

## Interpenetrating organometallic polymer networks in heterogeneous metal catalysis: a preliminary evaluation

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### Abstract

An organometallic copolymer and an organometallic interpenetrating polymer network, both containing palladium(II) centres, have been tested as catalysts for the hydrogenation of *p*-nitrotoluene in methanol under pure dihydrogen (5 atm) and at room temperature. After activation in situ by reduction of palladium(II) to metallic palladium, both materials promote the selective conversion of the substrate to *p*-toluidine. The apparent reaction rates are comparable with that observed when the same reaction is carried out in the presence of a commercial Pd/C catalysts.

**Keywords:** Organic support; Polymer networks; Palladium; Interpenetrating polymer networks; Supported catalysts

In recent years the strategy of supporting metal crystallites on synthetic polymer supports has led to significant results in industrial catalysis [1].

We have recently reported on the synthesis of an IPN material [1] (IPN = interpenetrating polymer network) [2] obtained upon dispersing an organometallic co-polymer derived from *cis*-PdCl<sub>2</sub>(3-IPA)<sub>2</sub> (3-IPA = 3-isocyanopropylacrylate) inside a macroporous poly-*N,N*-dimethyl-acrylamide-methylen-bisacrylamide (4% mol/mol) support (**M**) [3].

The resulting IOPN material (interpenetrating organometallic polymer network) (**1**) [4] turned

out to be a fairly efficient and quite reusable catalyst for the selective hydrogenation of *p*-nitrotoluene to *p*-toluidine in methanol, at ambient conditions. Catalytic activity is associated with the reduction of Pd<sup>II</sup> to Pd<sup>0</sup>. The possibility of recycling this IOPN catalyst is even more remarkable in comparison with commercial Pd/C catalysts, which are known to undergo a marked deactivation after each catalytic run, in the hydrogenation of nitroaromatics.

In general terms, the exploitation of the IOPN approach to the synthesis of polymer-supported metal catalysts seems to offer the advantage of tailoring, i.e. the combination of synthetic supports possessing specific properties, such as hydrophilicity, lipophilicity, chemical functionality, chirality, etc., with the electronic features of the desired metal centers.

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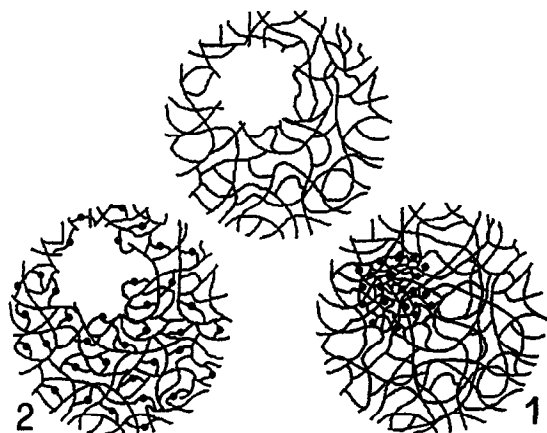


Fig. 1. Sketch of the macromolecular structure of matrix **M** and of the catalyst precursors **1** and **2**.

At atmospheric pressure the catalytic productivities of **1**, in beaded form, was found to be very close to that of a 'conventional' macroporous co-polymer of *cis*-PdCl<sub>2</sub>(3-IPA)<sub>2</sub>, *N,N*-dimethylacrylamide and methylenebisacrylamide, (**2**, Fig. 1), also in beaded form [2]. In both cases, *p*-nitrotoluene consumption vs. time plots turned out to be straight lines (*p*-nitrotoluene was monitored by GC).

We report here on the results of further experiments, based on the employment of materials **1** and **2**, under more severe and better controlled conditions, aimed at comparing the activities of these catalysts with that of a commercial Pd/C catalyst (Aldrich, catalog no. 20568-0, 5% Pd w/w).

