Catalytic activity of copper(II)complexes of immobilized 'polystyrene-bound 4-(*N*,*N*-dimethylamino)pyridine'* for the oxidative coupling of 2,6-disubstituted phenols

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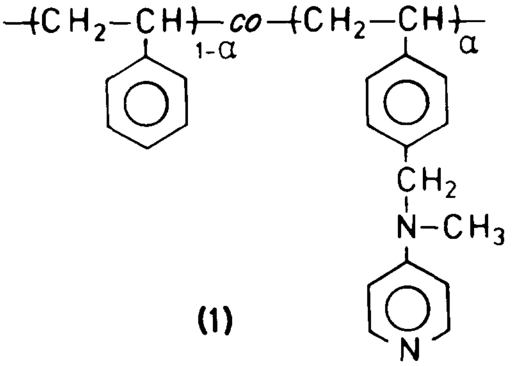
'Polystyrene-bound 4-(*N*,*N*-dimethylamino)pyridine'–copper (PS–DMAP–Cu(II)) catalysts for the oxidation of 2,6-disubstituted phenols were immobilized by grafting or by partial adsorption on silica and by crosslinking with 2% divinylbenzene. The most active immobilized catalyst is the most flexible, i.e. the grafted one, which however is still six times less active than unbound linear PS–DMAP–Cu(II). The less extended conformation of the adsorbed polymeric catalyst exhibits a significantly lower activity. For the crosslinked catalyst, indications were obtained that diffusional limitations occur. Application of all three types of immobilized PS-DMAP based catalysts in a continuous stirred tank (CST) reactor was unsuccessful. The phenol conversion drastically decreased in time. This loss of activity could be explained by the destructive effect of water: interaction of reaction water with the very basic DMAP ligands may result in the production of an excess of hydroxide which, according to our earlier work, deactivates the catalyst. A catalyst based on the less basic poly(styrene-*co*-4-vinylpyridine) adsorbed onto silica exhibited an invariable phenol conversion in the CST reactor for at least 230 h.

(Keywords: polystyrene-bound 4-(*N*,*N*-dimethylamino)pyridine–copper(II); polymeric catalysts; catalytic activity; phenol oxidation; immobilization; continuous stirred tank reactor)

INTRODUCTION

Recently we presented some papers on the oxidative coupling of 2,6-dimethylphenol by copper(II) complexes of 4-(*N*,*N*-dimethylamino)pyridine (DMAP)[1] and poly(styrene-*co*-4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine) (PS-DMAP)[2], **1**:



(1)

The structure of the complexes in solution and the catalytic properties were investigated in detail. In the present study, efforts to immobilize the polymer-bound catalyst are described.

In spite of some drawbacks, such as a possible reduction of catalytic activity and the possible existence of different kinds of sites which may influence the catalytic specificity, immobilization of a catalyst seems to be favourable for many industrial processes. The main benefits are the simplified separation of catalyst and products and the possibility of re-utilization of expensive catalysts in batch processes as well as in continuous processes.

Nowadays several immobilization techniques are known. This paper will be restricted to three of them. In the first place, a chemically silica-grafted PS-DMAP based catalyst will be investigated. A nice example of this technique was given by Verlaan *et al.*, who used silica-grafted copper complexes of poly(styrene-*co*-4-vinylpyridine) as catalysts for the oxidative coupling of 2,6-disubstituted phenols[3]. Secondly, attention will be paid to a very simple way of immobilization, namely the adsorption of polymeric catalysts on silica, as recently described by Bootsma *et al.*[4] and Koning *et al.*[5] In this paper this technique was used to immobilize both PS-DMAP (**1**) and poly(styrene-*co*-4-vinylpyridine) (PS-4VP) based copper catalysts. The adsorption is based on the formation of hydrogen bridges between the amine nitrogen atoms and the silanol groups of the silica surface. Thus, a significant part of the ligands may not be available for coordination to Cu(II). Finally, we will investigate a 'DMAP'-functionalized swellable 'Merrifield resin'[6], i.e. PS-DMAP (**1**) crosslinked with 2% divinylbenzene. A drawback of this type may be diffusional limitation of the reaction rate. In *Figure 1* all the above-mentioned ways of immobilization of reactive species are represented schematically.

The general reaction scheme for the oxidative coupling

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* Poly(styrene-*co*-4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine)
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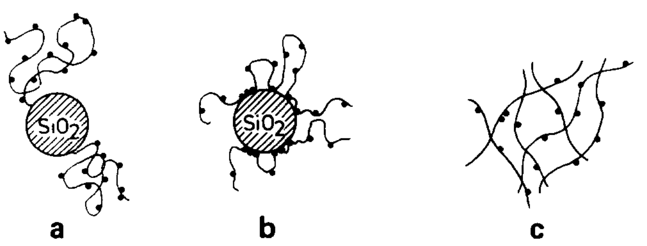
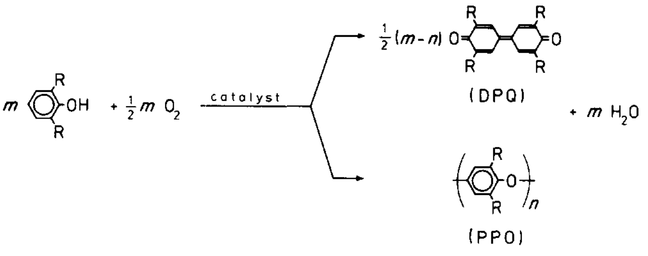


