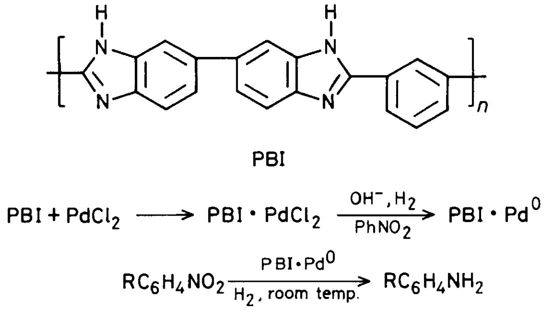
Polybenzimidazole-supported Heterogeneous Palladium Catalysts

Nai-Hong Li and Jean M. J. Fréchet*

Ottawa-Carleton Chemistry Institute, University of Ottawa, Ottawa, Ontario K1N 9B4, Canada

Polybenzimidazole is a useful ligand for the formation of highly active and thermally stable palladium catalysts.

Heterogeneous catalysts based on polymer-supported transition metals have been the object of much attention over the past few years.[1] In general, the catalysts used were based on modified polystyrene resins containing phosphine moieties such as those obtained by lithiation–phosphination of polystyrene.[2] The main disadvantage of these resins, coupled with their difficult preparation, is their lack of stability, both thermal and chemical.[3] Our interest in reactive polymers based on heterocyclic moieties such as the polyvinylpyridines[4] led us to consider other heterocyclic polymers such as the polybenzimidazoles[5] which exhibit remarkable thermal stability while incorporating the desirable benzimidazole ligand. Polybenzimidazole resins can be prepared in porous bead form by a precipitation polymerization process similar to that described recently by Milford[6] using readily available starting materials such as 3,3′-diaminobenzidine and isophthalic acid or derivatives. Although uncrosslinked, the polymer obtained by this process (PBI in Scheme 1) is insoluble in most organic solvents except for dimethyl sulphoxide (DMSO) and dimethylformamide (DMF). While numerous technological


PBI

$$\mathrm{PBI + PdCl_2 \longrightarrow PBI \cdot PdCl_2 \xrightarrow[PhNO_2]{OH^-,\,H_2} PBI \cdot Pd^0}$$

$$\mathrm{RC_6H_4NO_2 \xrightarrow[H_2,\ room\ temp.]{PBI \cdot Pd^0} RC_6H_4NH_2}$$

Scheme 1

Table 1. Reduction of nitro compounds to the corresponding amines.[a]

Substrate	Substrate : Pd^0	% Conversion (time/h)
$PhNO_2$	120 : 1	29(0.5), 41(1), 76(2), 91(2.5), 100(3)
$PhNO_2$	68 : 1	41(0.5), 78(1), 100(1.5)
$PhNO_2$	34 : 1	93(0.75), 100(1)
$PhNO_2$	23 : 1	100(0.5)
$PhNO_2$	17 : 1	100(0.5)
o-$HOCH_2C_6H_4NO_2$	17 : 1	58(2), 78(3), 100(4.5)
p-$HOCH_2CH_2C_6H_4NO_2$	17 : 1	33(1), 41(4), 73(18)
$EtNO_2$	17 : 1	54(1.3)
$EtNO_2$	19 : 1	39(1.3), 55(2.5), 80(8)
o-$MeC_6H_4NO_2$	17 : 1	41(0.5), 100(1.5)

[a] Reactions carried out in a standard low-pressure Parr hydrogenation apparatus using 1 mmol of PBI·Pd^0 in a closed system at 25 °C and under an initial pressure of 45 p.s.i. of H_2.

applications of polybenzimidazoles have been explored in areas such as structural engineering materials, fibres, and reverse osmosis membranes, we believe this to be the first report of an application of polybenzimidazole as a reactive polymer.

