the sample with high \(\bar{M}_n\) (\(\bar{M}_n = 1680\)). However, the presence of a CoPc(SO\(_3\)Na)\(_4\) molecule will strongly disturb the conformation of a polyam coil in solution. Because of the strongly complexing properties of CoPc(SO\(_3\)Na)\(_4\) towards polymer-bound RS\(^-\), it may be expected that a CoPc(SO\(_3\)Na)\(_4\) molecule is able to create a typical surrounding by RS\(^-\) species practically independent of the \(\bar{M}_n\) of the polymer sample. These considerations indicate that the observed molecular weight dependence of the catalytic activity is caused by shielding effects rather than by changes of coil density.

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CHAPTER 7

MACROPOROUS STYRENE-DIVINYLBENZENE COPOLYMERS AS CARRIERS
FOR POLY(VINYLAMINE)/COBALTPTHALOCYANINE OXIDATION
CATALYSTS

7.1 Introduction

Catalysis by complexes of transition metals anchored on macromolecular ligands currently receives considerable attention [1, 2]. Many polymer-metal complexes show a high catalytic efficiency because the polymer chains create a favourable micro-environment for the catalytic sites. Recently [3, 4, 5], we reported on a bifunctional catalyst for the autoxidation of thiols composed of a cobaltphthalocyanine (CoPc) and poly(vinylamine) (PVAm). The remarkable high activity of this catalyst could be explained by taking into account phenomena inherently connected with the polymeric character of PVAm.

A disadvantage limiting the practical applicability of the PVAm/CoPc catalyst is its solubility in the reaction medium preferentially applied (i.e. water), as the separation of the catalyst from the reaction product and the catalyst regeneration are difficult to achieve. Therefore, the idea appeared that the advantages might be retained and the disadvantages overcome if the PVAm/CoPc catalyst was chemically bound onto a solid carrier. This immobilization should be carried out in such a way that the polymeric character of PVAm, which is an essential requirement for a high catalytic activity [5], will be maintained. Macroporous copolymers of styrene (St) and commercial divinylbenzene (DVB) were used as carriers in this investigation. St-DVB copolymers may be prepared as spherical beads with a variety of particle size distributions (using suspension polymerization techniques), which strongly enhances the applicability of this class of supports in technical reactors. St-DVB copoly-
mers are being widely applied in the preparation of ion exchangers and as beads for analytical purposes [gel permeation chromatography and gas liquid chromatography] [6, 7]. More recently, this class of copolymers, which possesses good mechanical and chemical stability, has also been applied as carrier for homogeneous catalysts [1].

Macroporous polymer networks are heterogeneously cross-linked polymers, which may be obtained when high amounts of crosslinking agent are used and the monomers are diluted with an inert compound [6, 7]. During the preparation of these copolymers part of the divinylbenzene monomers are incorporated into the network with a single vinyl group only [8, 9]. So the resulting material will contain a certain amount of unreacted or pendent double bonds. When vinyl monomers are polymerized in the presence of these reactive carriers graft copolymers may be obtained [10]. The present paper describes the grafting of N-vinyl-tert-butylcarbamate onto St-DVB copolymers. The aim of the investigation was the preparation of poly(vinylamine) grafted onto a St-DVB carrier (III), by the hydrolysis of grafted poly(N-vinyl-tert-butylcarbamate) (I) and the subsequent removal of the amine-bonded hydrogen chloride (see scheme I). After coupling CoPc to the grafted PVAm (III) a heterogeneous bifunctional catalyst should be obtained, which may be expected to show activity in the autoxidation of thiols to disulfides.

\[
\begin{align*}
\text{I} & \xrightarrow{10 \text{N} \text{HCl}} \text{II} & \xrightarrow{6 \text{N} \text{NaOH}} \text{III} \\
\text{C=O} & \text{NH} & \text{NH} \\
\text{O-CH₃} & \text{NH₂} & \text{NH₂}
\end{align*}
\]

Scheme I. Preparation of grafted poly(vinylamine) from grafted poly(N-vinyl-tert-butylcarbamate).

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7.2 Experimental

Instrumentation
A Hewlett Packard (Model 185) apparatus was used for C, H, N analysis. Co-contents were determined by means of neutron activation analysis using a Ge(Li)-semiconductor detector. IR-spectra were recorded on a Hitachi EPI G spectrophotometer. Surface areas were determined with a Ströhllein Areameter. Scanning Electron Microscopy was carried out with a Stereoscan Mark 2A apparatus (Cambridge Scientific Instruments Ltd.). Number average molecular weights were determined with a Hewlett Packard High Speed Membrane Osmometer 502 (solvent: toluene, T=37°C). A Hewlett Packard gas chromatograph 5700 A equipped with a flame ionization detector and a Hewlett Packard integrator 3380 A were used. A stainless steel column (3.8m x 2mm, i.d.) has been applied packed with 10% Silicone oil DC 550 on Chromosorb P (60/80 mesh), operated with a helium flow rate of 30 ml·min⁻¹.

Reagents
Styrene (Merck) and commercial divinylbenzene (Merck) were washed with 2 N NaOH, neutralized, dried over CaH₂, and distilled in vacuo. GLC analysis of inhibitor-free commercial divinylbenzene gave the following results: 33.6 wt.-% m-ethylvinylbenzene, 11.2 wt.-% p-ethylvinylbenzene, 39.3 wt.-% m-divinylbenzene, 14.1 wt.-% p-divinylbenzene and some very small amounts of m- and p-diethylbenzenes and naphtalene (see also [11, 12]). N-vinyl-tert-butylcarbamate (VCb) was prepared from acryloylchloride on the analogy of the method given by Hughes et al. [13]: m.p. 65.5-66.5°C, Lit. [13] 67-68°C. 2,2'-Azobisisobutyronitrile (AIBN) (Merck) was purified by recrystallization from diethylether.

Preparation of macroporous styrene-divinylbenzene carriers [6, 7, 14, 15]

a) Polymers of inhibitor-free commercial divinylbenzene (3.0 g) were prepared by solution polymerization in the
presence of 6.0 ml diluents (mixtures of toluene and n-butanol) with AIBN as initiator. The reactions were carried out in sealed ampoules (under nitrogen) at 80°C in a thermo-
stated water bath, the reaction time was 8 h. The materials obtained were powdered, extracted with cyclohexane in a soxhlet-apparatus and subsequently dried in vacuo.

b) Polymers of purified commercial divinylbenzene
(27.0 g) and styrene (3.0 g) were prepared by suspension-poly-
merization in the presence of 60 ml diluent with 300 mg AIBN
as initiator. The reaction was carried out in 250 ml water
with 4 g/l polyvinyl alcohol (Koch-Light Laboratories Ltd.
Mn = 72,000) as suspension agent, reaction time 6 h at 80°C.
The polymerizations were run in a standard suspension poly-
merization apparatus (SPS) consisting of a 1 litre, double-
walled, round-bottomed cylindrical flask fitted with a
mechanical stirrer and nitrogen in- and outlet tubes.
Before starting the polymerization nitrogen was flushed
through the solution during 15 min, the stirring speed was
550 r.p.m. The reaction was stopped by the addition of p-
tert-butylpyrocatechol. Steam distillation was used to
remove unreacted monomers and the solvent-non solvent
mixture. The distillate was collected during 2 h in a flask
containing some inhibitor. Then, the organic layer was
separated and the aqueous part of distillate was extracted
twice with 50 ml n-hexane. The amounts of unreacted mono-
mers in the collected organic extraction liquids were de-
termined by GLC with α-methylstyrene as an internal refer-
ence. The obtained polymer beads were washed and dried, and
the size distribution was determined by sieve analysis. IR-
spectra of all carriers were recorded from KBr-pellets (1 wt.-% of polymer) and also from a nujol suspension using
finely powdered polymer with particle size < 20 μm [9]
(75 mg of polymer in 0.5 ml nujol, thickness 1 mm).