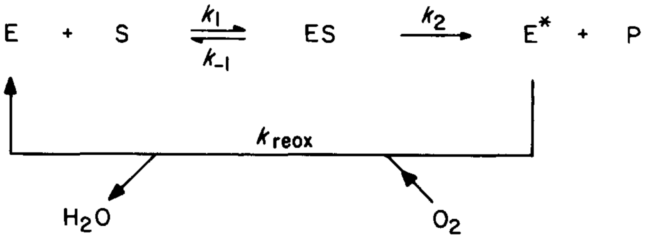
Figure 1 Schematic representation of the ways to immobilize the reactive species used in this paper (● = 'DMAP' (or pyridine in case (b))): (a) grafted onto silica; (b) adsorbed on silica; (c) swellable 'Merrifield' resin

of 2,6-disubstituted phenols is as follows:



When 2,6-dimethylphenol (DMP) is used as a substrate, then the corresponding 'diphenoquinone' (DPQ) as well as the polymer 'poly(phenylene oxide)' (PPO) are produced. The substrate 2,6-di-t-butylphenol (DTBP), however, exclusively yields the C–C coupled 'diphenoquinone'.

Generally the oxidative coupling reaction with polymeric copper catalysts is described by a Michaelis–Menten like scheme:



Here E stands for the Cu(II)–amine complex, S stands for the substrate DMP or DTBP, E* stands for the Cu(I)–amine complex and P stands for the products DPQ + PPO (S = DMP) or just DPQ (S = DTBP). When the k_2 step is rate-determining, then Michaelis–Menten kinetics in the substrate are valid and a plot of R^{-1} *versus* $[\text{phenol}]^{-1}$ yields a straight line intersecting the y-axis according to:

$$\frac{1}{R}=\frac{1}{k_2[\mathrm{E}]_0}+\frac{K_\mathrm{m}}{k_2[\mathrm{E}]_0[\mathrm{S}]_0} \qquad (1)$$

In equation (1) R is the dioxygen consumption rate, $k_2[\mathrm{E}]_0 \equiv R_\mathrm{max}$, the rate at infinite substrate concentration, and $K_\mathrm{m}=(k_{-1}+k_2)/k_1$ is the Michaelis constant.

In this paper some measurements of the catalytic activity of all three immobilized catalysts will be presented. In discussing the different activities, advantage will be taken of some results obtained in our laboratory on the conformation and the complex structure of the immobilized polymeric catalysts[7]. Moreover, the application in a continuous stirred tank (CST) reactor will be studied.

EXPERIMENTAL

Materials

1,2-Dichlorobenzene, $CuCl_2 \cdot 2H_2O$ and KOH were obtained from Merck and were analytically pure. The copper salt and the hydroxide were used as methanolic solutions in which the methanol was of Uvasol quality from Merck. DMP was from Aldrich and was purified by recrystallization from n-hexane. DTBP was from Janssen and was used without purification.

The non-porous silica was kindly provided by Degussa AG. According to the manufacturer, both Aerosil 200V (specific surface $\sim 200\,\mathrm{m^2\,g^{-1}}$ and average sphere diameter ~12 nm) and Aerosil OX50 (specific surface $\sim 50\,\mathrm{m^2\,g^{-1}}$ and average sphere diameter ~50 nm) contain $\sim(2\text{–}3)\times 10^{18}$ SiOH groups per square metre.

The 'Merrifield' resin, polystyrene crosslinked with 2% divinylbenzene, contained ~1.6 mmol of 4-(*N*-benzyl-*N*-methylamino)pyridine per gram of resin ($\alpha \simeq 0.21$) and was purchased from Fluka AG (abbreviated as 'Fluka resin').

Synthesis and characterization of unbound polymeric ligands

Both PS-4VP and PS-DMAP (**1**) were prepared by radical copolymerization in toluene using azobisisobutyronitrile (AIBN) as initiator. PS-4VP was synthesized according to Fuoss and Cathers[8] and PS-DMAP as described before[2]. The degree of functionalization α of the polymers was determined by elemental analysis. The number-average molar mass, $\bar{M}_\mathrm{n}$, of the polymeric ligands was determined in chloroform with a Knauer membrane osmometer, as follows:

PS-4VP	$\alpha = 0.360$	$\bar{M}_\mathrm{n} \simeq 1\times 10^5\,\mathrm{g\,mol^{-1}}$
PS-DMAP	$\alpha = 0.288$	$\bar{M}_\mathrm{n} \simeq 1.2\times 10^5\,\mathrm{g\,mol^{-1}}$

Synthesis and characterization of silica-grafted PS-DMAP

First a radical initiator was synthesized on Aerosil 200V according to Fery *et al.*[9] *p*-Nitrobenzyltrichlorosilane was coupled to the silanol groups. The nitro groups were transferred into the radical initiator by reduction, diazotization and reaction with thiophenol. The silica contained 0.02 mmol initiator per gram of silica, as determined by elemental analysis. Subsequently 4.8 g of the initiator was suspended under N_2 atmosphere in a mixture of 22.4 g of dry toluene, 18.1 g of freshly distilled styrene and 10.3 g of 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine (which was synthesized and purified as described before[2]). The continuously stirred mixture was allowed to copolymerize for 65 h at 75°C. As the radical initiator decomposes under N_2 elimination in a silica-bound radical and in a free radical, silica-bound copolymer as well as unbound copolymer are formed. In order to isolate the unbound copolymer the reaction mixture was diluted with 100 ml of $CHCl_3$ and centrifuged. The unbound copolymer was precipitated from the supernatant in petroleum–ether (40–60)/diethyl ether = 2/1 (v/v) and reprecipitated twice from chloroform. About 2 g of unbound copolymer was isolated, with $\alpha = 0.233$ and $\bar{M}_\mathrm{n} = 9.4\times 10^4\,\mathrm{g\,mol^{-1}}$. To

