Rhodium (1) Catalyst Supported on Polyethylene Hollow Fibers: Preparation and Hydrogenation Studies

JACQUELINE S. BUTLER, BERNARD GORDON III, and IAN R. HARRISON,* *Department of Materials Science and Engineering, Polymer Science Program, The Pennsylvania State University, University Park, Pennsylvania 16802*

Synopsis

In recent years polymers have been utilized as binding sites for transition metal catalysts (e.g. crosslinked polystyrene beads). However, general problems exist with the above system. The rate of reaction depends on the presence of solvents that adequately swell the polystyrene bead in order to allow access to the catalyst sites. Differences in polarity and reactant size can inhibit diffusion into the bead. Recently a new system has been developed where the catalyst is bound to polyethylene single crystal surfaces, this has solved the above problems. However, polyethylene single crystals are small and plate-like causing a new problem, when trying to filter the separate product the crystals cause clogging of the filtering system and limit the reactions to batch process. This paper describes the use of fine microporous polyethylene hollow fibers as the supporting polymer. This gives the advantages of the single crystal support, plus allows for the use of a fixed-bed flow reaction system.

INTRODUCTION

Commercial processes based on homogeneously catalyzed routes are becoming increasingly important. However, these processes can exhibit problems of product contamination and catalyst loss, where products are not readily separated from catalyst. In recent years several attempts have been made to combine the advantages of homogeneous and heterogeneous catalysis.[1] Anchoring homogeneous catalysts to polymers or other supports effectively "heterogenizes" them, allowing their use in "fixed-bed" type reactions and simplifying catalyst recovery. Thus the problems associated with anchoring homogeneous catalysts has recently been the object of much research.[2,3]

The most commonly used polymer for supporting catalysts has been crosslinked polystyrene (PS) beads.[1-3] Although PS-supported catalysts show many advantages over homogeneous catalysts, various problems associated with the system have prevented it from being used on an industrial scale. For example, the rate of reaction depends on the presence of solvents that adequately swell the polystyrene beads in order to allow access to the catalytic sites (in the

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*Author to whom inquiries should be addressed.

interior of the bead).[4,5] In addition, differences in polarity and reactant size can inhibit diffusion into the bead.

Recently a new polymer support has been developed whereby the catalyst was bound to the surface of a polymer substrate, eliminating many of the above problems.[6] In this latter case Wilkinson's catalyst [tris(triphenylphosphine) chlororhodium (I)][7] was bound to the surface of a polyethylene (PE) single crystal. The PE-supported Wilkinson's catalyst (PE catalyst) was compared to the PS-supported analogue (PS bead catalyst), using the rate of hydrogenation of various olefins in both polar and nonpolar solvents. The PE catalyst showed a dramatic increase in catalytic activity over that of the PS bead catalyst (six times as active) and was 75.5% as active as homogeneous Wilkinson's catalyst.[8] Because the catalyst was located on the surface of the PE crystals, swelling problems exhibited by PS bead catalysts in polar solvents were avoided. Overall, PE single crystals were shown to be a more effective means of catalyst support.

In the chemical industry large scale processes are typically carried out using a fixed-bed flow reaction process. In this case, reactants can continually flow over a supported catalyst where the reaction takes place. The main advantage of this system over that of the previously mentioned PS or PE-supported catalysts is that a continuous reaction process is maintained. It is not necessary to completely stop the reaction in order to remove the products, instead the product is removed with the flow of the reaction.

A new polymer support has been developed that shows potential for use in a fixed-bed flow reaction system. Fine microporous polyethylene hollow fibers (EHF) manufactured by Mitsubishi Rayon Co. have a very high porosity (approx. 60%) and a very small outer diameter (approx. 400 μm).[9] Wilkinson's catalyst has been bound to these polyethylene hollow fibers. Once again, many of the problems exhibited by the PS bead catalyst are avoided, namely: (1) the pore sizes in the hollow fiber are large; therefore diffusion into the fiber does not create a problem; (2) polar reactants can be exposed directly to the catalyst; (3) the catalyst is bound to the fiber hence there should be no site/site interactions.

At the present, the hollow fibers are used in a microfiltration cartridge (Sterapore-PKO) whereby each fiber is planted with polyurethane sealant in a polycarbonate cartridge.[10] The Sterapore-PKO module contains approximately 6 m^2 area consisting of 15,000 fibers. The system is used to remove germs and pyrogens from tap water thereby producing highly pure sterile water. A similar cartridge might ultimately be used for a PE fiber-supported catalyst, producing a fixed-bed flow reactor.

