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Citation for published version (APA):

Streun, van, K. H., Meuldijk, J., & German, A. L. (1989). Immobilization of 2,4-ionene on a macroporous poly(styrene-divinylbenzene) resin and its effect on the rate of the cobaltphthalocyanine-catalyzed oxidative coupling of mercaptoethanol. *Angewandte Makromolekulare Chemie*, 173(1), 119-135.
<https://doi.org/10.1002/apmc.1989.051730110>

DOI:

[10.1002/apmc.1989.051730110](https://doi.org/10.1002/apmc.1989.051730110)

Document status and date:

Published: 01/01/1989

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Immobilization of 2,4-Ionene on a Macroporous Poly(Styrene-Divinylbenzene) Resin and its Effect on the Rate of the Cobaltphthalocyanine-Catalyzed Oxidative Coupling of Mercaptoethanol

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(Received 10 October 1988)

SUMMARY:

A poly(quaternary ammonium) salt, 2,4-ionene, has been immobilized on a macroporous chloromethylated poly(styrene-divinylbenzene) resin (XAD-2). The ionene content of the resin, determined by CHN elemental analysis, was 50.2 g/kg resin. The most important side effect of the modified resin, catalyst (2,4-ionene) bleeding, can be detected by a spectrophotometric method capable of determining extremely low concentrations of free ionene in the supernatant of the resin.

The activity of these immobilized 2,4-ionene/cobalt(II)phthalocyanine-tetrasodiumsulfonate (CoTSPc) complexes towards the oxidative coupling of thiols is much lower than in the homogeneous case, but still considerably higher than for the polymer free system. The observed decrease in reaction rate does not originate from the considerable mass transfer resistances but predominantly from catalyst properties like a very low local N^+ / Co ratio. The active sites appear to be present in the outer shell of the resin particles only.

ZUSAMMENFASSUNG:

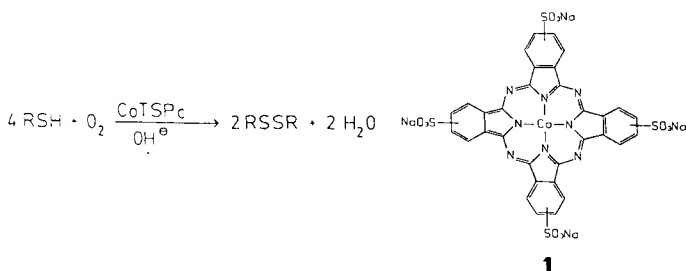
2,4-Ionen, ein polymeres quartäres Ammoniumsalz, wurde auf einem makroporösen chlormethylierten Poly(Styrol-co-Divinylbenzol)-Harz (XAD-2) immobilisiert. Der Ionen-Gehalt des Harzes, der durch CHN-Elementaranalyse bestimmt wurde, betrug 50,2 g/kg Harz. Der wichtigste Nebeneffekt des modifizierten Harzes, das Ausbluten des Katalysators 2,4-Ionen, kann durch eine spektrophotometrische Methode, die extrem geringe Konzentrationen an freiem Ionen an der Oberfläche des Harzes messen kann, ermittelt werden.

Die Aktivität der immobilisierten 2,4-Ionen/Kobalt(II)-phthalocyanin-tetranatriumsulfonat-Komplexe in bezug auf die oxidative Kupplung von Thiolen ist viel niedriger als im homogenen Fall, aber noch beträchtlich höher als im polymerfreien System. Die beobachtete Abnahme der Reaktionsgeschwindigkeit resultiert nicht aus

Behinderungen des Massentransports, sondern vorzugsweise aus den Katalysatoreigenschaften wie z. B. einem sehr niedrigen N^+ / Co -Verhältnis. Die aktiven Zentren scheinen nur in der äußeren Hülle der Harzpartikel vorhanden zu sein.

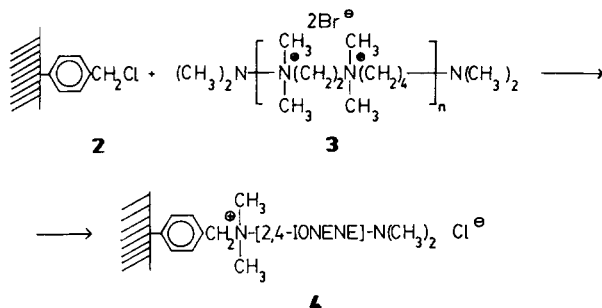
Introduction

In our laboratory we have studied the effects of positively charged polymers on the so-called Mercox-process, i.e. the oxidative coupling of thiols to disulfides in the presence of cobalt(II)phthalocyanine-tetrasodium-sulfonate (CoTSPc) (**1**, scheme 1)^{1,2}.



Scheme 1. Conventional (polymer free) thiol oxidation.

Especially polyvinylamine (PVAm) and 2,4-ionene (**3**, scheme 2), a poly(quaternary ammonium) salt showed a large enhancement as compared with the polymer free system.



