Activation of Cobalt–Phthalocyanine Catalyst by Polymer Attachment

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Summary Attachment of cobalt–phthalocyanine to cross-linked polyacrylamide produces a stable oxidation catalyst with enhanced activity.

RECENTLY, Rollmann[1] reported on the activity and stability of polymer-bonded metalloporphyrins for the oxidation of thiols. Some of them were effective catalysts, but

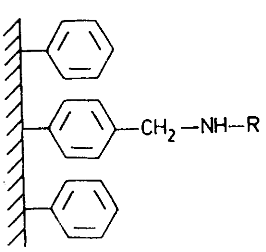
Table 1. Activities of the catalysts

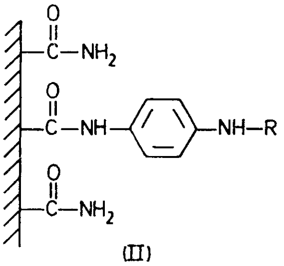
Catalyst	Support	Co/mol ($\times 10^9$)	Volume (ml min^{-1})	Volume per μmol Co (ml min^{-1} μmol^{-1})	Relative rate
CoTSPc	—	100	3·4	34	1
(I)	Merrifield resin	763	2·3	3·02	0·089
(II)	Enzacryl AA	13	1·75	135	4·0
(II)[a]	,,	13	2·6	200	5·88

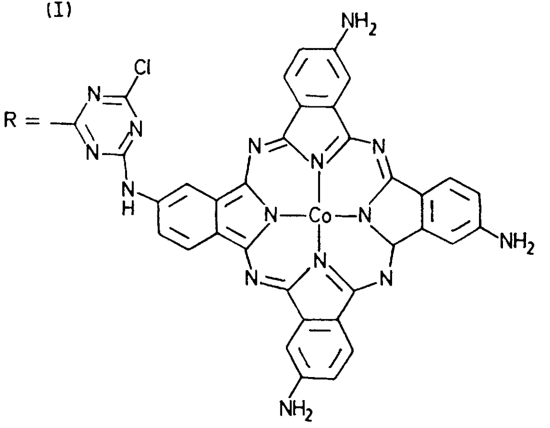
[a] This catalyst was ball-milled for 20 min immediately before use. Reaction conditions: 75 ml of H_2O per 6 mol of NaOH, 1 ml ME, catalyst, 22 °C, 1 atm of O_2, vigorous stirring.

during the reaction deactivation occurred. Our studies usually confirmed this but we now report a catalyst system which is both active and stable.

The active catalyst component is cobalt(II)-4,4′,4″,4‴-tetra-aminophthalocyanine ($CoTNH_2Pc$) prepared according to the method of Shirayaev *et al.*[2] It was coupled by means of cyanuric chloride[3] to NH_2 groups of a polymer matrix. The polymers used were aminated[4] Merrifield† resin and Enzacryl AA.‡ The resulting catalysts can be represented as (I) and (II).


(I)


(II)



The catalysts were tested for the oxidation of 2-mercaptoethanol (ME) by measuring the rate of oxygen consumption (equations 1 and 2).

$$4HSCH_2CH_2OH + 4OH^- \rightarrow 4\,^-SCH_2CH_2OH + 4H_2O \quad (1)$$

$$4\,^-SCH_2CH_2OH + O_2 + 2H_2O \rightarrow 2HOCH_2CH_2S\text{-}SCH_2CH_2CH_2OH + 4OH^- \quad (2)$$

In order to relate the performance of the polymeric catalysts to that of the corresponding soluble catalyst, we also studied aqueous solutions of cobalt–tetrasulphophthalocyanine (CoTSPc), which has proved to be one of the most active phthalocyanine catalysts for thiol oxidation.[5] The polymeric catalysts were powdered before use.§ Oxidation rates and catalytic activities relative to the soluble catalyst, and reaction conditions are given in Table 1.

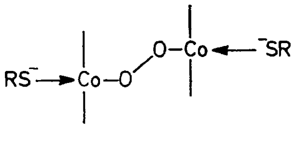
The catalysts were also tested for their stability in successive experiments. The results for catalyst (I) are given in Table 2. Similar results were obtained with catalyst (II).

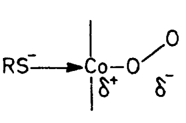
Table 2. Activity in successive runs[a]

No.	Rate /ml min^{-1}	Uptake of O_2 after 10 min ml
1	2·9	27·6
2	2·7	25·2
3	2·8	26·6
4	3·0	28·5
5	2·9	28·4
6	3·0	28·9

[a] After each run the catalyst was filtered and washed with water in preparation for the next run. Reaction conditions: 75 mg of catalyst (I) in 75 ml of H_2O per 9 mmol of NaOH, 1 ml ME, 22 °C, 1 atm of O_2.

The data demonstrate the following: (a) the catalysts (I) and (II) do not show deactivation, (b) activity is highly dependent on the supporting polymer used; catalyst (II) is more active than the soluble analogue, and (c) ball-milling to reduce the catalyst particle size led to an increase in the activity, which indicates diffusion limitations and suggests that a further enhancement of activity would result from a reduction in the diffusion resistance.


(III)


(IV)

The difference in activity between catalysts (I) and (II) is attributed to the difference in diffusion limitations, corresponding to the greater 'swellability' of the polyacrylamide in comparison to the polystyrene matrix. The reasons for the stability and the high activity of the catalysts are not clear at this stage.

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† Merrifield (Fluka) resin is a polystyrene cross-linked with 2% divinylbenzene and chloromethylated to give 3·5 mmol of CH_2Cl per g.

‡ Enzacryl AA (Koch-Light) is a cross-linked polyacrylamide with aniline-substituted acrylamide groups.

§ Catalysts (I) and (II) contained 0·06 and 0·21% Co, respectively. Because of the small amount of catalyst (II) necessary for an experiment, it was diluted by thoroughly mixing it with polystyrene powder (XAD-2, Rohm and Haas); the dilution factor for (II) was 15 and for ball-milled (II) was 75.

Preliminary results show that the kinetics of oxidation with the soluble and insoluble catalysts are different. The order of reaction in substrate in the solution reaction is *ca.* 1, whereas in the heterogeneous system it is appreciably lower than 1, indicating Michaelis–Menten kinetics.¶

The reactive intermediate in the solution, accounting for almost the total amount of catalyst, has been found by spectral studies to be (III). Since such a dimer may be prevented from forming in the matrix because the groups are held apart from one another, it is possible that the higher activity of the polymers is a consequence of the presence of a single cobalt species (IV). Higher activity may be related to the more highly activated oxygen present in (IV).

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¶ Catalysts (I), (II), and ball-milled (II) had K_M values of 19·2, 33·3, and 53·3 ml of ME per litre, respectively, and turn-over numbers of 1100, 70,000, and 153,000 mol of Me per mol of Co per min, respectively.

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[2] L. S. Shirayaev and V. N. Klyuev, *Trudy Tambovskogo Inst. Khim. Mashinostroeniya*, 1969, **3**, 101.
[3] 'The Chemistry of Heterocyclic Compounds,' ed. A. Weissberger, 1959, vol. 13, p. 55.
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[5] A. D. Simonov, N. P. Keier, N. N. Kundo, E. K. Mamaeva, and G. V. Glazneva, *Kinetics and Catalysis* (*U.S.S.R.*), 1973, **14**(**4**), 864.