EXPERIMENTAL

All solvents used were ACS reagent grade; benzene and tetrahydrofuran (THF) were further purified by distillation from sodium metal with benzophenone as blue anion indicator. Wilkinson's catalyst [chlortris(triphenylphosphine) rhodium (I)] bound to 2% crosslinked PS beads was purchased from Strem Chemical Co. (lot #123-D, 2.19 wt % Rh). Bromine and rhodium contents were determined for various catalyst systems used by neutron activation analysis at the Braezeale Nuclear Reactor (The Pennsylvania State

University); phosphorus analysis was performed by Galbraith Laboratories, Knoxville, TN. NMR spectra were recorded on a Varian EMS 360 spectrometer.

The PE hollow fibers used in this paper were produced by the Mitsubishi Rayon Co., Ltd., Tokyo, Japan. Hollow fibers can be obtained by spinning high-density polyethylene under a high-draft condition followed by cold stretching and hot stretching without the use of solvent or plasticizer. The porous hollow fibers have approximately rectangular micropores that are oriented in the long direction of the fibers, which have a porosity of approximately 60%.

Bromination

PE fibers were wound into small bundles (composed of 10 fibers each) weighing nearly 0.02 g per bundle. Each fiber bundle was secured by an additional PE fiber to prevent unraveling. A total of 5 PE fiber bundles (weighing approximately 0.80 g) was washed with distilled CCl_4 (via soxhlet extraction) for 10 h. The PE fibers were then placed in a reaction vessel kept at RT under a constant flow of nitrogen. Bromine was added in the ratio: 0.8 g PE fibers/300 mL CCl_4/8 mL Br_2. After illuminating the mixture with UV light for 24 h, the samples were washed (via soxhlet extraction) to remove excess bromine. The fiber bundles were than washed with acetone to remove CCl_4 and any residual bromine.

Phosphination

All steps were carried out under dry nitrogen with distilled solvents. Lithiodiphenyl phosphine was prepared by combining distilled diphenyl phosphine chloride in THF, with lithium wire in the ratio: 1 g Li wire/5.8 g diphenyl phosphine chloride/60 mL THF. The mixture was allowed to stir for 15 h. The red lithiodiphenyl phosphine solution was then added to a stirred suspension of brominated PE fiber bundles in THF. The mixture was allowed to reflux for 2 days, then cooled, and the supernatant pale yellow liquid was removed. Saturated NH_4Cl was added to the PE fibers and stirred for several hours; rinses of distilled water, distilled water with a trace of HCl, distilled water with THF, and finally dry THF followed. Elemental analysis found 2.48 wt % phosphorous on the PE fiber sample.

Rhodium Treatment

Tris(triphenylphosphine) chlororhodium $(PhCl(PPh_3))_3$ was dissolved in distilled benzene. Phosphinated PE fibers were added so that approximately equal amounts of Rh and poly-PPh_2 groups were present. The mixture was allowed to stir under nitrogen for 3 days. The PE fiber bundles were extracted repeatedly with distilled benzene (via soxhlet extraction) until the rinses showed no discernible coloration. Samples taken from each step in the reaction series were dried under vacuum for several days.

The above samples after bromination, phosphination, and rhodium treatment were tested for bromine and rhodium content by neutron activation analysis. Phosphorus content was determined by elemental analysis. Extent of

substitution was determined by the relative amounts of bromine, phosphorus, and rhodium content before and after each reaction.

Hydrogenations

Reductions were carried out using the method outlined by Brown and Brown.[11] Hydrogen gas was generated by dripping a standardized $1M$ ethanolic sodium borohydride solution into a $1.2M$ H_2SO_4 solution. Hydrogen gas was prepared in a three-neck round bottom flask connected to a smaller three-neck (reaction) flask by a small glass tube. A known amount of the PE fiber catalyst was suspended in distilled benzene and allowed to equilibrate under hydrogen for 1 h (using ca. 25–30 mL $1M$ $NaBH_4$ solution). The alkene to be reduced was then injected into the reaction flask so that a total solution volume of 30 mL was reached. The alkene was initially at $1M$ concentration in benzene. Hydrogen readings were taken every 15 min for 4 h. The PE fiber catalyst was rinsed in benzene and dried before further use.

Standardization of the $1M$ $NaBH_4$ was carried out by measuring the gas evolved when a known amount of the solution was added to $1.2M$ H_2SO_4. The presence of the reduced alkene was observed by NMR analysis.

RESULTS AND DISCUSSION

The substituted products (brominated PE fibers, phosphinated PE fibers and PE fiber-catalyst) were analyzed for bromine, phosphorus and rhodium content (Table I).