Table 1 Characteristics of the adsorbed polymeric catalysts used in this paper

Sample	Silica	Copolymer	α^a of offered copolymer	α^a of silica adsorbed copolymer	θ^b
I	Aerosil 200V	PS-DMAP	0.288	0.275	0.140
II	Aerosil OX50	PS-DMAP	0.288	0.329	0.037
III	Aerosil OX50	PS-4VP	0.360	0.268	0.031

[a] α = degree of functionalization of the copolymer as indicated in 1

[b] θ = degree of loading of the silica spheres = (weight of adsorbed copolymer)/(weight of adsorbed copolymer + weight of silica)

remove physically adsorbed copolymer the loaded silica spheres were twice suspended vigorously in chloroform and precipitated by centrifugation. Subsequently the loaded spheres were suspended in chloroform, 'precipitated' in n-pentane, filtered, washed with n-pentane (p.a.) and dried in vacuum at 50°C. The slightly yellow material was characterized by elemental analysis. The degree of loading of the silica spheres, θ (weight fraction of grafted copolymer), was 0.281 and the degree of functionalization of the grafted copolymer was $\alpha = 0.300$ ($\alpha > \alpha_{\text{unbound}}$, probably due to an enrichment around the silica of the basic 4-(*N*-methyl-*N*-*p*-vinylbenzylamino)pyridine monomer).

Adsorption procedure

Two grams of Aerosil 200V or 4.0 g of Aerosil OX50 was suspended in 60 ml of 1,2-dichlorobenzene/methanol = 13/2 (v/v). To the suspension, 0.5 g of copolymer was added, which was allowed to dissolve and adsorb for at least 24 h under gentle shaking at room temperature. Subsequently the loaded spheres were centrifuged, resuspended in 60 ml of solvent mixture containing again 0.5 g of copolymer, and again the suspension was shaken for at least 24 h. This procedure was repeated three times in order to have the high-molar-mass part of the polydisperse copolymer immobilized. (It is known that adsorbed short chains are replaced by longer chains because of the preferential adsorption of the latter ones[10,11].) This should be favourable for the catalytic activity because of the presence of longer loops and tails in the case of longer adsorbed chains[12].

After the above-mentioned adsorption procedure, possibly weakly adsorbed and 'entangled' chains were removed from the carrier material by suspending and shaking the loaded silica spheres twice in pure solvent mixture for at least 24 h. Further the material was centrifuged, dried in high vacuum at 60°C and characterized by elemental analysis. The different silica-adsorbed polymers used in this paper are listed in *Table 1*.

Oxidative coupling in a batch-type reactor

Dioxygen consumption rates were determined in batch experiments by measuring the dioxygen uptake with an automatic isobaric gas burette containing pure dioxygen[13]. The following standard reaction conditions were applied: $T = 298.2$ K; $P_{O_2} = 101.3$ kPa; solvent mixture 1,2-dichlorobenzene/methanol = 13/2 (v/v); total reaction volume = 0.015 dm^3; speed of shaking of the reaction vessel was 4–5 Hz, which is high enough to prevent dioxygen diffusion from the gas phase to become rate-determining.

Oxidative coupling in a continuous stirred tank (CST) reactor

The immobilized catalysts were suspended in a thermostatted stirred tank reactor, equipped with a membrane filter to keep the small loaded silica and resin particles in the system[14]. The substrate solution was injected at the top of the reactor via an electromagnetic valve switched by a contact barometer resulting in a constant volume of the reaction mixture. Dioxygen was bubbled into the stirred solution. The product stream left the reactor via the membrane at the bottom of the reactor and was collected in small fractions. The conversion was determined by a product analysis of these fractions. For the DTBP substrate the only reaction product is the corresponding DPQ, the concentration of which can easily be monitored by u.v./vis. spectroscopy (420 nm, $\varepsilon = 65.000$ dm^3 mol^{-1} cm^{-1} in chloroform). For the DMP substrate both PPO and DPQ are formed. [DPQ] in the product stream was determined spectrophotometrically (426 nm, $\varepsilon = 61.000$ dm^3 mol^{-1} cm^{-1} in 1,2-dichlorobenzene/methanol = 13/2 (v/v)). [PPO] in the product stream was determined gravimetrically by precipitating the polymer in an excess of acidified methanol.

RESULTS AND DISCUSSION

The catalytic activity and specificity of the immobilized complexes in a batch-type reactor

The silica with the grafted PS-DMAP was suspended carefully, and the dioxygen consumption rate R was determined as a function of [DMP] after a coordination period for Cu(II) and OH$^-$ of 72 h. (This is sufficient to establish an invariable complex structure[7].) Standard conditions were used (see 'Experimental') with [Cu(II)] = 0.83 mM, $(\text{OH/Cu})_0 = 1$ and $(\text{L/Cu})_0 = 4$. In *Figure 2*, R^{-1} has been plotted *versus* [DMP]$^{-1}$. The perfect linear relationship points to Michaelis–Menten kinetics in terms of DMP substrate.