Scheme 2. Synthetic route of immobilization of 2,4-ionene on an XAD-2 resin.

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It is believed that the cationic charge on the polymer backbone has a two-fold function: (a) binding the cobalt complex by coulombic interaction, (b) increasing the thiolate anion concentration in the polymer domain thus bringing the cobalt center and the substrate together. For both polymers Michaelis-Menten kinetics is observed in thiol and oxygen^{3,4}. 2,4-Ionene is preferred over PVAm for a number of reasons: (a) its simple synthesis, (b) its cationic charge independent of pH, and (c) its higher overall reaction rate.

Recently attempts were made to immobilize PVAm^{5,6}, often resulting in a collapse of the activity.

Immobilization of soluble precious catalysts is very interesting because it offers the possibility of an easy work-up of the reaction mixtures. Moreover, immobilized systems make continuous operations easier^{7,8}. One of the disadvantages of immobilization may be a decrease of the activity of the immobilized catalyst system as compared with the homogeneous system. This can be caused by a collapse of the intrinsic reaction rate due to loss of conformational freedom of the catalytic center, to a microenvironmental effect, to mass transport limitations, or to a combination of these.

In this paper we describe the immobilization of 2,4-ionene onto a macroporous chloromethylated XAD-2 resin and its effect on the oxidation of 2-mercaptoethanol (ME) by CoTSPc/ionene.

The strategy for the immobilization of 2,4-ionene/CoTSPc on a poly(styrene-divinylbenzene) resin implies the functionalization of the starting resin by chloromethylation, followed by a reaction of this activated resin with aminated 2,4-ionene and the subsequent binding of CoTSPc to the immobilized ionene. An organic support was preferred over a modified silica carrier since the former is insensitive to pH 8 – 12 in contrast to silica which solubilizes in this pH region⁹. The features of the catalyst connected with the observed lower activity of the immobilized system will be described.

Experimental

Immobilization

The macroporous XAD-2 resin (Rohm & Haas Co., average particle diameter 50 – 100 μm , specific surface area 300 m^2/g and average pore diameter 10 nm) was thoroughly cleaned before use as follows: washed twice with water, methanol, 1,4-dioxane and once with methanol and then dried at 50°C (0.1 kPa). The resin was chloromethylated as described by Bootsma et al.¹⁰. The amount of chloromethyl groups was determined by CHN elemental analysis from the diminishing percentage

of carbon as compared with the starting resin. CHN elemental analysis was carried out using a Perkin-Elmer 240 CHN elemental analyzer. 2,4-Ionene and aminated 2,4-ionene were synthesized and characterized as described previously¹¹. In a typical experiment the immobilization proceeds as follows: 2 g chloromethylated resin (2, scheme 2) and 1,63 g aminated 2,4-ionene (3, scheme 2; $\bar{M}_n = 1630$, as determined by titration) in 2 g methanol and 3,3 g water were reacted at 60 °C for two weeks. After filtration and washing with water, the resin was extracted with water in a Soxhlet apparatus for at least 48 h. Water was added to the resin and the supernatant was tested for the presence of free ionene by a spectrophotometric method based on considerations described in the results. The spectrophotometric measurements were performed on a Hewlett-Packard 8451A diode array spectrophotometer in a 1 cm cell at 25 °C. The amount of ionene per kilogramme resin was determined by CHN elemental analysis. Knowing the percentage of nitrogen of the pure ionene (8.37%), the ionene content on the resin can be calculated as $(\% \text{ N}/8.37) \cdot 10^3 \text{ g ionene/kg resin}$. The resin was stored in water, and filtered off and washed with water before use.

Kinetic Runs

CoTSPc was synthesized according to the method described by Weber and Bush¹². 2-Mercaptoethanol was used as substrate and distilled before use. Before the reaction was started a CoTSPc solution was added to the reaction vessel containing the resin. Different catalyst loadings were achieved by either changing the amount of added CoTSPc solution or the amount of resin in the reaction vessel. After 15 min the reaction was started by adding the substrate to the reaction mixture. The total reaction volume was 10^{-4} m^3 . The reaction rates were measured in an all glass double walled reactor (diameter = $6.5 \cdot 10^{-2} \text{ m}$) equipped with four symmetrically located baffles (widths = 10^{-2} m). A four bladed turbine impeller with a diameter of $2.5 \cdot 10^{-2} \text{ m}$ was used. The stirring speed was about 2500 rpm (41.7 rps). The reaction was carried out at 0.1 MPa partial pressure of oxygen and a temperature of $25.0 \pm 0.1 \text{ °C}$. The monitoring system was described earlier¹¹.