The PBI·$PdCl_2$ complex was prepared easily (Scheme 1) by refluxing a suspension of PBI dispersed in a solution of $PdCl_2$ in wet acetone containing 3—5% of acetonitrile. The colour of the polymer changed from light brown to orange-yellow as the complex was formed. In these experiments, the loading of $PdCl_2$ on the PBI can be controlled easily by varying the ratio of Pd to PBI used, as $PdCl_2$ is strongly retained by the reactive groups of the polymer. All the experiments reported here were carried out with a polymer containing 0.7 mmol of Pd^{II} per gram of dry PBI·$PdCl_2$ complex. Unlike its uncomplexed precursor, PBI·$PdCl_2$ is totally insoluble in all organic solvents including DMF and DMSO.

The reduction of PBI·$PdCl_2$ to PBI·Pd^0 can be carried out using methanolic sodium hydroxide in the presence of hydrogen. Only slight reduction occurs when the concentration of base is lower than 0.5 M; in 0.5 M NaOH the reduction is relatively rapid but a small amount of $PdCl_2$ can leach from the polymer, while no leaching is observed at lower concentrations. Further experiments showed that the reduction is best accomplished in the presence of nitrobenzene, which is itself reduced as the reaction proceeds. Thus, the best procedure for the preparation of PBI·Pd^0 involves the gradual addition of solid sodium hydroxide to a stirred suspension of PBI·$PdCl_2$ in methanol containing nitrobenzene under hydrogen atmosphere (40—50 p.s.i.), so that the final concentration of NaOH is 0.5 M; no leaching of palladium is observed under these conditions. Reduction to the PBI·Pd^0 complex can be followed visually as the bright orange material turns black. Extraction with 0.5 M NaOH following reduction does not result in any loss of palladium confirming that essentially no Pd^{II} remains in the polymer. The catalyst prepared in this fashion is extremely stable; it can be heated to 300 °C for several hours without decomposition and it shows excellent activity in the reduction of various nitro compounds as shown in Table 1. In contrast PBI·Pd^{II} is totally ineffective in the reduction of nitro compounds. All the reactions reported in Table 1 were carried out using the same batch of catalyst suspended in methanol in a standard 500 ml Parr shaker-type hydrogenation apparatus under an initial pressure of hydrogen of 45 p.s.i. at room temperature. The reaction proceeded rapidly, reaching completion in less than 30 min for nitrobenzene at a substrate to catalyst ratio of 23 : 1. This level of activity of the catalyst represents the production of >45 mol of aniline (mol of Pd)$^{-1}$ h^{-1}, operating in a closed vessel at room temperature and at an initial pressure of 45 p.s.i. In comparison, the recently described polymer-bound Pd catalyst of Baralt and Holy shows a comparable activity [40 mol of aniline (mole Pd)$^{-1}$ h^{-1}] but only at a much higher temperature and pressure (100 °C; 500 p.s.i.).[7] As expected, lowering the ratio of nitro compound to palladium increased the rate of reaction. At atmospheric pressure and room temperature the reaction was slower, consuming hydrogen at a rate of 4.8 ml/min for the reduction of nitrobenzene with a substrate to catalyst ratio of 23 : 1.

The catalyst may be recycled simply by washing with methanol to remove the reduced substrate from the polymer. The recycled catalyst showed no loss of activity or of Pd content after more than 20 cycles or after heating in air to 300 °C for 6 h. In fact, a small increase of activity upon recycling was observed in the first few cycles, perhaps owing to minor changes in microstructure within the polymer in the reaction solvent.

This polymer-supported hydrogenation catalyst shows great advantages over the the polymer-bound anthranilic acid·$PdCl_2$ catalyst reported recently by Baralt and Holy[7] as the reaction can be carried out easily at room temperature and low pressure and no lowering of activity upon recycling is observed.

Although the use of elevated temperatures was not required in this application owing to the high reactivity of PBI·Pd^0, the thermal stability of the complex makes it suitable for more demanding applications where most other polymer supports would fail.

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