

Macromolecule—Palladium Complexes as Catalysts for the Synthesis of Hydrogen Peroxide

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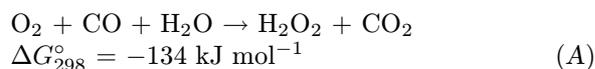
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Commercial resin supports containing aromatic nitrogen bases as functional groups have been used as macromolecular ligands for palladium(II), thus yielding insoluble macromolecule—metal complexes. Preliminary tests were run with these materials as catalysts for the preparation of hydrogen peroxide from carbon monoxide, oxygen, and water. Pretreatment of the catalyst with an organic solvent was found to be necessary in order to achieve catalytic activity. The best results (turnover number = 6) were obtained with pretreatment in dioxane.

The importance of hydrogen peroxide as an oxidant in industrial chemistry is rapidly growing, due to its high content of active oxygen and its “green” character, water being the only reaction by-product [1]. This is currently stimulating considerable research for novel, convenient methods for the manufacture of hydrogen peroxide which would not suffer from the drawbacks associated with the traditional technology, such as the involvement of relatively expensive organic intermediates [2]. The direct synthesis of hydrogen peroxide starting from oxygen, carbon monoxide, and water (A) was originally proposed by Zudin *et al.* [3], who utilized palladium—triphenylphosphine complexes as the catalyst.



They [3] were able to get the reaction (A) to work, but the employed catalyst turned out to be rather inefficient due to ligand oxidation and consequent decomposition to Pd black, its reported turnover number (TON) being equal to 5. Better results (TON = 87) were obtained some years later by Jacobson [4], who took advantage of the more stable triphenylarsine as the ligand. A major advance in the field, enabling to reach turnover frequencies (TOF) up to 600 h⁻¹ was recently reported by Bianchi *et al.* [5, 6], who introduced suitably substituted phenanthrolines as ligands, which are more stable under oxidative conditions. Another key feature was that the reaction was run in a biphasic system containing an aqueous phase acidified with an organic carboxylic or sulfonic acid acting as a phase-transfer species and a water-immiscible organic

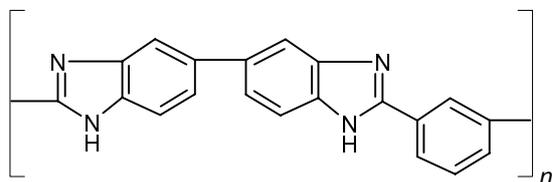
phase in which the catalyst was mainly dissolved. The partition in the organic phase apparently preserved the catalyst from decomposition under the reaction conditions.

We aimed at the development of suitable heterogeneous catalysts for the reaction (A) taking into account the advantages of the biphasic system described above. In this connection, we have investigated insoluble polymers with a proper degree of hydrophobicity and functionalized with nitrogen bases as macromolecular ligands for the catalytically active palladium(II) species. These supports should play the role of the organic phase in the reaction system, thus permitting the use of pure water (with acidic additives) as the reaction solvent. The insoluble macromolecule—metal complex catalyst can in principle be conveniently separated from the reaction mixture by simple filtration and recycled. Altogether, the requested features of such a polymer support can be summarized as follows:

1. The most suitable nitrogen bases are aromatic, chelating molecules such as phenanthroline [5, 6]. Therefore, the target polymer support should contain functional groups of similar nature. Monofunctional groups can in principle be employed, in which case the lack of chelate effect is supplied for by a sufficiently high concentration of functional groups within the polymer;

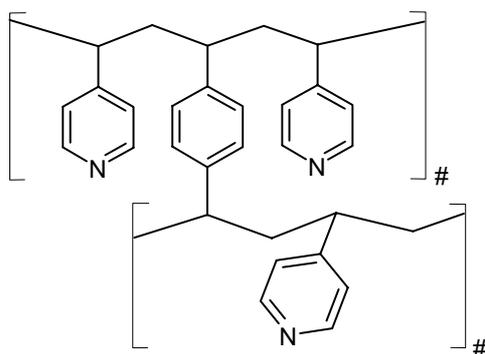
2. The resin should build up an analogue of the organic phase in the biphasic system [5, 6], yet it should be partially compatible with water in order to swell and be well accessible to gaseous reactants and to water itself. Therefore, the resin should be hydrophilic enough to be appreciably swollen in water, but not exceedingly hydrophilic;

3. The resin has to be sufficiently stable under oxidative conditions in order to withstand the presence of high-pressure oxygen and carbon monoxide as well as of hydrogen peroxide in the reaction solution.