Grafting of poly(α-vinyl-tert-butylcarbamate) (PVCA) onto
the monoporous styrene-divinylbenzene copolymers

A typical grafting experiment was performed in the
following way. In a sealed ampoule N-vinyl-tert-butylcarba-
mate (VCa) was polymerized (under nitrogen) in the presence of a carrier containing pendant vinyl groups. The polymerization was initiated with $1.2 \cdot 10^{-2}$ mol AIBN/mol VCa, cyclohexane was used as a solvent and the reaction was performed at 50°C during 72 h. The resulting reaction mixture was diluted with acetone/cyclohexane (1:1, v/v). The solid product was collected and extracted with acetone (3 h) and cyclohexane (1 h), successively, in a soxhlet apparatus; finally the product was dried in vacuo. The content of grafted VCa in the material was determined by N-analysis. The free homopolymer, PVCa, was obtained from the acetone/cyclohexane (1:1, v/v) solution, by precipitation with cold n-hexane.

**Hydrolysis of grafted PVCa**

Graded PVCa (I) was hydrolyzed by stirring or shaking the solid product in an ethanol/10 N hydrochloric acid (1:1, v/v) mixture in analogy to methods developed earlier for the hydrolysis of free PVCa [4, 13, 16]. This reaction was carried out during 8 h at ambient temperature. After neutralizing with ethanol/water mixtures and finally with pure ethanol, the product was dried in vacuo.

**Desalting of grafted PVAm-HCl**

Removal of bonded HCl was achieved by stirring or shaking the product for 7 h at ambient temperature (under nitrogen) in a 6 N NaOH/ethanol (1:1, v/v) mixture. The resulting material was washed with ethanol/water mixtures and subsequently dried in vacuo.

**Catalyst preparation**

Cobalt(II)-tetracarboxyphyphantocyanine (CoPc(COOH)$_4$) and its tetracosodium salt (CoPc(COONa)$_4$) were prepared as described in chapter 2. Complexation of CoPc(COONa)$_4$ with (III) and covalent attachment of CoPc(COOH)$_4$ to (II) were achieved analogous to methods developed earlier in behalf of the binding of CoPc derivatives to soluble PVAm [4].
Catalytic activity measurements

Activity measurements were carried out in an all-glass, thermostated \( T = 23 \degree C \), double-walled Warburg apparatus provided with a mechanical (glass) stirrer. The substrate, 2-mercaptoethanol (Merck) was distilled before use and carefully kept under nitrogen. The reaction rate was determined by measuring the initial oxygen consumption rate at constant oxygen pressure \( p(O_2) = 1 \text{ atm} \) and at constant stirring speed (3000 r.p.m.).

7.3 Results and discussion

7.3.1 Macroporous styrene-divinylbenzene copolymers

We aimed at preparing macroporous styrene (St)-divinylbenzene (DVB) copolymers with optimal characteristics, such as surface area, average pore diameter and amount of pendant vinyl groups accessible to the grafting of poly(N-vinyl-tert-butylcarbamate). The internal surface and the pore size distribution may be optimized by using a mixture of a solvent and a precipitant for the (uncross-linked) polymer during polymerization \[6, 7, 14\]. Good solvents will produce small pores, bad solvents large pores. In this investigation, toluene was used as a solvent and n-butanol as a nonsolvent.

In Fig. 1 the surface areas of the polymers obtained from the solution polymerization of commercial DVB are shown as a function of the composition of the diluent mixture. The maximum value of the surface area occurs at the ratio n-butanol: toluene = 1:3, in agreement with the results of Heitz \[7, 14\]. Scanning electron microscopy reveals the average pore diameter increases with decreasing toluene content in the inert phase. These findings are in accordance with literature \[6, 7, 14\].

The infrared absorption spectra of the crosslinked copolymers (in nujol) show a significant peak at 1630 cm\(^{-1}\) assigned to monosubstituted vinyl groups. The characteristic
absorption at 1600 cm\(^{-1}\) of the skeleton vibration of the aromatic nucleus of polystyrenes was used as a reference. The ratio of the extinctions at 1630 cm\(^{-1}\) and 1600 cm\(^{-1}\) (\(E_{1630} \text{ cm}^{-1}/E_{1600} \text{ cm}^{-1}\)) then may be used as a quantitative measure of the residual double bounds [9]. The results presented in Fig. 1 reveal that the relative content of pendent vinyl groups is rather constant at high toluene contents, but increases rapidly when the inert phase contains less than 25% toluene. This phenomenon may be explained by considering the mode of network formation [6-8, 17] as a function of the composition of the inert
phase. When the inert phase contains non-solvent (n-butanol) only, the polymer chains initially formed with pendant vinyl groups will be weakly solvated and therefore relatively highly contracted. During further polymerization the pendant vinyl groups will remain relatively inaccessible and the resulting network will contain a comparatively large amount of double bonds. When the amount of solvent (toluene) in the inert phase is increased the polymer chains will become more solvated and thus more expanded. As a result the pendant vinyl groups will remain more accessible to addition reactions.

It may be concluded that the St-DVB copolymers prepared at high n-butanol contents will contain relatively many residual double bonds, though poorly accessible.

Fig. 2. Macroporous St-DVB copolymers prepared by suspension polymerization. Surface areas (S) (particle size 200 μm < d > 300 μm) and residual double bonds (E 1630 cm⁻¹/E1600 cm⁻¹) as a function of the composition of the inert phase during preparation.
In Fig. 2 the IR-data and the surface areas of copolymers prepared by suspension polymerization of 10 wt.-% St and 90 wt.-% commercial DVB mixtures are shown as a function of the composition of the inert phase. The results given in Figs. 1 and 2 exhibit corresponding trends in accordance with the data reported in the literature for similar cases [7, 14].

The preparation of macroporous polymers by suspension polymerization has been investigated with respect to a number of characteristic phenomena. These characteristics include a higher reactivity of DVB as compared with styrene and ethylvinylenzenes (cf. [12]), which appears from Tab. 1 and Fig. 3.

Tab. 1. Composition of St-DVB macroporous copolymers\(^a\) prepared from a monomer mixture of 10 wt.-% St and 90 wt.-% commercial DVB\(^b\) using inert phases of varying composition.