Results and Discussion

Immobilization

For the immobilization of 2,4-ionene, a commercially available poly(styrene-divinylbenzene) resin (XAD-2) was used. This XAD-2 resin, a macroporous type resin, is preferred over gel type resins (e.g. Merrifield resin) because of its well-defined pore volume, specific area, and non-swellability (for specifications see the experimental part). After chloromethylation the chloromethyl content, determined by CHN elemental analysis, was 1.26 mol

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CH₂Cl/kg resin (Tab. 1). The immobilization of 2,4-ionene is accomplished by reacting the chloromethylated resin (2, scheme 2) with the aminated 2,4-ionene (3, scheme 2). The 2,4-ionene content of the resulting product (4, scheme 2), after thoroughly extracting the latter with water, was also determined by CHN elemental analysis to amount 50.2 g ionene/kg resin (= 31 mmol ionene/kg resin; chemical yield, based on chloromethyl groups = 2.5%, Tab. 1). Earlier results from our laboratory on homogeneous systems showed a dependence of the catalytic activity on the ionene concentration (expressed in [N⁺], calculated from the nitrogen content of ionene, 8.37%)^{11, 13}. Since even very low free ionene concentrations ([N⁺] = 10⁻² mol/m³) enhance the reaction, we developed a sensitive spectrophotometric method to determine these minor amounts of free ionene in the reaction mixture, based on the clear difference between the UV-Vis-spectra of non-complexed CoTSPc and ionene-complexed CoTSPc. Van Welzen et al.¹⁴ showed that a dimer peak around λ = 630 nm was observed for CoTSPc in the presence of low molecular mass ionene at a molar ratio (N:Co) of at least 2:1. If this ratio was less only the monomer peak around λ = 660 nm showed up. As the minimum detectable CoTSPc concentration is 2 · 10⁻⁴ mol/m³, the detection limit for ionene becomes two times higher, i.e. 4 · 10⁻⁴ mol N⁺/m³. By this method we proved that after extracting the resin with water in a Soxhlet apparatus for 48 h, the supernatant was free from non-immobilized 2,4-ionene.

In order to estimate the amount of quaternary ammonium groups on the resin available for CoTSPc binding, the concentration of CoTSPc in the supernatant was determined spectrophotometrically on increasing the total amount of CoTSPc in the system. The results are shown in Fig. 1. Curve A shows the dependence of the absorbance at λ = 660 nm as a function of the

Tab. 1. Elemental analysis of the resins used.

	C (%)	H (%)	N (%)	CH ₂ Cl/ resin (mol/kg)	Ionene/ resin (g/kg)
XAD-2	91.40	8.35	—	—	—
XAD-2/chloro- methylated	87.68	7.84	—	1.26	—
XAD-2/ionene	86.72	8.34	0.42	—	50.2*

* 31 mmol ionene/kg resin, based on $\bar{M}_n = 1630$; chemical yield = 2.5%, based on chloromethyl groups.

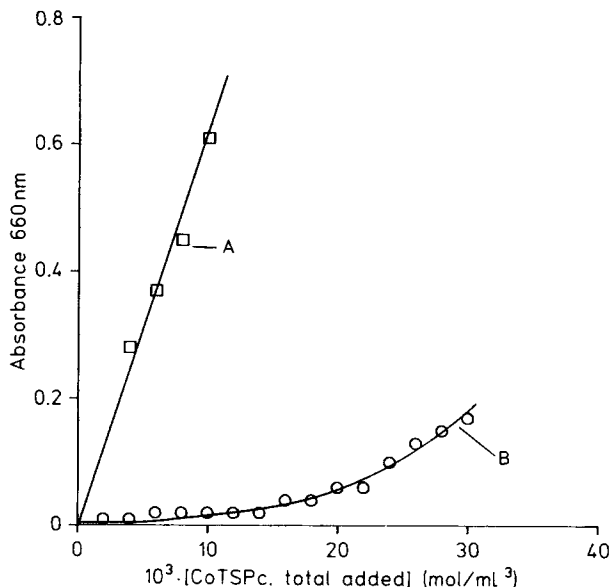


Fig. 1. Absorbance of non-complexed CoTSPc at 660 nm as a function of the total added amount of CoTSPc in water, 25 °C. (□) Chloromethylated resin, 3.75 kg/m³ (curve A); (○) immobilized ionene resin, 4.20 kg/m³ (curve B).

total amount of added CoTSPc in the presence of the chloromethylated resin. This curve coincides with the curve for CoTSPc alone, indicating there is no adsorption of CoTSPc on the chloromethylated XAD-2 resin. Curve B shows the dependence of the absorbance of CoTSPc on an increasing total amount of CoTSPc in the presence of the resin containing immobilized ionene. Up to a total concentration of $22 \cdot 10^{-3} \text{ mol CoTSPc/m}_L^3$ ($[\text{resin}] = 4.2 \text{ kg/m}_L^3$) hardly any absorbance is monitored, indicating that up to this value practically all CoTSPc added is being adsorbed on the resin. From these data one can estimate the total amount of CoTSPc on the resin used in the kinetic experiments as $5.2 \cdot 10^{-3} \text{ mol CoTSPc/kg resin}$. The maximum theoretical amount of absorption of CoTSPc on the ionene modified resin can be calculated from the nitrogen content of the immobilized ionene resin and an assumed maximum N:Co ratio of 4:1 (CoTSPc is fourfold negative), and amounts to $75 \cdot 10^{-3} \text{ mol/kg resin}$. This means that only 7% of the quaternary ammonium groups are available for CoTSPc complexation. We

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believe that interaction of CoTSPc with the immobilized ionene at the outer surface of the particles and at the entrance of the pores blocks off the "interior" of the resin, which was also observed in the case of crosslinked PVAm gel-type particles⁶.