The value of R for [DMP] = 0.06 M, which amounts to 12.9×10^{-6} mol O$_2$ dm^{-3} s^{-1}, will be used for comparison with other types of immobilized and unbound PS-DMAP-Cu(II) catalysts. For this DMP concentration the catalytic specificity was determined: 19% of DMP proved to be converted into DPQ (see *Table 2*). From *Figure 2*, R_{max} and K_m^{-1} were determined using a computer program for linear regression. The values obtained are listed in *Table 3*.

The dioxygen consumption rate R was also determined for a PS-DMAP-Cu(II) catalyst adsorbed on Aerosil 200V (sample I in *Table 1*). Standard conditions were used with [Cu(II)] = 0.83 mM, $(\text{L/Cu})_0 = 4$, $(\text{OH/Cu})_0 = 1$ and [DMP] = 0.06 M. The loaded silica was suspended carefully and the allowed coordination period for Cu(II) and OH^- was 72 h. (Again, sufficient to establish an invariable complex structure[7].) The result is given in *Table 2*, together with the fraction of DMP that was transformed into DPQ.

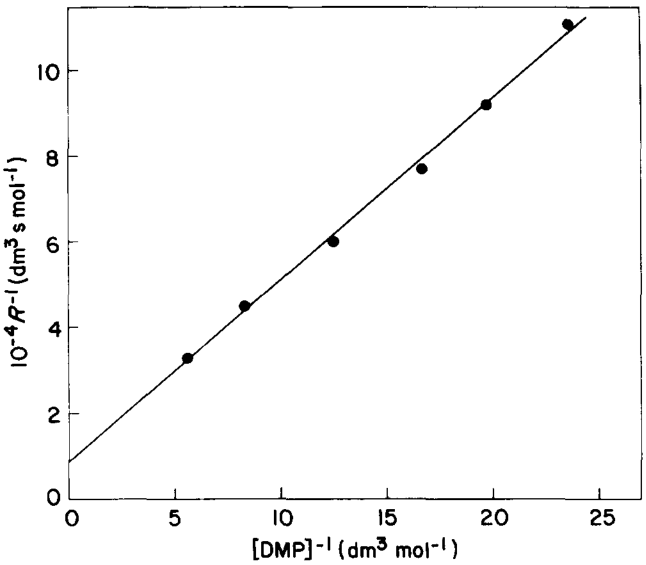


Figure 2 Lineweaver–Burk plot of R^{-1} *versus* $[DMP]^{-1}$ for Aerosil 200V grafted PS-DMAP with $\theta=0.281$ and $\alpha=0.300$. Standard conditions with [Cu(II)] = 0.83 mM, $((OH/Cu)_0)_0=1$ and $(L/Cu)_0=4$. Coordination equilibration period: 72 h

Table 2 Comparison of catalytic activity and specificity of the three types of immobilized PS-DMAP catalysts with unbound catalysts[a]. The coordination periods were long enough to establish invariable complex structures (see text). Standard conditions with $(L/Cu)_0=4$, $(OH/Cu)_0=1$ and [DMP] = 0.06 M

Type of PS-DMAP–Cu(II)	α^b	[Cu(II)] (mM)	R ($mol\,dm^{-3}s^{-1}$)	DPQ (%)
Unbound	0.187	0.83	66×10^{-6}	12
Unbound	0.251	0.83	70×10^{-6}	12
Unbound	0.251	1.66	–	11
Unbound	0.283	0.83	75×10^{-6}	12
Unbound	0.357	0.83	65×10^{-6}	13
Grafted, $\theta=0.281$	0.300	0.83	12.9×10^{-6}	19
Adsorbed, $\theta=0.14$ (sample I in *Table 1*)	0.275	0.83	2.8×10^{-6}	29
'Fluka resin'	0.206	1.66	9.4×10^{-6}	6
'Fluka resin'[c]	0.206	1.66	23.5×10^{-6}	5

[a] Data for the unbound catalysts have been derived from refs. 2 and 15

[b] α = degree of functionalization as indicated in **1**. In the case of the grafted and adsorbed catalysts, the α of the immobilized copolymer is given.

[c] In this case $(L/Cu)_0=8$, other variables as indicated

As already mentioned in the 'Introduction' a serious diffusional limitation of the reaction rate is to be expected for the 'Fluka resin' based catalyst. This already became evident from the Cu(II) coordination experiments[7]. As a coordination period of 72 h proved to be easily sufficient to establish an invariant complex structure, R and the selectivity were determined after 3 days of coordination of Cu(II) and OH^-. Standard conditions were used with [Cu(II)] = 1.66 mM, $(OH/Cu)_0=1$, [DMP] = 0.06 M and $(L/Cu)_0=4$ and 8. The results are listed in *Table 2*. For the 'Fluka resin' the dioxygen consumption rate R was further determined as a function of [DMP]. Again the coordination period for Cu(II) and OH^- was 72 h. Standard conditions were used with $(L/Cu)_0=8$, $(OH/Cu)_0=1$ and [Cu(II)] = 1.66 mM. In *Figure 3*, R^{-1} is given as a function of $[DMP]^{-1}$. The linear relationship points to Michaelis–Menten kinetics in the DMP substrate. From *Figure 3* the values of R_{max} and K_m^{-1} were calculated. These are listed in *Table 3* together with the values for the grafted PS-DMAP–copper catalyst (derived from *Figure 2*). For comparison, some values for unbound PS-DMAP–Cu(II) catalysts with comparable α are given as well.