<table>
<thead>
<tr>
<th>carrier</th>
<th>n-butanol (vol.-%)</th>
<th>St (%)(^c)</th>
<th>n-EVB (%)</th>
<th>p-EVB (%)</th>
<th>m-DVB (%)</th>
<th>p-DVB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>100/0</td>
<td>10.14</td>
<td>30.59</td>
<td>10.14</td>
<td>36.15</td>
<td>12.97</td>
</tr>
<tr>
<td>7</td>
<td>75/25</td>
<td>10.15</td>
<td>30.69</td>
<td>10.18</td>
<td>36.03</td>
<td>12.95</td>
</tr>
<tr>
<td>8</td>
<td>50/50</td>
<td>10.14</td>
<td>30.67</td>
<td>10.21</td>
<td>36.04</td>
<td>12.97</td>
</tr>
<tr>
<td>9</td>
<td>25/75</td>
<td>9.74</td>
<td>30.09</td>
<td>9.98</td>
<td>36.89</td>
<td>13.30</td>
</tr>
<tr>
<td>10</td>
<td>0/100</td>
<td>9.34</td>
<td>29.51</td>
<td>9.56</td>
<td>37.81</td>
<td>13.78</td>
</tr>
</tbody>
</table>

\(^a\)Composition is given in wt.-%, the values were calculated using the results of the GLC determination of the amounts of unconverted monomers.

\(^b\)Preparation by suspension polymerization technique; composition of commercial DVB is given in the experimental part.

\(^c\)Composition of inert phase during preparation.
Fig. 3. The relative amount of unreacted monomer as determined by GLC analysis versus the composition of the inert phase applied during the suspension polymerization of a monomer mixture initially containing 10 wt.-% St and 90 wt.-% commercial DVB (conditions: see Experimental). a styrene; b m-ethylvinylbenzene; c p-ethylvinylbenzene; d m-divinylbenzene (p-divinylbenzene was totally converted).
Fig. 4. Cumulative particle size distributions obtained from sieve analysis of St-DVB copolymers (prepared by suspension polymerization of 10 wt.% St and 90 wt.% commercial DVB). The composition of the inert phase applied during preparation was varied: a 100/0; b 75/25; c 50/50; d 25/75; e 0/100 (v/v) toluene/n-butanol.

It also appears that the mode of the cumulative particle size distribution curves (Fig. 4) tends to shift to higher values as the toluene content in the inert phase increases. Fig. 4 also reveals that the distributions become broader as the toluene content increases.

From scanning electron micrographs it appeared that with increasing n-butanol content the shape of the particles becomes less spherical. The latter observation is in agreement with the results of Wolf et al. [15], who observed that the percentage of deformed particles increased on addition of a water-soluble alcohol to the reaction medium. As expected [6, 7, 14], the micrographs confirm that the average pore diameter increases as the
n-butanol content in the inert phase increases. Simultaneously the materials become more brittle, which is in accordance with the literature data [14, 17].

7.3.2 Grafting of poly(N-vinyl-tert-butylcarbamate) onto macroporous styrene-divinylbenzene copolymers

a. Grafting method

Grafting of poly(N-vinyl-tert-butylcarbamate) (PVCa) is achieved by radical polymerization of N-vinyl-tert-butylcarbamate (VCA), initiated by AIBN, in the presence of the reactive St-DVB solid carriers. Graft copolymer is formed by chain propagation involving coupling of a growing VCA macroradical (P') to the solid bound double bonds (eq. 1, Scheme II).

Scheme II. Grafting of VCA macroradicals (P') on St-DVB carriers with pendant double bonds (R=-(CH₂)₂-C≡CN, M=VCA).

Grafting may also occur by termination of the growing VCA macroradicals with radicals generated on the carrier

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(eqs. 2 and 5). On the one hand efficient grafting will require solid carriers that possess a large internal surface, a sufficiently large average pore diameter and also a sufficient amount of accessible double bonds. Macroporous St-DVB copolymers [6-9, 14, 17] can meet those requirements within certain limits. On the other hand, the copolymerization kinetics will affect the grafting characteristics to a high degree. Because the copolymerization behaviour of VCa and VAc (vinylacetate) are comparable [18], the grafting mechanism of VCa onto these St-DVB carriers may be better understood when reviewing the literature on the attempted grafting of VAc on polystyrene [19, 20]. It is well established that the copolymerization parameters of styrene ($r_1$) and VAc ($r_2$) are quite unfavourable to copolymer formation ($r_1 = 55, r_2 = 0.01$) [21]. This indicates that grafting initiated by a radical on the solid surface, as represented by eqs. 3 and 6, will occur only rarely because of the low relative reactivity of the VAc and VCa monomers towards an unreactive styrene-type radical. Furthermore, it has been observed that AIBN is unable to initiate grafting of for instance methyl methacrylate on polystyrene by a radical transfer mechanism because the reactivity of the resonance stabilized $(\text{CH}_3)_2\text{C}-\text{CN}$ radical is too low [22]. Because of the relatively low reactivity of AIBN, it is very improbable that AIBN will initiate the graft copolymerization of VCa starting from the St-DVB carrier by a chain transfer mechanism.

b. Results of the grafting experiments

The experimental results of the grafting of FVCAs onto St-DVB carriers of various composition are presented in Tab. 2. St-DVB copolymers prepared in the presence of a relatively high content of n-butanol possess the highest density of pendant vinyl groups, but nevertheless they exhibit very low percentages of grafted FVCAs. Evidently, in the latter case the double bonds are not accessible to growing VCa macroradicals, as was anticipated in the
Tab. 2. Grafting of poly(N-vinyl-2-ethyl-2-butylycarboxylate) as a function of the specific surface and the amount of residual double bonds of the St-DVB carriers.

<table>
<thead>
<tr>
<th>Carrier no.</th>
<th>Toluene (vol-%)</th>
<th>n-Butanol (vol-%)</th>
<th>(S^c) (m²/g)</th>
<th>(\bar{S}_{1630}) cm⁻¹</th>
<th>(\bar{S}_{1600}) cm⁻¹</th>
<th>PVC(^d) (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100/0</td>
<td>569</td>
<td>0.17</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>75/25</td>
<td>600</td>
<td>0.17</td>
<td>12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>50/50</td>
<td>552</td>
<td>0.18</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>25/75</td>
<td>376</td>
<td>0.16</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0/100</td>
<td>244</td>
<td>0.23</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>100/0</td>
<td>504</td>
<td>0.17</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>75/25</td>
<td>477</td>
<td>0.17</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>50/50</td>
<td>468</td>
<td>0.19</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>25/75</td>
<td>35</td>
<td>0.22</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0/100</td>
<td>12</td>
<td>0.28</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Carriers 1-5 prepared from commercial DVB by solution polymerization technique, particle size \(d < 100 \mu m\); carriers 6-10 prepared from 10 wt.-% St and 90 wt.-% commercial DVB (see Tab. 1) by suspension polymerization technique, particle size 200 \(< d > 300 \mu m.\)

\(^b\) Composition of inert phase during preparation of carriers.

\(^c\) \(S\) = internal surface.

\(^d\) Grafting onto carriers 1-5 was carried out without stirring using 50 mg of powdered carrier, 150 mg VCA, 0.5 ml cyclohexane, 2.5 mg ATBN; grafting onto carriers 6-10, as described in the experimental part.

precending section.