On the other hand, the proposed CoTSPc distribution on the particles may be favorable for substrate accessibility in the kinetic experiments. The effect of the present immobilization on the CoTSPc catalyzed oxidative coupling of thiols will be described hereafter.

Kinetic Runs

Influence of pH

Fig. 2 shows the effect of pH on the rate of the oxidative coupling of 2-mercaptoethanol (ME) catalyzed by CoTSPc/ionene immobilized on XAD-2 resin (2,4-ionene/XAD catalyst). The optimum pH for this catalyst appears to be 7.3, being significantly lower and less pronounced than in the case of

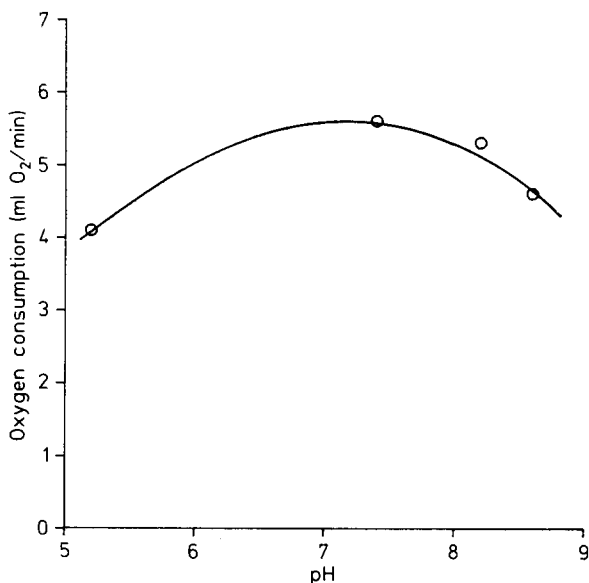


Fig. 2. Oxygen consumption rate as function of pH. $[\text{CoTSPc}] = 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$; $[\text{ME}] = 143 \text{ mol/m}_L^3$; $[\text{resin}] = 1.0 \text{ kg/m}_L^3$; $V_L = 10^{-4} \text{ m}^3$.

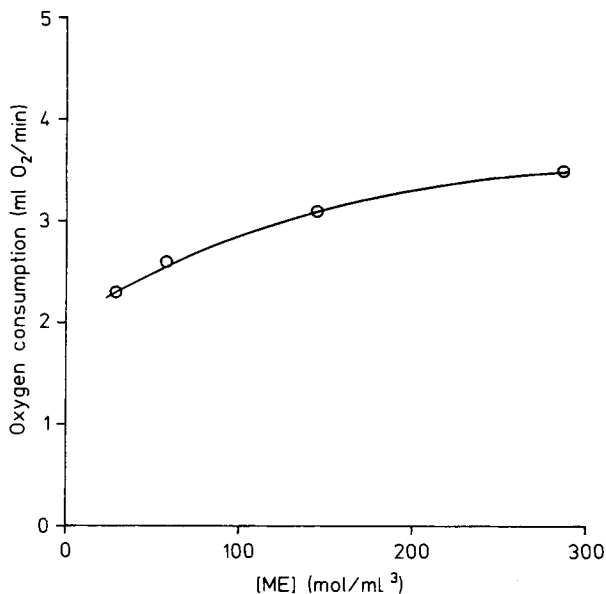


Fig. 3. Oxygen consumption rate as function of the mercaptoethanol concentration. $[\text{CoTSPc}] = 4 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$; $[\text{resin}] = 0.5 \text{ kg/m}_L^3$; $\text{pH} = 8.3$; $V_L = 10^{-4} \text{ m}^3$.

the homogeneous system¹¹. For the latter system a pH optimum around 8 was found. The relatively weak pH dependence of the reaction rates in slurries of the modified particles probably originates from the adsorption of the substrate at the resin surface. In the case of an almost complete saturation of ammonium groups on the resin particle with thiolate anions, a pH variation will hardly affect the concentration of reactive thiolate anions at the surface. This saturation effect is also clearly demonstrated by Fig. 3. In this figure the oxygen consumption rates are plotted as a function of the mercaptoethanol concentration. The relatively small increase of the oxygen consumption rate on increasing the substrate concentration indicates a tendency towards saturation with the thiolate anion for mercaptoethanol concentrations above 50 mol/m_L^3 . This saturation effect results in a relatively small influence of the pH for substrate concentrations above 50 mol/m_L^3 . The rather low activity of the immobilized system as compared with the homogeneous system will be explained hereafter.