Discussion of the catalytic results for the batch experiments

In the following discussion $(L/Cu)_0$ is the weighed-in and $(L/Cu)_{eff}$ is the effective ligand/copper ratio. For the adsorbed PS-DMAP, $(L/Cu)_{eff}<(L/Cu)_0$ due to the formation of hydrogen bridges between part of the basic

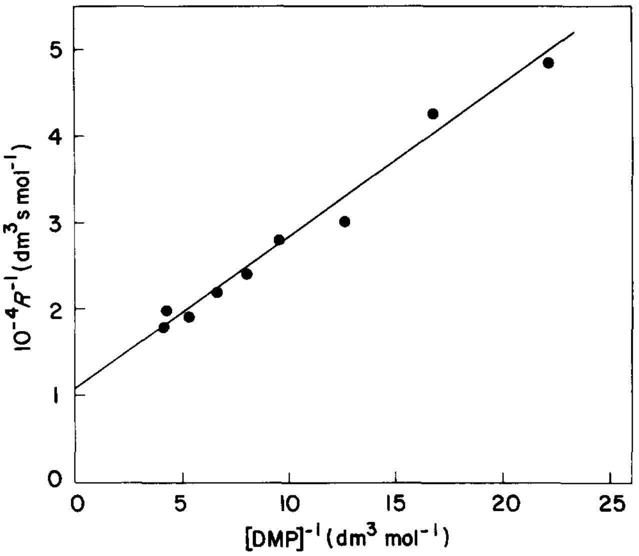


Figure 3 Lineweaver–Burk plot of R^{-1} *versus* $[DMP]^{-1}$ for the 'Fluka resin'. Standard conditions with [Cu(II)] = 1.66 mM, $(OH/Cu)_0=1$ and $(L/Cu)_0=8$. Coordination equilibration period: 72 h

Table 3 R_{max} and K_m^{-1} for the grafted PS-DMAP based catalyst, the Fluka resin based catalyst and some unbound Cu(II)–PS-DMAP catalysts with comparable α^a. (For definition of α, see *Table 2*)

Type of catalyst	α	[Cu(II)] (mM)	$(L/Cu)_0$	$(OH/Cu)_0$	R_{max} ($mol\,dm^{-3}s^{-1}$)	K_m^{-1} (dm^3mol^{-1})
Grafted	0.300	0.83	4	1	109×10^{-6}	2.2
Unbound	0.283	0.83	4	1	303×10^{-6}	5.2
Fluka resin	0.206	1.66	8	1	90.5×10^{-6}	6.5
Unbound	0.222	0.83	4	1	327×10^{-6}	5.0

[a] Data for the unbound catalysts have been derived from the experiments described in ref. 15

'DMAP' ligands and the acidic silanol groups of the silica. For the grafted polymeric catalyst, 50–60% of the silanol groups originally present vanish due to the grafting procedure[7], and consequently less H bridges are formed. Thus, the deviation from $(L/Cu)_0$ will be less pronounced in comparison with the adsorbed catalyst and, moreover, the conformation of the grafted polymeric catalyst will be more extended. In fact, for the grafted polymeric catalyst $(L/Cu)_{eff}$ was found to be close to $(L/Cu)_0$ (ref. 7).

In *Table 2* the catalytic results for the different types of immobilized PS-DMAP based catalysts are listed. Some results for unbound polymeric catalysts with comparable α are given as well. The very low activity of the adsorbed catalyst with respect to the unbound and grafted catalysts is obvious. Several reasons can be given. At first our investigations of the complex structure made clear that for the adsorbed catalyst $(L/Cu)_{eff}$ is lower than for the unbound catalyst[7]. In view of our earlier work[2] this implies a lower amount of the catalytically active species $CuL_4(OH)Cl$ and, consequently, a lower catalytic activity. Furthermore, the presence of the hydrophilic silica surface is likely to retard the process. The acidic silanol groups may react with added hydroxide, thereby lowering $(OH/Cu)_{eff}$. As a matter of fact a determination of R as a function of $(OH/Cu)_0$ for sample II in *Table 1*, with $(L/Cu)_0=5$, $[Cu(II)]=0.83$ mM and $[DMP]=0.06$ M, showed that the optimum activity is between 1.0 and 1.3. For unbound catalysts the optimum value was[2] $(OH/Cu)_0=1.0$. Another disadvantage of the hydrophilic silica is water enrichment around the spheres as reported by Verlaan *et al.*[16] They showed that water has a retarding effect on the oxidative coupling of 2,6-disubstituted phenols. An additional reason for the low activity of the adsorbed catalyst might be the following. The loops and tails of the adsorbed chain will be smaller than those of the grafted chain because of the higher silanol-group density on the unmodified silica[7]. Consequently, more catalytic sites feel the influence of the water layer around the silica and the catalytic activity is decreased with respect to the grafted chain. Of course, for the grafted chains on the modified silica, water enrichment and reduction of $(OH/Cu)_{eff}$ will be less pronounced. Furthermore, our study on the complex structures showed that for the grafted material more DMAP ligands are available for Cu(II) coordination than in the case of the adsorbed material. So, $(L/Cu)_{eff}$ will be higher, the conformation will be more extended (fewer H bridges), and consequently R will be higher for the grafted catalyst. In addition, the degree of loading (θ) of the grafted sample is twice the degree of loading of the adsorbed sample. In general a higher θ yields a more extended conformation of the immobilized polymer chain[12], which in view of the above would lead to a more active catalyst. Finally one should realize that the dimerization of mononuclear Cu(I) complexes, which proved to be necessary to reoxidize Cu(I) to Cu(II)[2], may be retarded in the case of catalysts with a slightly rigid character, such as the adsorbed and (to a lesser degree) the grafted catalysts, with respect to unbound PS-DMAP–copper catalysts. However, for the immobilized catalysts the oxidation of DMP (step k_2 in the scheme above for oxidative coupling with polymeric catalysts) is retarded as well (see above), and for the grafted catalyst k_2 remains the rate-determining step. This is shown by the perfect linear relationship between R^{-1} and $[DMP]^{-1}$ in *Figure 2*, which is a feature of Michaelis–Menten kinetics in terms of substrate.