It appears that the internal surfaces of the carriers (S) and the amount of grafting are not directly related, though it is evident that a too low internal surface should have a deleterious effect on the grafting efficiency.

In conclusion, it appears that the materials prepared in the presence of an inert phase consisting of 75 vol.-%
toluene and 25 vol.-% n-butanol are the most suitable carriers for the grafting of PVCl. These carriers combine a large surface area with a sufficiently large average pore diameter, while they possess a reasonable amount of accessible pendant double bonds.

As no grafting occurred in the absence of AIBN, a radical initiator appears to be essential in order to obtain grafting. Also PVCl was allowed to react with the macro-porous copolymers (50°C, 24 h, in cyclohexane). The materials obtained, after purification, contained no detectable amounts of PVCl (i.e. < 1.5 wt.-%). The latter result also proves that the extraction method applied efficiently removes the free (physically attached) PVCl from the carrier.

c. Average block length of the grafted PVCl

An important prerequisite for obtaining an active catalytic system is a sufficiently large [15] average block length of the grafted PVCl. As a first approximation the block length might be obtained from the number of grafting sites and the total amount of grafted PVCl. The number of grafting sites may be determined by IR-measurement of the number of pendant vinyl groups [9] before and after the grafting reaction. Application of this method provides an indication of $\bar{P}_n$ in the grafted PVCl(I) samples investigated, i.e. $4 < \bar{P}_n < 12$. However, it has been shown experimentally that the initiator (AIBN) can also consume the pendant double bonds (eq. 4), which does not necessarily result in an effective grafting site. Consequently, the described method leads to too low values for the average block length. The number average degree of polymerization ($\bar{P}_n$) of the extracted free homopolymers were found to be approximately 400 (using $1.2 \cdot 10^{-2}$ mol AIBN/mol PVCl). Up to now no reliable method have been available for the determination of the average block length of the grafted PVCl.

d. IR-characterisation of the grafted PVCl samples

In a mixture containing (for example) 50 wt.-% PVCl
(obtained from a regular homopolymerization of VCa) and 50 wt.-% St-DVB copolymer the main IR-absorption of the NH-group (see Fig. 5a) is found at 3350 cm⁻¹ (NH-group with interaction), while a distinct shoulder shows up at 3440 cm⁻¹ (NH-group without interaction). In this sample the C=O absorption was found at 1700 cm⁻¹ (Fig. 5b).

The IR-spectrum of grafted PVCa (St-DVB carrier 2, see Tab. 2) shows that the main absorption of the NH-group is found at 3420 cm⁻¹ (Fig. 5c), indicating the practical absence of hydrogen bonding. In the latter case the C=O absorption (Fig. 5d) is shifted to 1715 cm⁻¹. From these shifts, it may be inferred that the grafted PVCa occurs as relatively isolated chains within the pores of the carrier. However, these phenomena should depend on the pore size of the carrier applied. Using a carrier with larger pores (St-DVB carrier 5, see Tab. 2), indeed led to a spectrum (see Fig. 5e and 5f) similar to that of a physical mixture (compare with Fig. 5a and 5b). Evidently, the larger pore size allows the grafted PVCa chains to form hydrogen bonds, and consequently the IR-spectrum shows interactions similar to those in the physical mixtures of PVCa and St-DVB copolymer.

7.3.3 Preparation of grafted poly(vinylamine) from grafted poly(N-vinyl-tert-butylcarbamate)

Previous investigations [4, 13, 16] have revealed that the hydrolysis of the homopolymer PVCa can be achieved properly using 10 N hydrochloric acid (HCl) in ethanol (1:1, v/v). Therefore, in this investigation the hydrolysis of grafted PVCa (I) was also carried out under these conditions (see Experimental). After hydrolysis, IR-spectra of the reaction products showed that the C=O absorption of the samples (spectra in nujol) had practically vanished, indicating the grafted carbamate polymer (I) was almost completely converted into the grafted hydrogen chloride salt of poly(vinylamine) (PVAm-HCl, II).

Since the PVAm-HCl is grafted on insoluble carriers
Fig. 5. IR absorption spectra (recorded from KBr-pellets): a, b 50/50 (w/w) mixture of St-DVB carrier and PVCa; c, d PVCa grafted onto carrier 2; e, f PVCa grafted onto carrier 5.
the removal of bonded HCl cannot be carried out in the usual manner (i.e. passage of an aqueous solution of PVAm-HCl through an ion-exchange column [3, 4, 16]). In the present case we have resorted to a 6 N NaOH/ethanol (1:1, v/v) mixture for the conversion of (II) into (III). This method was proved to be effective since no chloride could be detected with AgNO₃.

A reliable proof of the versatility of the described method was obtained by hydrolysing (I) with nitric acid (HNO₃) instead of HCl. Although HNO₃ has a strong absorption at 1380 cm⁻¹, no remaining HNO₃ was observed by IR-analysis after desalting of the HNO₃-analogon of (II).

7.3.4 Catalytic activities of the heterogeneous bifunctional catalysts

Attachment of CoPc moieties to the grafted PVAm (III) was achieved either by complexation through the polymeric amine groups or by formation of a peptide linkage between the grafted PVAm and the phthalocyanine ring system (see Experimental and cf. [4]). The catalytic properties of the resulting heterogeneous bifunctional catalysts were tested for the autooxidation of thiols to disulfides:

\[
\frac{3}{2}[C-\text{C}]_n + n\text{RSH} \rightarrow \frac{3}{2}[C-\text{C}]_n\text{NH}_3^{+}\text{SR}
\]

\[
\frac{3}{2}[C-\text{C}]_n + \frac{n}{2}\text{O}_2 + \text{CoPc} \rightarrow \frac{3}{2}[C-\text{C}]_n + \frac{n}{2}\text{RSSR} + \frac{n}{2}\text{H}_2\text{O}_2
\]

The results presented in Tab. 3 indicate that both methods of coupling CoPc to the grafted PVAm provide bifunctional catalysts, which do not require additional alkaline base to obtain high activities. Most of the heterogeneous bifunctional catalysts prepared are found to be sub-
Tab. 3. Catalytic activities of the polymeric catalysts for the autoxidation of 2-mercaptoethanol.