Influence of Catalyst Loading

The reaction rates, $-r_{O_2}^W$ (expressed in $\text{mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$) as a function of the mean CoTSPc concentration in the resin are collected in Fig. 4. This figure shows that for CoTSPc concentrations below $2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ an almost linear relationship exists between the reaction rate and the CoTSPc concentration. For CoTSPc concentrations above $4 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ the reaction rate becomes almost independent of $[\text{CoTSPc}]_{\text{resin}}$.

According to the Michaelis-Menten mechanism which holds for the homogeneous CoTSPc/ionene catalyzed oxidative coupling of thiols^{4,11}, a linear relationship is to be expected between reaction rate and CoTSPc concentration. The observed deviation from linearity for CoTSPc concentrations above $2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ may be attributed to a limited number of residual sites on the 2,4-ionene/XAD resin after binding of relatively small number of CoTSPc molecules. In that case, excess CoTSPc would only have a relatively small contribution to the observed catalytic activity. The influence

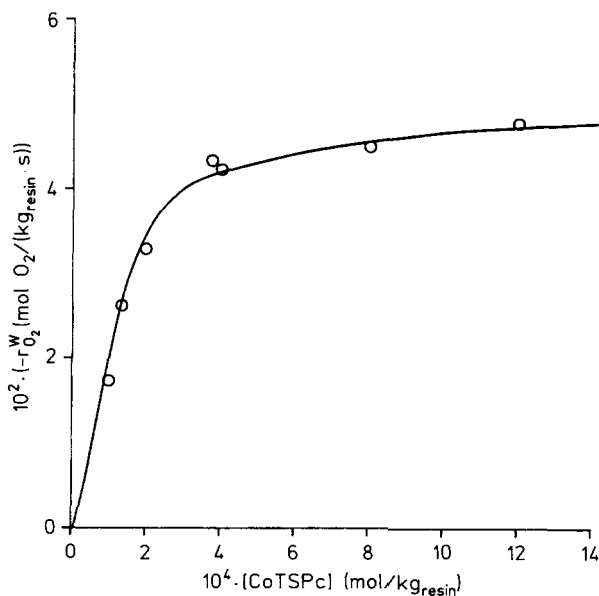


Fig. 4. Reaction rate ($-r_{O_2}^W$, $\text{mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$) as a function of the CoTSPc concentration in the resin. $[\text{ME}] = 143 \text{ mol}/\text{m}_l^3$; $\text{pH} = 8.3$; $V_L = 10^{-4} \text{ m}^3$.

of catalyst loading on the reaction rate can also be caused by mass transfer limitations. A detailed discussion on the importance of the various possible resistances against mass transfer will therefore be presented.

Mass Transfer

Only mass transfer of molecular oxygen has to be considered because the initial concentration of ME ($[ME] = 143 \text{ mol/m}_L^3$) is much higher than the equilibrium concentration of oxygen in the bulk liquid ($[O_2]_L = 1.4 \text{ mol/m}_L^3$ at 0.1 MPa partial pressure of oxygen). As a result of the macroporous character of the 2,4-ionene/XAD resin it is quite obvious that also in the resin phase mercaptoethanol is present in large excess over oxygen. The resistance against oxygen transport from the gas phase into the liquid phase is negligible under the experimental conditions. This can be derived from the homogeneous ionene system where no mass transport limitation was observed at even much higher oxygen consumption rates than those occurring in the present study^{4,11}.

So, possible remaining barriers are the oxygen transport from the bulk liquid to the outer surface of the resin (film diffusion limitation) and the oxygen conversion in the resin particle (pore diffusion limitation). These two effects constitute resistances in series, leading to a relation between $-r_{O_2}^w$ and the difference between the oxygen concentrations in the bulk liquid ($[O_2]_L$) and at the outer surface of the resin ($[O_2]_S$), given by

$$-r_{O_2}^w = k_{LS} \cdot a_{LS} ([O_2]_L - [O_2]_S) \quad (1)$$

where k_{LS} (expressed in $\text{m}_L^3/(\text{m}_S^2 \cdot \text{s})$) stands for the oxygen mass transfer coefficient between the liquid and the outer catalyst surface, and a_{LS} for the outer catalyst surface per unit of mass of the water-swollen resin. A value for a_{LS} can be obtained from

$$a_{LS} = 6/(d_p \cdot \rho_{\text{resin}}) \quad (2)$$

where d_p is the mean diameter of the resin particles and ρ_{resin} is the density of the water-swollen resin. For $d_p = 80 \cdot 10^{-6} \text{ m}$ and $\rho_{\text{resin}} = 10^3 \text{ kg/m}^3$, a_{LS} becomes $75 \text{ m}_S^2/\text{kg}_{\text{resin}}$. The parameter k_{LS} can be estimated with an accuracy of about 30% from the experimental relation derived by Sano et al. for mass transport to spherical ion exchange resin particles in a stirred tank reactor¹⁵:

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$$k_{LS} \cdot d_p / D_{O_2} = 2 + 0.4 \cdot (\varepsilon \cdot d_p^4 / \nu^3)^{1/4} \cdot (\nu / D_{O_2})^{1/3} \quad (3)$$

where D_{O_2} stands for the molecular diffusion coefficient of oxygen in the free liquid ($D_{O_2} = 2 \cdot 10^{-9} \text{ m}^2/\text{s}$)¹⁶, ν for the kinematic viscosity of the liquid ($\nu_{H_2O} (25^\circ\text{C}) = 0.9 \cdot 10^{-6} \text{ m}^2/\text{s}$) and ε (expressed in m^2/s^3) for the energy input rate per unit of mass due to stirring. For agitated vessels ε can be obtained from¹⁵:

$$\varepsilon = N_p \cdot d_s^5 \cdot N^3 / V_L \quad (4)$$

For our experimental setup a power number $N_p \approx 5$ is reasonable^{15,17}, leading to $\varepsilon = 35.3 \text{ m}^2/\text{s}^3$ (the values of the impeller diameter (d_s), the stirring speed (N) and the reaction volume (V_L) are given in the experimental section). Substitution of the values of ε , d_p , ν and D_{O_2} into eq. (3) leads to $k_{LS} = (5.6 \pm 1.7) \cdot 10^{-4} \text{ m}_L^3/(\text{m}_S^2 \cdot \text{s})$.

From the observed values of $-r_{O_2}^W$ and eq. (1) the oxygen concentrations at the outer surface of the resin ($[O_2]_S$) can now be calculated. $[O_2]_S$ decreases from $0.95 \pm 0.14 \text{ mol}/\text{m}_L^3$ for $[\text{CoTSPc}] = 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}$ to $0.53 \pm 0.27 \text{ mol}/\text{m}_L^3$ for $[\text{CoTSPc}] = 2.0 \cdot 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}$. Although the values of $[O_2]_S$ decrease on increasing the catalyst loading there is linear relationship between $-r_{O_2}^W$ and $[\text{CoTSPc}]_{\text{resin}}$ for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}$. This linear relationship between $-r_{O_2}^W$ and $[\text{CoTSPc}]_{\text{resin}}$ is only possible for a reaction order in oxygen close to zero and in absence of intraparticle diffusion limitation of the reaction rate. A reaction order in oxygen close to zero for the $[O_2]_S$ values found for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}$ agrees with the dependence of the rates on the oxygen concentration as observed for homogeneous CoTSPc/ionene system⁴. Hereafter it will be shown that on the basis of a homogeneous distribution of CoTSPc over the resin particles a linear relationship between $-r_{O_2}^W$ and $[\text{CoTSPc}]_{\text{resin}}$ for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol}/\text{kg}_{\text{resin}}$ cannot be expected. Therefore, it becomes most probable that CoTSPc is only present in the outer shell of the 2,4-ionene/XAD catalyst.

Assuming a homogeneous distribution of the active sites through the particle the catalyst effectiveness factor can be obtained from observed reaction rates using the Weisz-modulus. The latter can be estimated from the observed rates¹⁷. The Weisz-modulus Φ for an n -th order irreversible reaction in a spherical catalyst particle is defined as:

$$\Phi = \frac{(n+1) \cdot (-r_{O_2}^W) \cdot \rho_{\text{resin}} \cdot (d_p/6)^2}{2 \cdot D_{O_2} (\text{eff}) \cdot [O_2]_S \cdot \lambda} \quad (5)$$

where n stands for the reaction order in oxygen, $D_{O_2}(\text{eff})$ for the effective diffusion coefficient in the resin particle and λ for the partition coefficient of oxygen between the resin phase and the surrounding liquid. For oxygen λ is taken unity. $D_{O_2}(\text{eff})$ can be estimated from the molecular diffusion coefficient of oxygen D_{O_2} according to¹⁸:

$$\frac{D_{O_2}(\text{eff})}{D_{O_2}} = \frac{F}{\alpha \cdot \lambda} \quad (6)$$

where F is the "drag" factor representing the reduction of the mobility of a spherical molecule in a cylindrical pore and α is a parameter depending on the porosity and tortuosity of the resin.