In comparing the activity of the 'Fluka resin' with the other types of catalyst in *Table 2* one should note that for the resin $[Cu(II)]_0$ has been enhanced by a factor 2. As the resin particles can be regarded as separate micro-reactors, the reaction order in catalyst is unity. So, the R values for the resin in *Table 2* can be divided by 2 in order to allow good comparison. The activity is much lower than for unbound linear PS-DMAP based catalysts and even significantly lower than for the grafted catalyst, in spite of the fact that for the resin (L/Cu) and (OH/Cu) are not reduced by silica. Obviously the resin yields a bad catalyst. Exactly the same trend in activity for unbound, silica-anchored and crosslinked catalysts was observed by Brouwer *et al.*[17] for the autoxidation of thiols with Co(II) phthalocyanine tetrasodium sulphonate attached to poly(vinylamine). The structural investigations already showed that even the diffusion of small particles such as Cu(II) and OH^- ions proceeds very slowly[7]. More than about 20 h were necessary to establish an invariable complex structure. It is highly likely that such diffusional limitations occur for DMP and O_2 as well, and that only the outer shell of the resin particles acts as a catalyst. Moreover, the formation of highly active mononuclear complexes with four 'DMAP' ligands coordinated to one Cu(II) ion[1,2] proved to be very difficult in the crosslinked resin. The presence of crosslinks may also retard the dimerization of mononuclear Cu(I) complexes which is needed to reoxidize Cu(I)[2]. The increase of R with increasing $(L/Cu)_0$ for the 'Fluka resin' was also observed for unbound PS-DMAP[2] and can be ascribed to an increasing amount of the catalytically active species $Cu(II)(DMAP)_4(OH)Cl$.

At this stage comments on the catalytic specificity of all types of catalysts listed in *Table 2* should be made. It is known from earlier work[1,2] that the amount of DMP which is transformed into DPQ is reduced on enhancing $(L/Cu)_0$ and $(OH/Cu)_0$, in other words on enhancing the basicity. For the 'Fluka resin' based catalyst the amount of DPQ produced decreases with increasing $(L/Cu)_0$. For comparable $(L/Cu)_0=4$ the adsorbed catalyst is the least specific and the 'Fluka resin' based catalyst is the most specific for PPO formation. For the adsorbed catalyst $(OH/Cu)_{eff}$ and $(L/Cu)_{eff}$ are lower than for the grafted catalyst (see earlier). Therefore the grafted catalyst yields more PPO. For the unbound catalyst $(L/Cu)_{eff}$ and $(OH/Cu)_{eff}$ are maximal and consequently the amount of DPQ produced is still lower. The relatively high specificity of the 'Fluka resin' can be explained by the relatively high values of $(L/Cu)_{eff}$ and $(OH/Cu)_{eff}$. In addition, the resin particles are rather compact, which leads to a relatively high local concentration of uncoordinated DMAP ligands with respect to the linear PS-DMAP based catalysts. This relatively high local basicity is favourable for PPO formation.

Table 3 shows that the intrinsic activity as indicated by R_{max} of the grafted catalyst is much lower than that of an unbound catalyst with comparable α. The explanation is the same as given above for the dioxygen consumption rates listed in *Table 2*. Although for the 'Fluka resin' based catalyst both [Cu(II)] and $(L/Cu)_0$ were raised by a factor 2, R_{max} is lower than for the grafted material. This lack of catalytic activity was also explained earlier. At this stage

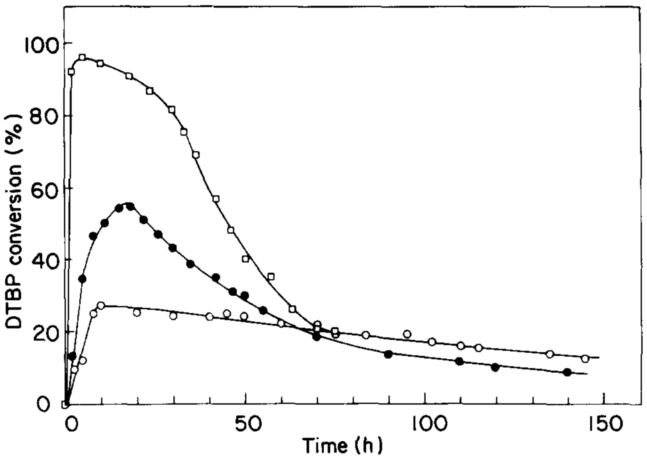


Figure 4 DTBP conversion in the stirred flow reactor as a function of time. $T = 308$ K, $P_{O_2} = 101.3$ kPa, $(OH/Cu)_0 = 1$, solvent = 1,2-dichlorobenzene/methanol = 13/2 (v/v). (□) 'Fluka resin' based catalyst: total copper content = 0.50 mmol, $(L/Cu)_0 = 4$, [DTBP] = 0.06 M, flow rate = 0.65 cm^3 min^{-1}, total reaction volume $V = 0.15$ dm^3. (●) Aerosil 200V grafted PS-DMAP–Cu(II): total copper content = 0.036 mmol, $(L/Cu)_0 = 4$, [DTBP] = 0.02 M, flow rate = 0.40 cm^3 min^{-1}, $V = 0.20$ dm^3. (○) Aerosil OX50 adsorbed PS-DMAP–Cu(II) (sample II in *Table 1*): total copper content = 0.034 mmol, $(L/Cu)_0 = 4$, [DTBP] = 0.02 M, flow rate = 0.35 cm^3 min^{-1}, $V = 0.16$ dm^3. The coordinating equilibration period for all experiments was 72 h.