<table>
<thead>
<tr>
<th>Carrier no.</th>
<th>Amine (mmol)</th>
<th>CoPc (μmol)</th>
<th>Method of coupling&lt;sup&gt;c&lt;/sup&gt;</th>
<th>v (mol&lt;sub&gt;2&lt;/sub&gt;·mol&lt;sup&gt;-1&lt;/sup&gt;·min&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reaction medium (ml/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.01</td>
<td>0.01</td>
<td>A</td>
<td>20</td>
<td>water/toluene 1/70</td>
</tr>
<tr>
<td>7</td>
<td>0.01</td>
<td>0.01</td>
<td>A</td>
<td>50</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.01</td>
<td>A</td>
<td>8</td>
<td>&quot;</td>
</tr>
<tr>
<td>6</td>
<td>0.01</td>
<td>0.004</td>
<td>B</td>
<td>81</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>0.01</td>
<td>A</td>
<td>13</td>
<td>&quot;</td>
</tr>
<tr>
<td>9</td>
<td>0.01</td>
<td>0.04</td>
<td>B</td>
<td>4</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>0.01</td>
<td>A</td>
<td>74</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.01</td>
<td>B</td>
<td>442</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.17</td>
<td>B</td>
<td>77</td>
<td>&quot;</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>0.01</td>
<td>A</td>
<td>300</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.01</td>
<td>B</td>
<td>444</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.01</td>
<td>0.17</td>
<td>B</td>
<td>77</td>
<td>water 75</td>
</tr>
<tr>
<td>7</td>
<td>0.02</td>
<td>0.01</td>
<td>A</td>
<td>408</td>
<td>&quot;</td>
</tr>
<tr>
<td>4</td>
<td>0.10</td>
<td>0.01</td>
<td>B</td>
<td>444</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: see Experimental, 1 ml (14.25 mmol) substrate was used in all cases.

<sup>b</sup> St-DVB copolymer, see Tab. 2.

<sup>c</sup> A = CoPc(COONa)<sub>4</sub> coupled through complexation to PVA<sub>m</sub>, time of complexation 1 h; B = CoPc(COONa)<sub>4</sub> covalently coupled to PVA<sub>m</sub> (see text).

<sup>d</sup> Without polymeric base, but with 1.0 mmol NaOH.

Substantially more active than the traditional catalytic systems (i.e., without polymeric base in the presence of NaOH).
Since the soluble as well as the immobilized polymeric catalysts require far less basic groups per cobalt site than the traditional systems to obtain even higher catalytic activities, it may be inferred that the polymeric catalytic systems are characterized by an efficient cooperation between basic sites and oxidation sites. However, it also appears that using grafted PVAm the catalytic activity is significantly lower than when using ungrafted PVAm. It is assumed that the hydrophobic environment created by the St-DVB matrices and diffusion limitation (i.e., restricted transport of reactants to the active sites) are responsible for this phenomenon. At present, however, it cannot be excluded that too small an average block length (\( \bar{F}_n \)) of the grafted PVAm also contributes to the relatively low activities observed. When \( \bar{F}_n \) becomes too low the CoPc units will not be protected sufficiently by the PVAm chains against dimerization reactions, which causes deactivation of the catalyst [3, 5].

The hydrophobic character of the St-DVB carriers prohibits the formation of a proper dispersion of the catalyst particles in pure water, consequently experiments in pure water have not been subjected for further investigation. Addition of ethanol to the reaction medium gave improvement of the dispersability and activity of these catalysts. In the present as well as in a previous [4] investigation bifunctional catalysts have also shown remarkable activities in toluene provided that small amounts of water are present (see Tab. 3). Up to now, no straightforward relationship between the specific catalytic activities observed and the properties of the macroporous St-DVB carrier could be determined. However, it appears that the PVAm/CoPc catalysts immobilized on carriers with a low internal surface (i.e., large average pore diameter) exhibit a low catalytic activity (see for instance Tabs. 2 and 3, carrier 9). This result fits in with the observed effect of the pore size on intermolecular interactions of grafted polymer chains (see the preceding section). When a constant \([\text{CoPc}]/[\text{amine}]\) ratio is applied, the increased
interaction between grafted PVAm chains in wide pores compared with narrow pores will cause an enhanced probability of CoPc dimerization reactions (i.e. deactivation).

Obviously a high surface area (i.e. relatively small average pore diameter) is an important prerequisite for obtaining a good catalytic activity. From the results presented in Tab. 2 it appears that efficient grafting also calls for a high surface area. On the other hand it is evident that both grafting efficiency and catalytic performance impose restrictions on the minimum pore diameter. Finally, it may be concluded that within the present series of St-DVB carriers, the most effective catalysts are obtained from those carriers allowing the highest percentage of PVAm grafting.

References

18 C.J. Bloys van Treslong, private communication.
In the previous chapters it is shown that cobalt-phthalocyanines (CoPc) attached to a non-crosslinked polymeric base, poly(vinylamine), possess a much higher activity per cobalt site for thiol oxidation (i.e. a factor of about 50) than CoPc in the presence of NaOH (see also [1]). In chapter 6 it is proven, that prevention of the normally-occurring aggregation of CoPc molecules is a very important reason for the high activity of the water-soluble polymeric catalysts. Another phenomenon, intrinsically connected with the coil structure of the polymeric base in solution, is the high local concentration of basic groups in the micro-environment of the oxidation sites.

In addition to these two effects there may be other phenomena contributing to the high activity of the polymeric system, that have not been described before. Firstly, the water molecules near the catalytic sites in the polymeric coil will be restricted in their mobility because of the strong hydrophilic character of poly(vinylamine) (see [2]). This may result in a decrease of the effective hydration of reactants, which may have a positive effect on the reaction rate (cf. chapter 5). Secondly, since the oxidation reaction occurs in the polymeric coils and these occupy only a small fraction of the total reaction volume, a slight oxygen shortage within the coils may easily arise. A limited availability of oxygen may to some extent enhance the catalytic activity, because the formation of highly reactive Co(I)-species will be favoured under these circumstances (see [1]). Finally, the replacement of NaOH by the polymeric base may influence the ligand exchange rates on the cobalt center of the phthalocyanine. In both cases the base can occupy an axial site on the CoPc and this will strongly influence the exchange rate of the opposite axial
ligand (i.e. a trans-effect) [3]. It has to be studied whether or not the polymeric base is also in this respect preferable to NaOH.

Unfortunately, the bifunctional system enhances only the rate of the first step (Eq. (1)) of the coupled oxidation of thiols, whereas the second step (Eq. (2)) is not accelerated as compared to the conventional CoPc/NaOH system.

\[
\begin{align*}
2\text{RSH} + \text{O}_2 & \xrightarrow{\text{CoPc/base}} \text{RSSR} + \text{H}_2\text{O}_2 & (1) \\
2\text{RSH} + \text{H}_2\text{O}_2 & \xrightarrow{\text{base}} \text{RSSR} + 2\text{H}_2\text{O} & (2)
\end{align*}
\]

Evidently, CoPc is a very efficient catalyst for the reduction of \( \text{O}_2 \) into \( \text{H}_2\text{O}_2 \), but not for further reduction of \( \text{H}_2\text{O}_2 \) into \( \text{H}_2\text{O} \). In the presence of accumulated \( \text{H}_2\text{O}_2 \), thiols are partly converted to sulphur-containing oxo-acids, which deactivate the catalyst by poisoning the basic sites (cf. chapter 3). No catalyst for decomposition of the redundant \( \text{H}_2\text{O}_2 \) during thiol oxidation was found, but a suitable method to avoid peroxide-induced deactivation was found to be the addition of small amounts of NaOH. This promotes the conversion of \( \text{H}_2\text{O}_2 \) by reaction (2) and does not substantially increase the production of \( \text{H}_2\text{O}_2 \) by reaction (1). The kinetics of consecutive reactions [4] implicate, that the concentration of the intermediate product \( \text{H}_2\text{O}_2 \) in the reaction mixture will also be reduced, when applying a lower initial concentration of thiol. In the experiments described in this thesis we have used a fairly high initial thiol concentration and probably this is an important reason for the observed fast loss of activity of the bifunctional catalyst.