Analysis by neutron activation shows an addition of 11.38 wt % bromine to the PE fibers. After the phosphination reaction was completed 2.48 wt % P was bound to the PE fiber while nearly all the bromine was removed, leaving only 0.69 wt % Br. Upon reaction with Wilkinson's catalyst, the bromine content stayed approximately the same (0.67 wt % Br) with an addition of 1.65 wt % rhodium to the PE fibers (PE fiber catalyst). An additional PE fiber catalyst sample, which had been used a minimum of seven times, was also tested for rhodium content (PE fiber catalyst). Neutron activation results show that the rhodium content stayed essentially constant at 1.63 wt % Rh. The Rh content can also be calculated as 0.159 mmol Rh/g PE fiber, and also corresponds to 4.8 PE fiber-bound P ligands per Rh catalyst.

TABLE I
Neutron Activation Analysis

Sample	%Br	%Rh	%P
Original PE fibers	0.00	—	a
Brominated PE fibers	11.38	—	a
Phosphinated PE fibers	0.69	—	2.48
PE fiber catalyst	0.67	1.65	a
PE fiber catalyst[b]	0.67	1.63	a

[a] Not sent for analysis.
[b] After a minimum of seven hydrogenations with the same fiber catalyst.
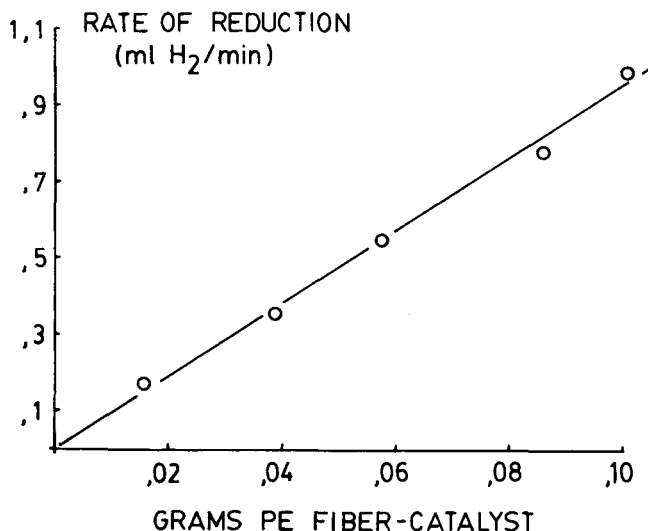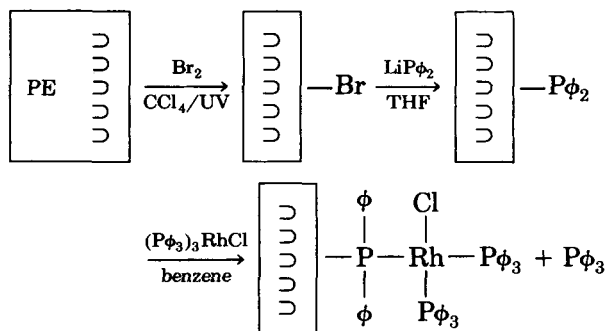
Fig. 1.   Plot of reduction rate of cyclohexene versus quantity of PE fiber catalyst used.

The manner by which Wilkinson's catalyst was bound to the PE hollow fibers is shown pictorially by the following procedure:

Hydrogenation reactions were carried out at room temperature and pressure, and hydrogen uptake followed as a function of time. The reaction rate is taken as the initial slope of the hydrogen uptake vs. time curve for each particular weight of the PE fiber catalyst used. A linear relationship was found between the quantity of PE fiber catalyst used and the observed rate of reduction of cyclohexene (Fig. 1).

The catalytic activity of four catalyst systems namely, Wilkinson's catalyst, PS bead catalyst, PE catalyst (described in the Introduction), and PE fiber catalyst were compared based on their rate of reduction of cyclohexene at equivalent levels of Rh in the four systems (Table II).[12] The results show a dramatic increase in activity of both the PE catalyst and the PE fiber catalyst over that of the PS bead catalyst (approximately a sixfold increase). While one might argue that porous beads optimized for pore size and surface area would give better results, similar statements may be made for the PE fiber support.

TABLE II
Comparison of Catalytic Activity

Catalyst	Rate of reduction of cyclohexene (%)
Wilkinson's catalyst	100
PS bead catalyst	12
PE catalyst	75.5
PE fiber catalyst	69.3

Despite the marked increase in activity of the PE catalyst systems relative to the PS bead system, it is also possible to compare catalytic activity of the four catalyst systems based on their relative rates of reduction of a variety of olefins of different molecular sizes. The relative rates were determined by normalizing each rate, relative to the rate of reduction of cyclohexene, for each catalyst system. The results (Table III) show a marked decrease in rate of reduction of the PS bead catalyst as the size of the olefin increased, as also evidenced in previous publications.[12,13] Random crosslinks in the PS bead inhibit diffusion into the interior of the bead where the majority of the catalytic sites are located, thereby causing a decrease in the rate of reduction. The PS bead catalyst also showed a marked reduction in rate when reducing polar olefins. This is presumable due to the nonpolar character of the PS support; polar olefins do not readily diffuse into nonpolar PS beads.

