'Caging' of and Catalysis by a Complex inside a Polymer Matrix

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Utilizing solvent dependent swelling, it is possible to physically trap molecules inside a polystyrene matrix; catalysis by a 'caged' rhodium complex is demonstrated.

Heterogenization of homogeneous transition-metal catalysts by chemical attachment to organic polymers has gained considerable attention because of the possibility of easy catalyst recovery and sometimes enhanced selectivity.[1] Instances where the supported complex is catalytically more active than its homogeneous analogue are also known.[2] Preparation of the functionalized polymer followed by catalyst attachment normally involves several synthetic steps.[1,3] We thought that it may be possible to physically entrap a relatively large complex molecule inside polymer voids, circumventing chemical attachments. This idea is based on an earlier observation[4] that one could trap 4-aminoazobenzene (**1**) in 2% cross-linked polystyrene and carry out quantitative acylation reactions on the amino group to give (**2**), as shown in Scheme 1. A methylene chloride solution of (**1**) was mixed with polystyrene. After evaporation and removing most of (**1**) by Soxhlet extraction with methanol, 'caged' (**1**) is obtained, which cannot be extracted with methanol even after prolonged treatment. However, on adding acetic anhydride to the methanolic solution, a quantitative acylation occurred as proved by extraction of all the products by leaching with methylene chloride and analysis by TLC. Pure (**2**) was obtained.

The rationale of this experiment was that by shrinkage of the polymer on the addition of methanol, a small fraction of (**1**) was trapped. The polymeric cage was small enough not to allow (**1**) to leach out and big enough to allow small molecules, such as acetic anhydride, to penetrate and react. Our approach for 'caging' a metal complex is similar: (a) introduction of the complex inside the polymer matrix, using a solvent in which the polymer exhibits a high degree of swelling; (b) evaporation, and (c) use of a second solvent in which the polymer exhibits little swelling, entrapping the complex in the contracted polymer. The free catalyst, which should be soluble in the second solvent, is washed away.

Using this approach, we have been able to entrap complex (**3**) in 1% cross-linked polystyrene. The solvents used were THF (tetrahydrofuran) and methanol, both of which dissolve the complex. The degree of swelling of this polymer in THF is approximately 3 times larger than in methanol.† The following procedure is representative: 1% cross-linked polystyrene (5 g) was added to a solution of (**3**) (200 mg) in THF (50 ml). After stirring the mixture overnight, under nitrogen, the solvent was slowly evaporated off and the polymer beads were Soxhlet-extracted with methanol for 24 h. A pale yellow polymer was obtained. Elemental analysis revealed the presence of 0.025% P, corresponding to 1.35×10^{-2} mmol (10 mg) of 'caged' complex.

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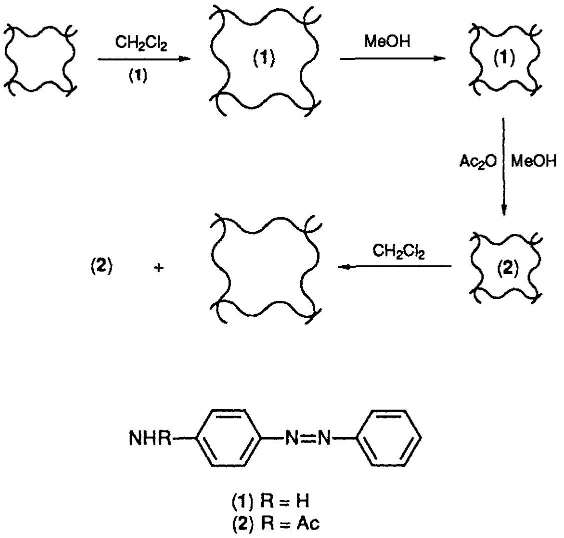
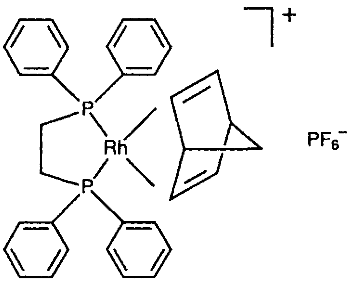
† 1 g of a 1% cross-linked polystyrene (Rohm & Haas Co. No. XE-73-S), whose dry volume is 0.62 cm^3, swells to a volume of 2.56 cm^3 in methanol and 8.04 cm^3 in THF at 23 °C.



Scheme 1



(3)

The supported complex catalyses the hydrogenation of hex-1-ene. Thus, stirring a suspension containing this polymer (0.5 g), hex-1-ene (1 ml), and methanol (4 ml) under 52 psi of hydrogen resulted, after 18 h, in quantitative H_2 absorption to yield hexane. Filtration of the mixture to give the polymer under nitrogen and re-use resulted in similar catalytic activity, showing quantitative conversion after 20 h. To exclude the possibility that the leached catalyst is responsible for the hydrogenation catalysis, we used poly(butadiene) impregnated on silica as a substrate, resulting in no catalytic activity. Apparently, this polymeric alkene is too large to reach the entrapped catalyst. In accord with this, addition of a solution of complex (**3**) to the same reaction mixture resulted in hydrogenation catalysis.

It should be emphasized, however, that the long-term stability of the catalytic system has not been evaluated yet and that the possibilities for multiple recycling or continuous use still have to be determined.

In conclusion, (a) complex (**3**) appears to be physically entrapped inside the cross-linked polymer, (b) it is catalytically active, and (c) small molecules have access to entrapped (**3**), whereas large ones do not. This concept can potentially lead to high degrees of selectivity, perhaps even larger than those obtained with catalysts chemically bound to polymers, for which catalytic reaction takes place mainly at the surface of the polymer. Although we have not tried to trap other metal complexes so far, the success of this approach with molecules as different as (**1**) and (**3**) suggests that this concept may be of broad applicability.

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