The application of the bifunctional catalyst allows in principle simplification of the industrially applied two-phase process for the oxidation of thiols, because this catalyst can be used in a predominantly apolar medium (see chapter 5). However, a one-phase process with a polymeric catalyst in the absence of NaOH and with a high in-
itial thiol concentration can only be adopted when a relatively high rate of deactivation can be accepted. The enhancement of the activity of conventional COFC/NaOH systems by addition of salt or application of mixed alcohol/water media is a very important new aspect revealed by the present investigation. These remarkable observations deserve more thorough investigation, the more so as in this case the increase in activity apparently is connected with a relatively small decrease of the stability.

In the present study one of the first examples of the immobilization of a soluble polymeric catalyst onto solid supports is described. The special properties of polymeric catalysts are dependent on the adaptability of the polymeric structure in the vicinity of the catalytic centers and, therefore, the mobility of the polymer chain should not be affected by immobilization. Apparently, our system consisting of macroporous styrene (St)/divinylbenzene (DVB) supports with attached poly(vinylamine)/COFC does not fulfill this requirement completely. IR-measurements (Fig. 5 in chapter 7) have indicated that conformational changes of PVAm occur due to immobilization, whereas the hydrophobic St/DVB matrices will unfavourably influence the performance of the catalytic site. Probably, these problems can be circumvented by the application of more hydrophilic carriers and the use of spacer groups. Furthermore, in the future further attention should be devoted to the optimization of the porosity of the supports in order to avoid diffusional limitations of the transport of reactants to the catalytic sites.

References

SUMMARY

This thesis describes the results of an investigation on the catalytic oxidation of thiols (RSH) to disulphides (RSSR) with molecular oxygen. An effective catalyst for this autoxidation should possess oxidation sites and basic sites in cooperative interaction. Such a bifunctional catalyst was prepared by using poly(vinylamine) (PVAm), that acts both as a supplier of basic sites and as a carrier for the oxidation catalyst cobalt(II)-tetracarboxyphthalocyanine (CoPc(COOH)₄). Polymer attachment of this cobalt-phthalocyanine (CoPc) was achieved by complexation through polymeric amine groups (catalyst I) as well as by formation of a peptide linkage between the carboxylic groups of the phthalocyanine ring system and the polymeric carrier (catalyst II). Both methods of coupling provided bifunctional catalysts not requiring additional base and having extremely high activities (chapter 2).

During the autoxidation of RSH with bifunctional catalysts hydrogen peroxide (H₂O₂) is produced and consumed simultaneously. A mechanistic interpretation of the production of H₂O₂ is presented. It is demonstrated that the base-catalyzed reaction of RSH with H₂O₂ can account for the measured conversion of H₂O₂ (chapter 3), while the conversion of H₂O₂ by reaction with polymeric amine groups and the disproportionation into O₂ and H₂O (catalyzed by CoPc) are found to be of minor importance. The reaction of RSH with H₂O₂ results mainly in the formation of RSSR, but it is shown by IR-measurements that also small amounts of sulphur-containing oxo-acids are formed. The observed deactivation of the bifunctional catalytic system results from the poisoning of the basic sites of the catalysts by these sulphur-acids. Decomposition of CoPc by H₂O₂ is proved not to be an important reason for the deactivation.

The presence of low amounts of alkaline base did not influence the initial activity of the PVAm/CoPc catalysts appreciably, but it had a positive influence on the stability. Presumably, the addition of NaOH inhibits the formation...
of acidic by-products. However, addition of higher amounts of alkaline base resulted in a decrease of the activity due to a reduction of the local substrate concentration. In case of catalyst I this decrease is more pronounced because of rupture of the polymer/CoPc linkage.

Since the deactivation of the bifunctional catalysts is connected with the accumulation of $H_2O_2$ in the reaction system, it was investigated whether in situ conversion of the redundant peroxide could be achieved (chapter 4). Metallic oxides ($MnO_2$, $PbO_2$ and $Ag_2O$), activated carbons and metallophthalocyanines were applied as catalysts for the decomposition of $H_2O_2$ into $O_2$ and $H_2O$. It was found that these substances are powerful catalysts, but all of them (with the exception of $PbO_2$) have the disadvantage of a rather fast deactivation. Furthermore, the ability to decompose $H_2O_2$ is almost entirely suppressed during thiol oxidation with PVAm/CoPc catalysts and therefore none of the mentioned compounds gave an improvement in the deactivation of the bifunctional catalysts. Most probably, the catalytic decomposition of $H_2O_2$ is inhibited because the thiol molecules expel the $H_2O_2$ molecules from the active sites on the catalysts.

It has been found that the bifunctional catalysts can be applied in an apolar medium like toluene, provided that a small amount of water (i.e. about 0.5 vol.-%) is present as proton-transfer medium (chapter 5). This observation might be of technological interest since it offers the opportunity for simplification of the method for oxidation of thiols in oil-products (i.e. avoiding the usually applied two-phase process). Experiments with conventional CoPc/NaOH systems, as well as with PVAm/CoPc catalysts, have revealed that remarkable kinetic effects can be obtained when applying water/alcohol mixtures of varying composition as reaction medium. The activity of both types of catalysts decreases on increasing the ethanol content from 0 to 50 vol.-%. Above 50 vol.-% alcohol however, the activity of the CoPc/NaOH system increases again and a pronounced maximum was found at about 90 vol.-% (i.e. an increase of
a factor of 10 as compared to pure water). Visible light spectral measurements and experiments with various types of alcohols indicated that the observed activity pattern might be caused by solvation effects. Presumably, the maximum in activity can be ascribed to an increased reactivity of the catalyst and reactants due to a decreased hydration. It has also been observed, when using water as reaction medium, that addition of electrolytes can enhance the rate of thiol oxidation in conventional CoPc/NaOH systems by a factor of about 40. Although various classical and specific salt effects may play a role here, probably a decrease of the hydration of the catalyst and reactants is an important reason for the increase in activity in this case too. Evidently, a certain amount of water is necessary for the catalytic reaction to proceed, but the amount of water in the micro-environment of the catalytic sites must be kept to a minimum in order to attain high activities.

Optical and catalytic experiments with complexes of the tetrasydiamine salt of cobalt(II)-tetrathiaporphyrinocyanine and PVAm give supporting evidence to the hypothesis, that the isolation of cobalt centers and the catalytic activity can be promoted by increasing the relative amount of polymeric base. It is found that the specific activity of the polymeric catalysts depends on the number average degree of polymerization \( \bar{P}_n \) of the applied polymer samples (chapter 6). In particular at relatively high cobalt content, samples with comparatively low \( \bar{P}_n \) give more protection against aggregation of cobalt sites (i.e. inactivation) and, therefore, effect a higher specific activity. A statistical calculation suitable to determine the distribution of cobalt sites over the polymeric coils, supports the interpretation of the experimental data.