For diffusion of oxygen in the XAD-2 resin $F = 1$, because the mean pore diameter (10 nm) is much larger than the diameter of the oxygen molecule (0.46 nm as calculated from the Van der Waals equation¹⁹)²⁰. For poly(styrene-divinylbenzene) resins $\alpha = 4$ seems to be a reasonable value¹⁸. Substitution of the values into eq. (6) gives $D_{O_2}(\text{eff}) = 5 \cdot 10^{-10} \text{ m}^2/\text{s}$. For $-r_{O_2}^W = 1.73 \cdot 10^{-2} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$ (as determined for $[\text{CoTSPc}]_{\text{resin}} = 10^{-4} \text{ mol/kg}_{\text{resin}}$) and $n = 0$, $\Phi = 3.2$. For this value of Φ the effectiveness factor η then can be calculated according to¹⁷:

$$\eta = 1/\Phi \quad (7)$$

resulting in $\eta = 0.31$.

For zeroth order reactions in catalyst particles with an homogeneous distribution of active sites and $\Phi > 1$ an increase of the number of active sites by a factor m results in the following expression for the ratio of the rates before ($-r_{O_2}^W$ (1)) and after ($-r_{O_2}^W$ (2)) the change of the catalyst activity¹⁷:

$$\frac{-r_{O_2}^W(1)}{-r_{O_2}^W(2)} = \frac{1}{\sqrt{m}} \cdot \sqrt{\frac{[O_2]_{S,1}}{[O_2]_{S,2}}} \quad (8)$$

In eq. (8) $[O_2]_{S,1}$ and $[O_2]_{S,2}$ stand for the oxygen concentration at the outer surface of the particles before and after changing the number of active sites. Relation (8) shows that for a homogeneous distribution of the active sites an increase of the rate from $1.73 \cdot 10^{-2} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$ ($[\text{CoTSPc}]_{\text{resin}} = 10^{-4} \text{ mol/kg}_{\text{resin}}$, $[O_2]_S = 0.95 \text{ mol/m}_L^3$) to $3.29 \cdot 10^{-2} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$ ($[\text{CoTSPc}]_{\text{resin}} = 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$, $[O_2]_S = 0.53 \text{ mol/m}_L^3$) should only be reached for an increase of $[\text{CoTSPc}]_{\text{resin}}$ from $1 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ to $6.5 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$. Experimentally the rate of $3.29 \cdot 10^{-2} \text{ mol O}_2/(\text{kg}_{\text{resin}} \cdot \text{s})$ is

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already found for $[\text{CoTSPc}]_{\text{resin}} = 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$. The measured behaviour of the rates as a function of the catalyst loading for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ strongly suggests that the diffusion rates of oxygen in the pores of the resin do not have a significant influence on the observed rates. The experimentally found linear relation between the rate and $[\text{CoTSPc}]_{\text{resin}}$ for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ could only be obtained for a reaction order in oxygen close to zero and an effectiveness factor $\eta \approx 1$. Using these arguments the intrinsic activity of the CoTSPc sites on the XAD/ionene catalyst in terms of the turnover frequency can now be calculated from the rates as a function of $[\text{CoTSPc}]_{\text{resin}}$ for $[\text{CoTSPc}]_{\text{resin}} \leq 2 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$.

For a mercaptoethanol concentration of 143 mol/m^3 , a pH value of 8.3 and a temperature of 25°C a turnover frequency of $175 \text{ mol O}_2/(\text{mol CoTSPc} \cdot \text{s})$ is found for the XAD/ionene catalyst. Later in this paper the difference between this turnover frequency and those of other CoTSPc catalyst systems used for the oxidative coupling of 2-mercaptoethanol will be discussed.

CoTSPc Loading

An effectiveness factor η of almost unity, indicating an almost complete use of the active sites can only be achieved when active CoTSPc is present in the outer shell of the resin particle. This is confirmed by the adsorption experiments of CoTSPc on ionene-XAD catalyst, as shown previously in this article. The sudden change of the reaction rate dependence on increasing the catalyst loading above $[\text{CoTSPc}]_{\text{resin}} > 4 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$ into a more saturations type behaviour cannot be explained by mass transport limitation alone. In that case a much slower change of the reaction rate dependence on increasing the catalyst loading would have been observed. These considerations allow the conclusion that another feature must anyhow be at least partially responsible for this rapid change.

Apparently, the reaction rate is hardly influenced by increasing the already high catalyst loading above $4 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$. This is probably caused by a lesser accessibility of the immobilized 2,4-ionene for CoTSPc molecules due to the already high local CoTSPc concentration. Based on the considerations described above the oxygen concentration profile in the liquid and resin phase can be represented as shown in Fig. 5. The film layer around the resin particle, the region between R_f and the particle radius $R (=0.5 \cdot d_p)$, seriously influences the concentrations of oxygen. As the outer

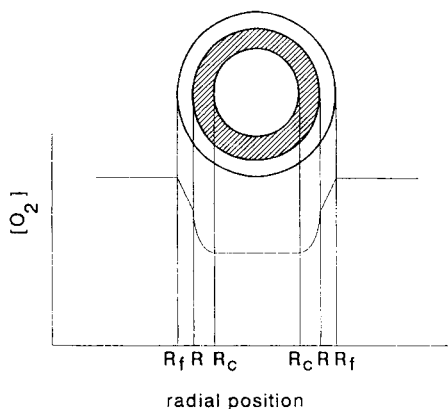


Fig. 5. Schematic representation of the immobilized CoTSPc/ionene system on XAD-2 and the oxygen concentration profile as a function of the particle radial position (see text).

shell of the spheres between R and R_c of the particle contains most of the reactive CoTSPc moieties, oxygen conversion will take place in this shell. The proportions of the layers are not properly scaled. In the interior of the support, where no CoTSPc is present, will be no change in oxygen concentration.