Before any treatment, the polymeric materials were analyzed with a scanning electron microscope, in order to disclose their macroscopic (on the molecular scale) morphology. The SEM micrographs of **M** (for comparison), **1** and **2** are shown in Fig. 2. It can be seen that catalyst **2** possesses a defined macroporous morphology (comparable to that exhibited by matrix **M**), featured by pores diameter of 0.1–0.2 μm. On the contrary, the SEM picture of **1** reveals the expected [4] compact morphology caused by the occupation of the macropores featuring matrix **M** by the guest organometallic copolymer.

The polymeric catalysts **1** and **2** were ground

and sieved (particle size < 180 μm) before use and Pd<sup>II</sup> was pre-reduced to Pd<sup>0</sup> with excess NaBH<sub>4</sub> (ca. 5:1, mol/mol, vs. metal) in absolute ethanol. After metal reduction the catalysts,

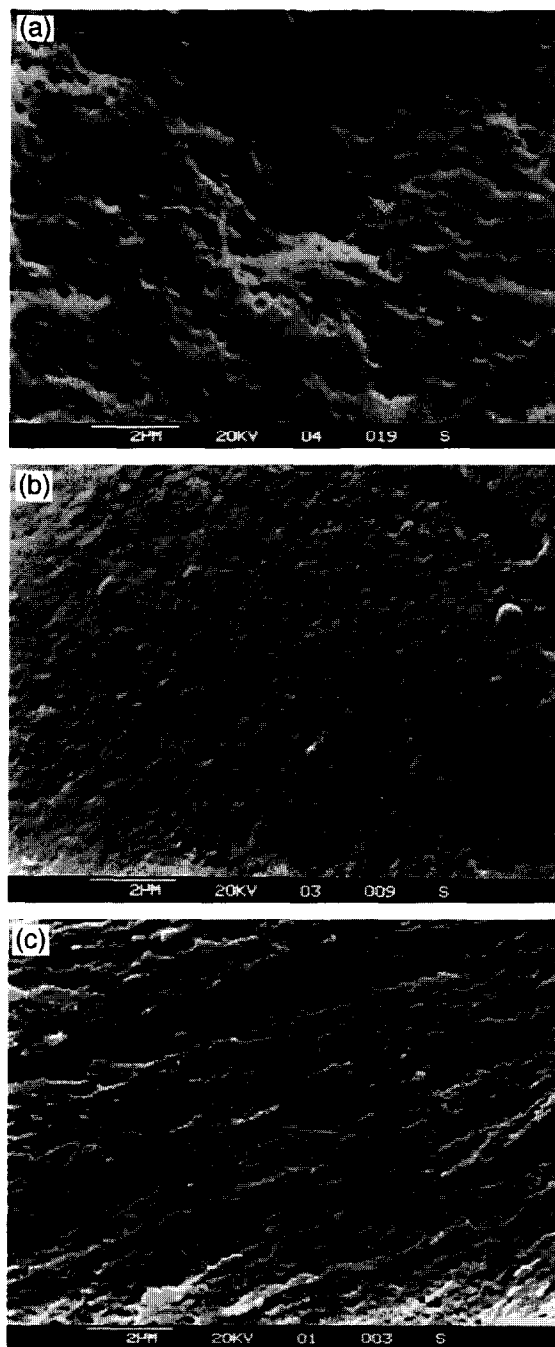


Fig. 2. SEM pictures of (a) matrix **M** and of catalyst precursors (b) **1** and (c) **2**.

including Pd/C, were checked for palladium distribution throughout catalyst particles. Some particles of each catalyst were cut and the whole surface of the obtained sections was analyzed by scanning X-ray microprobe. The relevant scanning micrographs are shown in Fig. 3 and demonstrate a homogeneous metal distribution throughout the particles of **1** and **2**, while palladium is evidently inhomogeneously distributed in the case of Pd/C, the external shell being more rich in metal crystallites.