Formula 1

In order to meet at least partially these requirements, two commercial resin supports may be of interest. The first one is polybenzimidazole (PBI, Formula 1), a thermooxidatively very stable polymer that in spite of being uncrosslinked is virtually insoluble in the vast majority of solvents. PBI can be prepared in beaded, porous form exhibiting after contact with suitable liquids, including water, high surface area due to nonpermanent pores of diameter 10–20 nm with walls formed by dense polymer mass [7]. PBI can conveniently coordinate metal species through the benzimidazole moieties present in the main chain [8, 9], yielding polymer-supported metal complex species which have already been successfully applied as oxidation catalysts [9]. The second resin is a 2 % crosslinked poly-4-vinylpyridine (PVP, Formula 2), a gel-type resin which, in spite of being presumably less oxidatively stable than PBI, possesses functionalities which are closer in nature to the ligands utilized by *Bianchi et al.* [5, 6]. PVP itself is poorly water-compatible, but compatibility can be dramatically increased upon partial protonation of the pyridine moieties with suitable acids.



Formula 2

EXPERIMENTAL

Polybenzimidazole (beads 0.25–0.5 mm) was from the Hoechst-Celanese Corporation. Poly-4-vinylpyridine crosslinked with 2 mole % of divinylbenzene

(beads 0.2–0.5 mm) as well as other chemicals (all of anal. grade) were supplied by FLUKA.

PBI-supported catalyst. 1 g of PBI was swollen for 1 h in 20 cm³ of acetone, after which a solution of 67 mg of Pd(OAc)₂ (0.1 equivalents in respect to the available benzimidazole moieties) in 20 cm³ of acetone was added. The resulting mixture was gently stirred for two days, after which the supernatant became colourless, indicating that Pd incorporation was quantitative. The polymer was filtered off, washed several times with acetone and dried under vacuum to constant mass.

PVP-supported catalyst. 5 g of PVP were swollen for 1 h in 50 cm³ of acetone, after which a solution of 110 mg of Pd(OAc)₂ in 30 cm³ of acetone was added. The resulting mixture was stirred overnight, after which time the supernatant was still strongly coloured. 1.36 cm³ of acetic acid (0.5 equivalents in respect to the available pyridine moieties) and 10 cm³ of water were then added and the mixture was stirred for additional 24 h, after which time the supernatant was colourless. The resin was filtered off, washed several times with acetone and dried under vacuum to constant mass.

Catalytic tests. The catalytic tests were carried out in an autoclave containing a glass liner and a teflon-lined mechanical stirrer. After charging the reaction mixture, the reactor was pressurized with 600 kPa CO and 6 MPa O₂ and stirring was started. After the given reaction time, stirring was stopped and the reactor was depressurized. An aliquot of the aqueous phase was treated with an excess of an acidified KI solution and the iodine, which evolved upon reaction with H₂O₂, was titrated with 0.01 M-Na₂S₂O₃. The lower detection limit for hydrogen peroxide by this titration was 2 μmol.

RESULTS AND DISCUSSION

Initial tests were run in water containing 40 equivalents (in respect to Pd) of sulfuric acid. The resin-supported catalysts were swollen for 1 h in the reaction solvent prior to reaction; no leaching of Pd species due to the acidic environment was detected. The results are collected in Table 1.