Because the applicability of the PVAm/CoPc catalyst is limited by its solubility in the reaction medium that is applied most frequently (i.e. water), the polymeric catalyst was immobilized on a solid support (chapter 7). In this investigation macroporous highly crosslinked styrene (St)—divinylbenzene (DVB) copolymers prepared by solution and
suspension polymerization techniques have been applied. These materials allowed the grafting of poly(N-vinyl-tert-butylcarbamate) (PVCa) either by addition of VCa macro-radicals to the solid bound double bonds or by termination involving the reaction of VCa macro-radicals present on the carrier. PVAm grafted on St-DVB carriers was obtained after the hydrolysis of grafted PVCa with HCl and the subsequent removal of amino-bonded HCl by means of NaOH. Heterogeneous bifunctional catalysts were obtained by attachment of CoPc(COOH)$_4$ to the grafted PVAm. The prepared catalysts were shown to be active in the autoxidation of RSH, both in predominantly apolar media and in aqueous media. It is demonstrated, that important prerequisites for the applicability of macroporous St-DVB copolymers as carriers for the CoPc(COOH)$_4$/PVAm catalyst include a high surface area, a sufficiently large average pore diameter and accessibility of the pendant double bonds.
SAMENVATTING

In dit proefschrift worden de resultaten beschreven van een onderzoek naar de katalytische oxidatie van thiolen (RSH) tot disulfides (RSSR) met moleculaire zuurstof. Een effectieve katalysator voor deze oxidatie moest oxidatie- en basische plaatsen met een goede onderlinge wisselwerking bezitten. Een dergelijke bifunctionele katalysator werd bereid door gebruik te maken van poly(vinylamine) (PVAm), dit polymer fungeert als leverancier van basische groepen en dient tevens als drager voor de oxidatiekatalysator Co(II)-tetracarboxyftalocyanine (CoPc(COOH)₄). Het cobaltftalocyanine (CoPc) werd aan het polymer gekoppeld door complexering met de aminogroepen van het polymer (katalysator I) en ook door een peptide-binding tot stand te brengen tussen een carboxyl-substituut van het CoPc en een aminogroep van de polymere drager (katalysator II). Beide koppellingsmethoden hebben bifunctionele katalysatoren opgeleverd, die geen toevoeging van loog vereisten en zeer actief waren (hoofdstuk 2).

Gedurende de autooxidatie van RSH met bifunctionele katalysatoren vindt zowel productie als consumptie van waterstofperoxide (H₂O₂) plaats. Er wordt een mechanistische voorstelling van de productie van H₂O₂ gepresenteerd. De door base gekatalyseerde reactie van RSH met H₂O₂ blijkt de gemeten H₂O₂ consumptie te kunnen verklaren, terwijl de omzetting van H₂O₂ door reactie met de aminogroepen van het polymer en de disproportionering in O₂ en H₂O (gekatalyseerd door CoPc) van geen belang is (hoofdstuk 3). De reactie van RSH met H₂O₂ levert hoofdzakelijk RSSR op, maar met IR-metingen werd aangetoond dat ook kleine hoeveelheden zure produkten worden gevormd. De waargenomen deaktivering van het bifunctionele katalysatorsysteem wordt veroorzaakt door vergiftiging van de basische plaatsen op de katalysator door deze zuren. De ontleding van CoPc door H₂O₂ blijkt geen belangrijke oorzaak van de deaktivering te zijn.
De aanwezigheid van kleine hoeveelheden loog heeft geen grote invloed op de activiteit van de PVAm/CoPc katalysatoren, maar blijkt wel een positieve invloed op de stabiliteit te hebben. Waarschijnlijk wordt door de toevoeging van NaOH de vorming van zure bijprodukten voorkomen. De toevoeging van grotere hoeveelheden base veroorzaakte een daling van de activiteit, hetgeen wordt toegeschreven aan een afname van de lokale substraat concentratie. In het geval van katalysator I wordt deze activiteitsverlaging veroorzaakt door verbreking van het polymer/CoPc complex.

Vanwege het feit dat de deaktivering van de bifunctionele katalysator samenhangt met de accumulatie van $H_2O_2$ in het reactiesysteem, werd onderzocht of in situ omzetting van het overtoplauw peroxide kon worden verkregen (hoofdstuk 4). Metaaloxide ($MnO_2$, $PbO_2$ en $Ag_2O$), aktieve kool en metaalhalogeenines werden als katalysator voor de ontekening van $H_2O_2$ in $O_2$ en $H_2O$ getest. Het is gebleken dat deze stoffen actieve katalysatoren zijn, maar helaas trad in alle gevallen (met uitzondering van $PbO_2$) een vrij snelle deaktivering op. Tijdens thiol oxidatie met PVAm/CoPc katalysatoren is bovendien het vermogen om $H_2O_2$ te ontekenen vrijwel geheel verdwenen en daarom kon geen van de genoemde verbindingen verbetering van de deaktivering van de bifunctionele katalysator berekenen. Waarschijnlijk wordt de katalytische ontekening van $H_2O_2$ belemmerd, doordat de thiol moleculen de $H_2O_2$ moleculen van de aktieve plaatsen op de katalysator verdrijven.

De bifunctionele katalysatoren blijken te kunnen worden toegepast in een apolair medium, zoals toluol, op voorwaarde dat een kleine hoeveelheid water (ongeveer 0,5 vol.-%) aanwezig is voor het verzorgen van het protonentransport (hoofdstuk 5). Deze waarneming opent de mogelijkheid om het process voor de verwijdering van thijlen uit olieprodukten te vereenvoudigen, omdat het gebruikelijke twee-fase proces zou kunnen worden vermijden. Experimenten zowel met conventionele CoPc/NaOH
systemen als met PVAm/CoPc katalysatoren hebben uitgewezen dat opmerkelijke kinetische effecten kunnen worden verkregen, wanneer water/alkohol mengsels van verschillende samenstelling als reactiemedium worden gebruikt. De activiteit van beide katalysatortypen daalt wanneer men het ethanolgehalte van 0-50 vol.-% laat toenemen. Boven 50 vol.-% stijgt de activiteit van het CoPc/NaOH systeem echter weer en er treedt een duidelijk maximum op bij ongeveer 90 vol.-% ethanol. De activiteit op het maximum is een factor 10 hoger dan de activiteit in alcoholvrij water. Spectroscopische metingen en experimenten met verschillende alkoholen wijzen erop, dat het waargenomen activiteitsverloop wordt veroorzaakt door solvatatie-effecten. Het maximum in de activiteit mag wellicht worden toegeschreven aan een toegenomen reactiviteit van de katalysator en de reactanten als gevolg van een verminderde hydratatie. In het geval dat water als reactiemedium wordt gebruikt blijkt, dat door toevoeging van electrolyten de snelheid van thiol oxidatie in conventionele CoPc/NaOH systemen met een factor van ongeveer 40 kan toenemen. Hoewel verschillende klassieke en specifieke zouteffecten hierbij een rol kunnen spelen, is wellicht ook in dit geval een afname van de hydratatie van de katalysator en reactanten een belangrijke reden voor de stijging van de activiteit. Er kan worden geconcludeerd, dat een bepaalde hoeveelheid water noodzakelijk is om de katalytische reactie te doen verlopen, echter om een hoge activiteit te verkrijgen moet de hoeveelheid water in de directe omgeving van de aktieve plaatsen tot een minimum worden beperkt.