some attention will be paid to the values of K_m^{-1} for the different types of catalysts. According to *Table 3* the grafting of PS-DMAP causes a significant reduction of K_m^{-1}. A similar reduction was observed by Verlaan *et al.*[16] for silica-grafted Cu(II) complexes of poly(styrene-*co*-4-vinylpyridine) as catalysts for the oxidation of DTBP. For Verlaan's system the grafting procedure did not affect k_2, and thus the change in $K_m^{-1} = k_1/(k_{-1} + k_2)$ reflected a change in $K_1 = k_1/k_{-1}$. So, the reduction of K_m^{-1} implied that phenol complexation becomes less complete on grafting. Verlaan showed further that the presence of water around the silica spheres has an important negative effect on complexation: the same catalyst grafted on hydrophobic silica yielded an increase of K_m^{-1} with respect to the unbound catalyst[16].

It is obvious that for the grafted PS-DMAP based catalyst both K_m^{-1} and $k_2[\mathrm{Cu(II)}]_0 (\equiv R_{max})$ are reduced with respect to the unbound catalyst. The reduction of K_m^{-1} might be caused by the above-mentioned influence of water (k_1/k_{-1} is reduced).

For the 'Fluka resin' based catalyst K_m^{-1} is higher than for a comparable linear catalyst (see *Table 3*). It might be that water, produced during the oxidation reaction, is pushed out of the outer, catalytically active, shell of the hydrophobic resin particles. In view of the foregoing discussion, this would lead to an increase of K_1 (and K_m^{-1}).

The application of the immobilized polymeric catalysts in a CST reactor

In this laboratory Verlaan and Kok have demonstrated that an Aerosil 200V grafted Cu(II)–poly(styrene-*co*-4-vinylpyridine) catalyst can be used for at least 50 h in a membrane-containing continuous stirred tank reactor without loss of activity (in ref. 18). One of our aims is the continuous production of PPO oligomers out of DMP. Therefore the immobilized DMAP based catalysts looked promising, as unbound PS-DMAP based copper catalysts were highly active and very specific for PPO formation under a lot of experimental conditions[2]. In *Figure 4* the conversion of the substrate, in this case DTBP, yielding only the easily detectable dimer DPQ, has been plotted as a function of time for three types of immobilized Cu(II)–PS-DMAP catalysts. Experimental conditions have been given in the figure caption. After a coordination period for Cu(II) and OH$^-$ of 72 h (see earlier) the reaction was started by pumping the DTBP solution into the reactor. In the case of the adsorbed catalyst, Aerosil OX50 had to be used as carrier material as the small loaded Aerosil 200V particles escaped from the reactor (pore diameter = 2×10^{-8} m). This phenomenon was not observed for the Aerosil 200V grafted material. Obviously, the more extended conformation of the grafted PS-DMAP with respect to the adsorbed PS-DMAP prevents the grafted spheres from passing through the membrane.

The results presented in *Figure 4* are disappointing. For all types of immobilized PS-DMAP based copper catalysts most of the catalytic activity is lost within the relatively short period of one day. Like the Aerosil 200V grafted and the Aerosil OX50 adsorbed catalyst, the resin particles ($\phi = (3.0\text{–}7.4) \times 10^{-5}$ m) also stayed in the reactor. (Therefore, this possible reason for the loss of activity can be excluded.) Moreover, the copper content of the output of the reactor was negligible. For all types of catalyst only 0.1–0.3% of the initially added total amount of Cu(II) escaped from the reactor during a period of 40 h. Thus, leaching of Cu(II) out of the polydentate as well as detachment of immobilized catalyst from the silica can be neglected. Obviously the stability of the DMAP based copper catalysts in the oxidation of phenols is very poor.

Now we will try to explain the observed loss of activity (*Figure 4*). The possible influence of water on K_m^{-1} has already been discussed. In order to get more insight into this phenomenon, measurements with varying DMP concentration were carried out for an unbound PS-DMAP–Cu(II) catalyst ($\alpha = 0.288$), and for the same polymer catalyst after addition of 20 μl of water. Standard conditions were used with $(L/Cu)_0 = 4$ and $(OH/Cu)_0 = 1$. The dioxygen consumption rates were measured 3 days after the addition of water. Lineweaver–Burk plots were constructed both for the 'water-free' and the 'water-enriched' polymeric catalysts. In sharp contrast with the experiments with poly(styrene-*co*-4-vinylpyridine)[16] the added water proved to have affected not only K_m^{-1} but also the intrinsic activity (R_{max}) of the DMAP based catalyst: the addition of 20 μl of water reduced R_{max} by some 15%. Additional experiments showed that the retarding effect of the initially added water is more pronounced when $(L/Cu)_0$ is higher and when the time between water addition and the start of the kinetic experiment is longer. In our earlier work it has already been mentioned that the very basic DMAP ligands may abstract a proton from water molecules[1,2]. This, of course, may occur to a larger extent for higher values of $(L/Cu)_0$ and probably also for longer interaction periods. The protonated DMAP ligands can no longer coordinate to Cu(II) and $(L/Cu)_{eff}$ is reduced, resulting in loss of activity (see earlier). Moreover, the generated OH$^-$ ions enhance the value of $(OH/Cu)_{eff}$, which may exceed the optimum value of $(OH/Cu) = 1$. In view of earlier experiments this also leads to deactivation of the