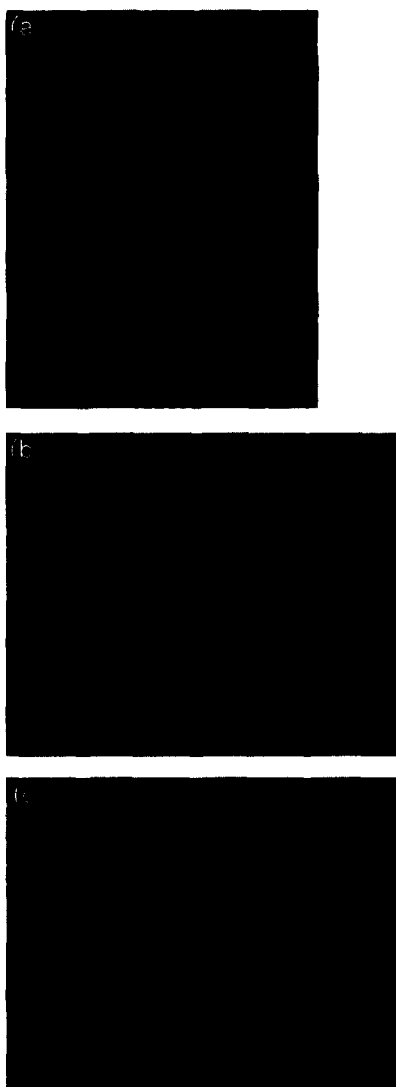


Fig. 3. X-ray microprobe analysis (scanning pictures through entire particle sections) of activated catalysts **1**, **2** and of commercial Pd/C.

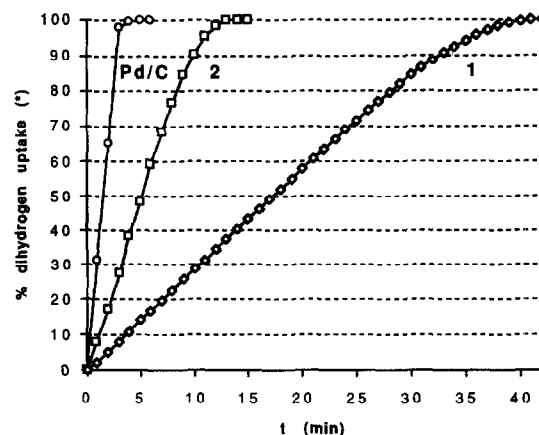


Fig. 4. Observed catalytic productivity of **1**, **2** and Pd/C in the hydrogenation of *p*-nitrotoluene to *p*-toluidine in methanol.  $[Pd] = 5 \times 10^{-3}$  M (analytical),  $[substrate] = 1$  M,  $T = 20^\circ\text{C}$ ,  $P(\text{H}_2) = 5$  atm. (\*): Percent dihydrogen uptake was calculated as the ratio between the volume of absorbed  $\text{H}_2$  and the total volume of absorbed  $\text{H}_2$  at full conversion).

The catalytic runs were carried out under dihydrogen, at a pressure of 5 atm. The employed apparatus has been designed to continuously feed dihydrogen to the reaction mixture while keeping its pressure carefully constant [5]. The progress of the reaction was monitored by measuring the volumetric consumption of  $\text{H}_2$ . However, the consumption of  $\text{H}_2$  actually reflects the decrease of the concentration of *p*-nitrotoluene (the stoichiometrically limiting reagent) in the reaction mixture, in that the pressure of  $\text{H}_2$  (and thus its concentration in the liquid phase) is kept strictly at 5 atm. Thus, the plots of dihydrogen consumption vs. time (Fig. 4, see captions for details), which again turn out to be straight lines, actually show the response of the reaction rate to the *p*-nitrotoluene concentration. Under the employed conditions, the apparent reaction order with respect to *p*-nitrotoluene is zero for all the tested catalysts.

The results reported herein do confirm in a quantitative form that the observed productivity of an IOPN-based metal catalysts is comparable to that of conventional ones so that the 'burying' of an organometallic catalytically active comonomer (or of the metal crystallites stemming therefrom) within a moderately cross-link-

ked polymer network does not cause a dramatic dumping of catalytic activity, thus lending credit to the IOPN approach to polymer-supported metal catalysis.

As a final remark, we speculate that the moderate activity dumping observed in this work for the IOPN catalyst might be potentially exploited for reaching conditions of size selectivity.

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