M.b.v. spectroscopische en katalytische experimenten aan complexen van het tetranatriumzout van cobalt(II)-tetrasulfofoetacocyanine en PVAm werd bewezen, dat zowel de isolatie van het CoPc als de katalytische activiteit toenemen door stijging van de relatieve hoeveelheid PVAm. De specifieke activiteit van de polymere katalysatoren blijkt afhankelijk te zijn van de aantalgemiddelde polymerisatiegraad ($\bar{F}_n$) van het gebruikte PVAm monster.
(hoofdstuk 6). In het bijzonder bij een relatief hoog cobalt gehalte blijken monsters met een betrekkelijk lage $F_n$ een hoger specifieke activiteit op te leveren, omdat dan de CoPc moleculen meer tegen aggregatie worden beschermd. Een statistische berekening, waarmee de verdeling van het CoPc over de polymerklamers kan worden berekend, ondersteunt de interpretatie van de experimentele gegevens.

Vanwege het feit dat de praktische toepasbaarheid van de PVAm/CoPc katalysator wordt belemmerd door de oplosbaarheid in het oplosmiddel dat meestal wordt toegepast (water), werd de polymere katalysator geimmobiliseerd op een vaste drager (hoofdstuk 7). In dit onderzoek werd gebruik gemaakt van macroporeuze sterk vernette styreen-St-divinylbenzeen (DVB) copolymeren als dragers, deze werden bereid m.b.v. oplossings- en suspensiepolymerisatie-technieken. Poly(N-vinyl-tert-butylcarbamaat) (PVCa) kon op deze materialen worden geënt d.m.v. aditie van VCa makroradikalen aan de in de drager aanwezige dubbele bindingen of wel door reactie van VCa makroradikalen met radikalen op de drager (terminiatie). Hydrolyse van het geënte PVCa met HCl en vervolgens verwijdering van het aan de aminogroepen gebonden HCl met NaOH heeft op St-DVB geënt PVAm opgeleverd. Heterogene bifunctionele katalysatoren werden verkregen door CoPc(COOH)$_4$ aan het geënte PVAm te koppelen. De gesynthetiseerde katalysatoren zijn, zowel in hoofdzakelijk apolaire als in waterige media, aktief voor de autooxidatie van RSH. Het wordt aangetoond dat een groot specifiek oppervlak, een voldoende grote gemiddelde poriën diameter en toegankelijkheid van de dubbele bindingen belangrijke randvoorwaarden zijn voor de toepasbaarheid van macroporeuze St-DVB copolymeren als dragers voor CoPc(COOH)$_4$/PVAm katalysatoren.
CURRICULUM VITAE


In februari 1977 kwam hij in dienst van de vakgroep anorganische chemie op de Technische Hogeschool te Eindhoven, waar in nauwe samenwerking met de (sub-)vakgroep polymeer-chemie het in dit proefschrift beschreven onderzoek werd uitgevoerd.
DANKSETIJGING

Dit proefschrift is mede tot stand gekomen door de inzet van diverse medewerkers en studenten van de afdeling scheikundige technologie van de Technische Hogeschool Eindhoven. Met name geldt dit voor de leden van de vakgroepen anorganische chemie en chemische technologie. Aan allen hiervoor mijn hartelijke dank.


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Tenslotte dank ik mijn vrouw voor de verzorging van het vaste typswerk en Mevr. C.J. van 't Blik-Quax voor de hierbij verleende assistentie.
STELLINGEN

behorende bij het proefschrift van

J.H. Schutten

Eindhoven, 30 januari 1981
1. De door Sallier et al. beschreven methode om door middel van pyrolyse-gaschromatografie het divinylbenzeen gehalte van styreen-divinylbenzeen copolymeren te bepalen is aan bedeningen onderhevig.

2. Rajadhyaksha et al. vonden een lage activiteit voor de conversie van ethaan over met NH₄NO₃ verkregen HY-SSM-5 zeoliet t.o.v. de met HCl bereide katalysator. Deze lage activiteit en ook de gevonden produktverdelingen gevonden aanleiding tot de veronderstelling dat de auteurs gebruik gemaakt hebben van zeoliet-preparaten met een behoorlijk percentage amorf verontreiniging.

3. In tegenstelling tot wat Bucknall en Hoare et al. suggereren, mag de overeenkomst tussen het mechanisch gedrag van respectievelijk oplosmiddel- en spanningsgeïnduceerde crises niet als vanzelfsprekend worden aanvaard.
   J. Hoare en D. Hall, Phil. Mag., 26 (1972) 448.

4. Bij de bepaling van monomere reaktiviteitsverhoudingen in copolymerisatieonderzoek wordt vaak ten onrechte gesteld dat oplosmiddel-effecten op de kinetische parameters kunnen worden geëlimineerd door geen oplosmiddel te gebruiken.
5. De bewering van Wagnerova et al., dat het cobalt-tetra-
sulfoftalocyanine niet actief is voor de katalytische
ontleding van $\text{H}_2\text{O}_2$, is onjuist. De schijnbare in-
aktiviteit is het gevolg van blokkering van de katal-
lytisch aktieve plaatsen door het aanwezige EDTA.

D. N. Wagnerova, E. Schubertnerova en J. Veprek-
2066.

Dit proefschrift, hoofdstuk 3 en 4.

6. Het verdient aanbeveling om waterstof-chemisorptie
experimenten voor de karakterisering van metaal-op-
dragers katalysatoren te standaardiseren; bij voorkeur
dient een correctie voor de reversibel geabsorbeerde
waterstof te worden toegepast.

446.

G. S. MoVicker, H. T. K. Bakker, R. L. Garren en

7. Bij de bepaling van monomere reaktiviteitsverhoudingen
(z-vaarden) bevatten alle variabelen een meetfout.
Berekeningsmethoden voor z-vaarden, die hiermee geen
rekening houden, zijn aan ernstige bedenkingen onder-
hevig.

H. Patino-Leal, F. M. Reilly en K. F. O’Driacoli,
319.

8. De Raman-spectra die door respectievelijk Villa et al.
en Madema et al. worden toegeschreven aan ijzer-molybdentaat
$(\text{Fe}_2\text{MoO}_4)_3$ zijn niet met elkaar in overeenstemming.
Waarschijnlijk hebben de laatstgenoemde auteurs niet
gemeten aan het door hen veronderstelde produkt.

P. L. Villa, A. Saba, F. Trifiro en
W. Madema, C. van Stam, F. H. W. de Beer,
A. J. A. Koning en B. C. Koningh, J.
9. Het gebruik van de uitdrukking "chemisch afval" kan ten onrechte de indruk wekken, dat er ook afval bestaat dat niet uit scheikundige verbindingen is samengesteld.

10. In het licht van het gezegde "die het kleine niet eert, is het grote niet waard" is het verschil in maatschappelijke reactie op het aantreffen van aardolieprodukten in respectievelijk Lekkerkerk en Schoonebeek enigzins bevredigend.