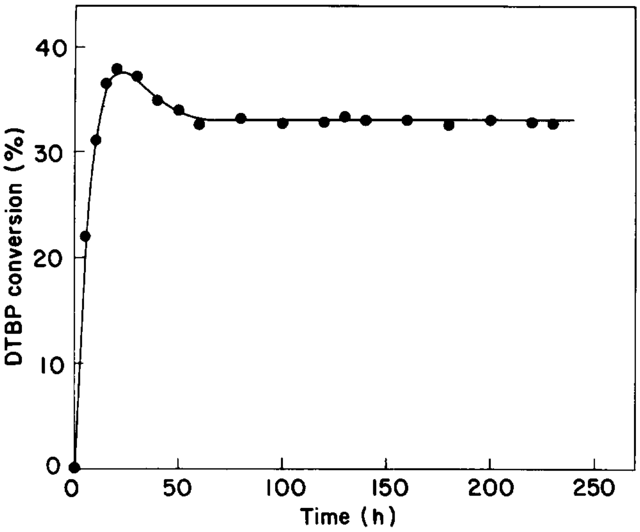


Figure 5 DTBP conversion in the stirred flow reactor as a function of time for an Aerosil OX50 adsorbed poly(styrene-*co*-4-vinylpyridine)–Cu(II) catalyst ($\theta=0.031$ and $\alpha=0.268$, sample III in *Table 1*). $T=308\,K$, $P_{O_2}=101.3\,kPa$, solvent = 1,2-dichlorobenzene/methanol = 13/2 (v/v), total copper content $=1.45\times10^{-4}$ mol, $(OH/Cu)_0=1$, [pyridine]/[Cu(II)]$_0$ = 2, [DTBP] = 0.06 M, flow rate = $0.35\,cm^3\,min^{-1}$, $V=0.16\,dm^3$. Coordination equilibration time for Cu(II) and OH^-: 72 h

catalyst[1,2]. Obviously, the basicity of the pyridine ligands used by Verlaan *et al.*[16] is not high enough to produce hydroxide out of reaction water. So, R_{max} remains unaffected, and when a steady water concentration is established in a stirred flow reactor after a certain period, the influence of water on K_m^{-1} and on the reaction conversion does not change with time (Verlaan and Kok, in ref. 18).

Although application in a stirred flow reactor was unsuccessful, the immobilized PS-DMAP based copper catalysts can be used in batch experiments to produce PPO which is hardly contaminated with catalyst. A batch experiment with the 'Fluka resin' based catalyst yielded 0.1 g of PPO as a white powder containing only 0.38 ppm of copper.

In order to achieve a constant phenol conversion in the CST reactor, a copper ligand should be used which is less basic than DMAP, e.g. pyridine. In *Figure 5* it is shown that a constant phenol conversion is obtained for at least 230 h with an Aerosil OX50 adsorbed poly(styrene-*co*-4-vinylpyridine)–Cu(II) catalyst. It is clear that no desorption occurs. The experimental conditions have been given in the figure caption. The drawback of the pyridine based catalyst with respect to the DMAP based catalyst is its at least 10-fold lower intrinsic activity[2]. Moreover, the specificity for PPO formation of the DMAP based catalyst can be raised to some 97%[2], whereas for the pyridine based catalyst under comparable conditions 80% of PPO is formed[13]. The great benefit, however, will become clear when *Figures 4* and *5* are compared. The maximum in the conversion in *Figure 5* after around 20 h is caused by the fact that at $t=0$, the value of [DTBP] in the reactor is already 0.06 M, contrary to the situation in *Figure 4*, where no substrate was present in the reactor at $t=0$. As the initial water concentration is low, this results in a high initial activity. After some 50 h the steady water concentration is established, the influence of water on K_m^{-1} becomes invariant and the conversion remains constant. For this experiment the amount of copper in the output of the reactor was even smaller than for the experiments described in *Figure 4*.

In spite of the low activity and specificity for PPO formation of the pyridine based catalysts, we succeeded in the continuous production of PPO oligomers out of DMP. For this experiment Aerosil 200V grafted poly(styrene-*co*-4-vinylpyridine)–Cu(II) ($\theta=0.465$, $\alpha=0.243$) was used. The total copper content was 1.0 mmol, [pyridine]:[Cu(II)]$_0$:[OH$^-$]$_0$ = 2:1:1, the flow rate was $0.4\,cm^3\,min^{-1}$, [DMP] = $0.06\,mol\,dm^{-3}$ and the total reaction volume was $0.12\,dm^3$. The rest of the conditions were as indicated in the caption of *Figure 4*. For 80 h an invariable conversion of DMP into DPQ and PPO, 37% and 33% respectively, was obtained. With time intervals of 10 h the intrinsic viscosity $[\eta]$ of the produced and isolated PPO oligomers was determined by the Ubbelohde technique in chloroform at 298.2 ± 0.1 K. The value of $[\eta]$ fluctuated between 7 and 13 ml g^{-1}. This corresponds to $\bar{M}_v=2.4\times10^3$ and 6.4×10^3 respectively, using the Mark–Houwink relation with $K=4.83\times10^{-2}\,ml\,g^{-1}$ and $a=0.64$ (ref. 19).

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