No formation of hydrogen peroxide was detected with PBI–Pd, whereas H₂O₂ in less than stoichiometric amount (in respect to Pd) was formed with PVP–Pd. Under the reaction conditions employed, the catalysts appeared to be quite unstable towards reduction to metallic Pd. They turned black in all cases and some release of Pd black in the solution was observed with PBI–Pd. Remarkably, the formation of Pd metal in this catalyst was apparently less extensive at lower reaction temperature (the third entry in Table 1), at least judging from the colour of the spent catalyst, but in spite of this no formation of H₂O₂ took place. Apparently, our macromolecule—

Table 1. Catalytic Tests Carried out in Water^a

Catalyst	$n(\text{Pd})/\text{mmol}$	$\theta/^\circ\text{C}$	t/min	$n(\text{H}_2\text{O}_2)/\text{mmol}$
PBI—Pd	0.06	70	60	n.i. ^b
PVP—Pd	0.08	25	145	0.078
PBI—Pd	0.06	25	145	n.i.
PVP—Pd	0.06	25	120	0.040

a) Reaction conditions: 600 kPa CO, 6 MPa O₂, 30 cm³ of water, 40 mole equivalents (in respect to Pd) of H₂SO₄. b) n.i. – not identified.

Table 2. Catalytic Tests Carried out in Water/Organic Solvent^a

Catalyst	$n(\text{Pd})/\text{mmol}$	Organic solvent	t/min	$n(\text{H}_2\text{O}_2)/\text{mmol}$
PVP—Pd	0.03	Dioxane	60	0.18
PVP—Pd	0.03	Toluene	60	0.025
PVP—Pd	0.03	Butan-1-ol	60	0.073
PBI—Pd	0.06	Dioxane	60	0.35

a) Reaction conditions: 600 kPa CO, 6 MPa O₂, 25 cm³ of water + 5 cm³ of organic solvent, 40 and 1 mole equivalents (in respect to Pd) of H₂SO₄ and HCl, respectively.

palladium complexes are not stable enough under the employed reaction conditions. The reason for this could lie in the nature of the macromolecular ligands themselves or in the nature of the microenvironment inside the swollen resin support, the hydrophobicity of which could not be sufficient to effectively protect the metal complex catalyst. We took the latter argument as a working hypothesis and we let samples of the resin-supported catalysts swell overnight in 5 cm³ of an organic solvent, either water-miscible or -immiscible. 25 cm³ of water containing 40 equivalents (in respect to Pd) of sulfuric acid and 1 equivalent of HCl – a stabilizing agent for the metal complex catalyst according to *Bianchi et al.* [5, 6] – were then added. The resulting reaction mixture was stirred for 30 min, after which it was poured in the autoclave and the reaction was run as above. The reaction temperature was 25 °C in all cases. The results are reported in Table 2.

The PVP—Pd catalyst was tested after swelling in dioxane, toluene or butan-1-ol. The first solvent is water-miscible whereas the others are water-immiscible. The affinity of the solvents for the PVP—Pd catalyst, as apparent from the swelling volume of the resin, decreases in the sequence butan-1-ol, dioxane, toluene. It needs to be remarked that toluene was apparently displaced by water once the water phase was added, hence the resin was mainly water-swollen in the course of this reaction (second entry in Table 2). Accordingly, the yield in hydrogen peroxide was very low and quite comparable to the results obtained in pure water. On the other hand, much higher yields were obtained with butanol-1-ol and especially with dioxane. In the latter case, a TON of 6 was reached with PVP—Pd and also with PBI—Pd.

All these findings suggest that the preliminary

swelling of the catalyst with an organic solvent having a high affinity for the resin support provides a significant improvement in the performance of the catalyst. Best results are obtained with water-miscible organic solvents such as dioxane, possibly as a consequence of the lower number of phase boundaries. On the contrary, the effect of the added chloride ion appears to be very limited, as the result obtained with catalyst PVP—Pd in toluene shows. It must be remarked that even under these reaction conditions the catalysts do not appear to be much stable towards reduction and turn invariably black in the course of the reaction.

On the basis of the obtained results, it is possible to state that insoluble macromolecule—palladium complexes based on polymer supports containing nitrogen ligands can catalyze the formation of hydrogen peroxide from carbon monoxide, oxygen, and water. This represents the first example of the catalysis of this reaction by a solid heterogeneous catalyst. However, significant improvements are needed for this catalytic system to become technologically relevant. A maximum TON of 6 was reached at 25 °C, which is lower than others previously reported [4, 5]. We are currently focusing our attention on the careful optimization of the reaction conditions, as well as on improving the stability of the catalyst, in order to prevent its reduction to palladium metal under the reaction conditions employed.

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