Effect of Immobilization of Ionene on the Activity

The catalytic activities of some CoTSPc catalysts at the optimum pH and 25°C expressed in terms of the turnover frequencies are collected in Tab. 2. This Tab. shows that attaching 2,4-ionene to XAD-2 resin results in a considerable lower activity as compared with that of a homogeneous solution of 2,4-ionene. However, the activity of the immobilized system is still much higher than that of the polymer free system. The difference in activity between a solution of 2,4-ionene and the 2,4-ionene/XAD-2 catalyst can be explained in terms of the N^+/Co ratio in these catalysts. For solutions of 2,4-ionene an optimum activity is observed for $300 < N^+/\text{Co} < 800$ ¹¹. Lowering this ratio dramatically decreases the reaction rate. Since the CoTSPc complexes appear to be present in the outer shell of the ionene modified resin particles only, the local concentration of CoTSPc is much

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Tab. 2. Turnover frequencies in the oxidative coupling of mercaptoethanol at optimum pH and 25 °C, catalyzed by various CoTSPc containing systems.

System	pH	[N ⁺]	Turnover frequency* (mol O ₂ / (mol CoTSPc · s))
Aqueous OH ⁻	8.2	—	8.4**11
Aqueous PVAM	8	1***	700 ⁶
Aqueous 2,4-ionene	8	0.1****	1000 ¹¹
2,4-Ionene/XAD-2	7.3	0.3*****	175*****

* [ME] = 143 mol/m³.

** [CoTSPc] = 2 · 10⁻⁴ mol/m³.

*** In mol/m³; [CoTSPc] = 2 · 10⁻⁴ mol/m³.

**** In mol/kg_{resin}; [CoTSPc] < 2 · 10⁻⁴ mol/kg_{resin}.

***** As determined by the slope of the reaction rate vs. catalyst loading (Fig. 3), for [CoTSPc] < 2 · 10⁻⁴ mol/kg_{resin}.

higher than the overall concentration in the resin. This results in a rather low N⁺/Co ratio in the outer shell of the resin (for 5 vol.-% occupation of the resin volume with CoTSPc, corresponding to a thickness of the CoTSPc containing layer of 7 · 10⁻⁷ m, and an overall CoTSPc concentration of 2 · 10⁻⁴ mol/kg_{resin}, the local N⁺/Co ratio can be estimated to amount 0.3/4 · 10⁻³ = 75). In this train of thought the rather low activity of the 2,4-ionene/XAD-2 catalyst can be explained in terms of too low N⁺/Co ratios in the outer shell of the resin particles as compared with homogeneous solutions of 2,4-ionene/CoTSPc.

Conclusions

The strongly cationic polymer 2,4-ionene can be chemically bonded onto chloromethylated macroporous poly(styrene-divinylbenzene) resins. The ionene content on the resin, determined by CHN analysis, was 50.2 g/kg resin. Due to limited accessibility of the polymeric quaternary ammonium groups on the macroporous particles, only 7% of these groups are available for complexation with CoTSPc indicating that CoTSPc is being adsorbed at the outer shell of the particle. A spectrophotometric method that has been

developed proves the absence of (any possible) traces of ionene in the supernatant, that would highly disturb the kinetic measurements.

Immobilization of 2,4-ionene/CoTSPc on a macroporous poly(styrene-divinylbenzene) resin (XAD-2) results in a considerable reduction of the reaction rate of the oxidative coupling of 2-mercaptoethanol as compared with homogeneous 2,4-ionene/CoTSPc systems. Although there is a significant resistance against oxygen transport from the bulk liquid to the active sites, this decrease is not the result of the limited rate of mass transfer but originates from the rather low N^+/Co ratio around the active centers which are localized in the outer shell of the resin particle. The number of binding sites for CoTSPc in the 2,4-ionene modified resin is therefore rather limited resulting in only a small increase of the activity on increasing the CoTSPc concentration on the resin for $[\text{CoTSPc}] > 4 \cdot 10^{-4} \text{ mol/kg}_{\text{resin}}$. A more reactive catalyst may be prepared by a strong enhancement of the concentration of N^+ -groups in the resin phase. These N^+ -groups should be available for CoTSPc binding and thus preferably be located in the outer shell of the particle. This leads to the conclusion that the reaction rates per unit mass of catalyst can also be considerably increased by drastically reducing the particle size. In this way a larger volume of the support may become accessible to the CoTSPc moieties.

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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