Wacker Oxidation of Oct-1-ene Using a Palladium(II) Complex Supported on Cyano-Functionalized Polyimide Beads

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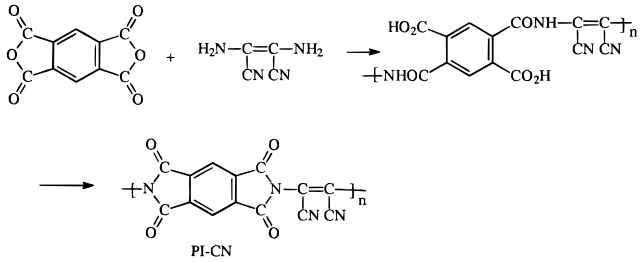
Introduction. Polystyrene-based resins have been used widely as supports for metal complex catalysts[1] and other reactive species.[2,3] These polymers, however, have a drawback in their limited thermo-oxidative stability. The scope for application is therefore restricted, particularly in polymer-supported transition metal complex oxidation catalysts. Consequently, there is a need for the development of polymer supports with a much higher intrinsic thermo-oxidative stability. Polybenzimidazoles and polyimides are likely candidates in this respect.

We have developed a research program involving the preparation of polybenzimidazole[4] and nonfunctional[5,6] and functional[7] polyimide particulates using a nonaqueous suspension polycondensation methodology. Successful results using polybenzimidazole-supported oxidation catalysts have been reported already.[8,9] We have now found that a polyimide bead carrying cyano groups is a useful support material for anchoring a Pd(II) complex, the nitrile ligand being employed to coordinate Pd(II).[10−12] We now report on the preparation of such polyimide beads and their application as a catalyst support in a Wacker-type oxidation.

Experimental Section. The functional polyimide carrying cyano groups (PI-CN) was prepared according to Scheme 1. A typical procedure for the preparation of spherical polyimide particles is as follows. A three-necked round-bottomed flask was charged with *N*,*N*′-dimethylacetamide (68.5 g) and flushed thoroughly with N_2. Diaminomaleonitrile (7.57 g, 7.0×10^{-2} mol) was added and dissolved. Under stirring, pyromellitic dianhydride (15.27 g, 7.0×10^{-2} mol) was added in small portions initially at 0 °C. Stirring was continued for 20 h at room temperature to yield a poly(amic acid) solution. Subsequently, this solution was suspended in paraffin oil (200 g) containing poly(maleic anhydride-*co*-octadec-1-ene) (1.0 g) as a suspension stabilizer. The stirring speed was 400 rpm. After equilibration for 2 h at 60 °C, imidization was initiated by dropwise addition of a mixture of acetic anhydride (20.3 g, 19.9×10^{-2} mol) and pyridine (13.8 g, 17.4×10^{-2} mol). After 20 h the polyimide particulates were collected by filtration, extracted with dichloromethane for 24 h, and dried at 80 °C in a vacuum oven. The yield of polymer beads was 20.2 g (99.4%). The particle size distribution is 5.1 wt % (38−75 μm), 70.3 wt % (75−106 μm), 21.9 wt % (106−212 μm), 2.3 wt % (212−425 μm), and 0.4 wt % (>425 μm).

The polyimide-supported Pd(II) complex (PI-CN/$PdCl_2$) (Figure 1) was prepared by stirring a mixture of palladium(II) chloride and polyimide beads in methanol for 24 h at room temperature using a rotary evaporator

Scheme 1. Synthesis of the Functional Polyimide Containing Cyano Groups



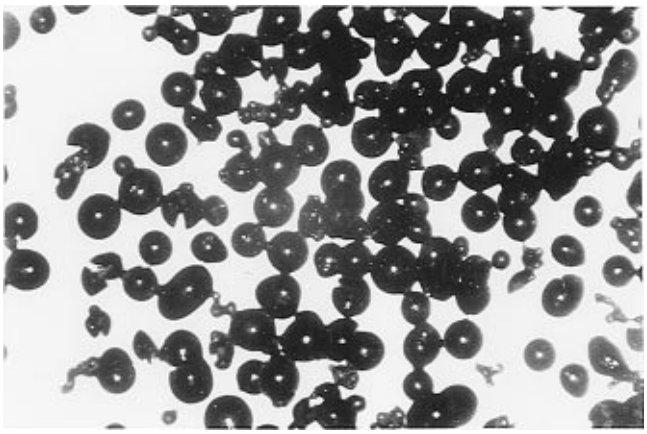
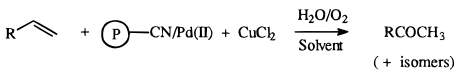


Figure 1. Optical photograph of spherical polyimide beads (PI-CN/$PdCl_2$) (~100 μm diameter).

Scheme 2. Waker-Type Oxidation of Alk-1-ene



followed by exhaustive extraction with methanol in a Soxhlet apparatus and vacuum drying.

The palladium content was measured by inductively coupled plasma (ICP) to be 1.08 mmol g^{-1}. The polyimide-supported Pd(II) catalyst was employed in Wacker-type oxidation of oct-2-ene (Scheme 2). A typical reaction was performed as follows. The reactor was a three-necked glass flask fitted with a water jacket. The reactor, equipped with a mechanical stirrer, a condenser, and an air inlet, was charged with a mixture of polyimide-supported Pd(II) catalyst (0.1 g, 0.108 mmol Pd) and $CuCl_2$ (0.1 g, 0.745 mmol) in ethanol (7.5 mL) and water (1.5 mL). The catalyst was suspended in the solution by stirring, and the temperature was maintained at 60 °C with air bubbled (~100 mL/min) through the solution for 30 min. Then oct-1-ene (0.8 mL, 5.10 mmol) and bromobenzene (0.3 mL) as an internal standard were added. The oxidation reaction was monitored by GC. Successive reactions were carried out in an identical manner. The supernatant solution from each reaction was analyzed for Pd using ICP.

Results and Discussion. The polyimide containing −CN groups exhibits characteristic FTIR bands at 1788, 1735 (heterocyclic carbonyl vibration), 1353 (C−N stretch vibration), 728 (imide ring deformation), 1618 (olefinic vibrations), and 2219 cm^{-1} (C≡N stretch vibration). The bands are similar to those of the polyimide powder obtained by thermal conversion.[13] Extraction of the beads with methylene chloride was directed primarily toward removing small organic fragments from the polymer. We anticipate that at least a portion of the suspension stabilizer will be trapped in, or bound to,

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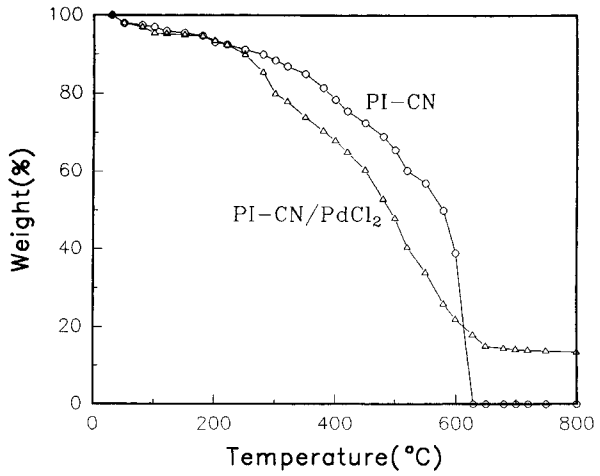

Figure 2. Thermogravimetric analysis curves of functional polyimide beads (air flow 50 cm^3/min; heating rate 10 °C/min).

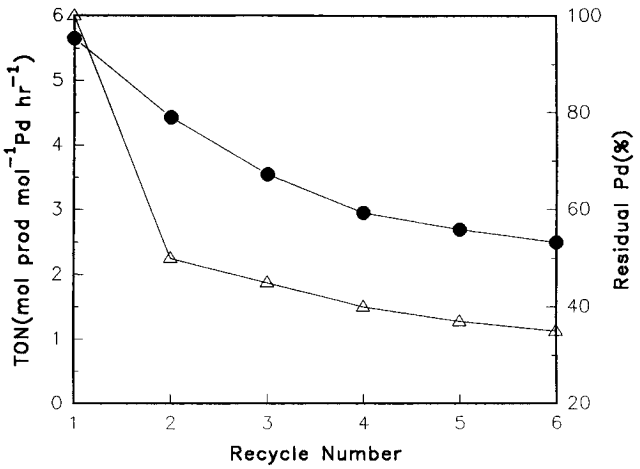

Figure 3. Catalytic activity and Pd(II) leaching data during recycling in Wacker oxidation of oct-2-ene: (●), turnover number at 8 h; (△) residual Pd(%) on the PI-CN support.

the bead surface. The level, however, is low and spectroscopic detection of this was unsuccessful.

Figure 2 shows the thermogravimetric analysis curves of PI-CN and PI-CN/$PdCl_2$. The mass loss (∼7%) below 200 °C for PI-CN may be due to completion of cyclohydration (imidisation) and may also represent loss of residual tenaciously trapped organic fragments since a similar loss appears for PI-CN/$PdCl_2$. Most importantly, however, the TGA traces indicate good stability in O_2 to at least ∼200 °C. PI-CN is decomposed completely at ∼600 °C, while the PI-CN/$PdCl_2$ retains a residue even at 800 °C. The latter, however, may be Pd-based.

The supported Pd(II) complex is active in the aerobic oxidation of oct-1-ene, yielding octan-2-one and other isomeric ketone products. One of the most attractive potential advantages of polymer-supported catalysts is that they might be easily separated from the reaction solution and recycled several times, and in the longer term used in packed or fluidized bed reactors. Figure 3 shows data for the activity of the catalyst and the level of Pd(II) retained on the support over six successive cycles. Significant Pd leaching occurs in the first cycle, but thereafter Pd loss is arrested. The activity of the PI-CN-supported catalyst falls in the initial runs but gradually stabilizes over six cycles. The activity of the catalyst correlates best with the level of Pd(II) immobilized on the support, and this supported Pd(II) complex therefore seems to be the primary catalytic species. It is possible to speculate that the loss of Pd in the earlier cycles probably occurs from sites at which the Pd is bound by a single nitrile ligand, the more strained sites succumbing first. The more stable Pd centers are probably bound by two nitrile ligands or are immobilized in a local polymer conformation which provides a surplus of nitrile ligand sites. The product distribution is typically octan-2-one (62%), octan-3-one (26%), and octan-4-one (12%) since rapid isomerization occurs concurrently with oxidation, as observed previously.[14]

In the context of producing polymer-supported catalysts with enhanced thermo-oxidative stability, this PI-CN-supported Pd complex now offers exciting prospects for operating in more severe oxidative conditions. In due course we will be reporting in more detail on a range of polyimide-based metal complex catalysts we have under study. These are proving to be robust and versatile.

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References and Notes

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