Both PE catalyst and PE fiber catalyst systems showed a marked improvement in catalytic activity compared with the PS bead catalyst. In both cases, diffusion problems exhibited by the PS bead catalyst seem to be largely eliminated. For the PE catalyst, the catalyst sites are located on the surface of the crystal allowing for greater ease of reaction. In the PE fiber catalyst, large micropores in the fiber walls virtually eliminate concern for solvent diffusion. Overall the rates of reduction obtained by both PE catalyst and PE fiber catalyst were similar for all olefins tested.

To gain a more comprehensive understanding of the behavior of PE fiber catalysts in increasingly polar environments, hydrogenation reactions of cyclohexene were carried out in 100% benzene, 1 : 1 benzene-ethanol, and 100% ethanol. Reaction rates obtained were compared to those of PE catalyst and PS bead catalyst.[6,14] Figure 2 shows that both PE fiber catalyst and PE

TABLE III
Relative Rates of Reduction

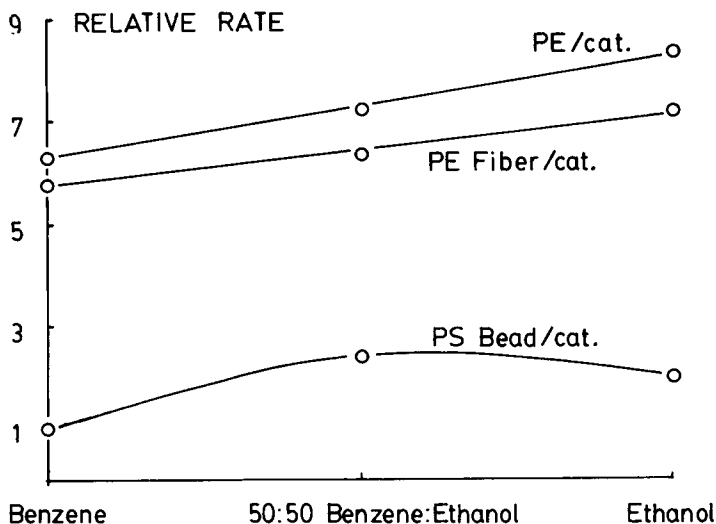| Olefin	Wilkinson's catalyst	PS bead catalyst	PE catalyst	PE fiber catalyst
Cyclohexene	1.0	1.0	1.0	1.0
1-Dodecene	1.23	0.60	0.95	0.91
Cyclododecene	1.29	0.23	0.78	0.74
Allyl alcohol	1.09	0.62	0.92	0.84
Cholesterol	1.2	a	0.68	0.58

[a] Unable to detect.

Fig. 2. Reaction rate of PS bead catalyst, PE fiber catalyst, and PE catalyst vs. solvent polarity.

catalyst give a linear increase in rate of reduction as solvent polarity is increased. However, PS bead-catalyst showed an initial increase followed by a subsequent decrease in rate of reduction upon increasing solvent polarity.

This difference in rates with changes in polarity is presumable due to the fact that both PE fiber catalyst and PE catalyst are not affected by diffusion problems; this is not the case with the PS bead system. PS bead catalyst contains catalytic sites surrounded by nonpolar aromatic groups. Consequently, if solvent surrounding the polymer bead is more polar than benzene, two major changes should occur in the catalyst. First, solvent pores will decrease in size; in addition, a "polar" gradient will be built up between bulk solvent and the localized environment of the catalytic center. The former should cause a decrease in reaction rate, in contrast the latter should cause an increase in reaction rate (higher diffusion rate).

From Figure 2, the PS bead catalyst showed an initial increase in reaction rate upon increasing polarity from 100% benzene to 1:1 benzene–ethanol (polar gradient). However, the reaction rate subsequently dropped after increasing the solvent polarity to 100% ethanol (pore size decrease). In contrast, both PE fiber catalyst and PE catalyst are largely unaffected by an increase in solvent polarity and avoid all swelling problems exhibited by the PS bead catalyst. As a result, both PE fiber catalyst and PE catalyst show an overall increase in reaction rate with increasing solvent polarity.

CONCLUSION

It has been shown that PE fiber-supported Wilkinson's catalyst is very effective for the hydrogenation of both large and polar olefins and in both polar and nonpolar solvents. Diffusion and swelling problems exhibited by PS bead catalyst systems are virtually eliminated. PE fiber catalyst is comparable

in activity when compared to PE catalyst, and is 69.3% as active as homogeneous Wilkinson's catalyst and approximately six times as active as a PS bead catalyst.

PE fiber catalyst, like other PE supported catalysts, can be easily separated and reused with no loss of activity within experimental limits. These initial results show the great potential for PE fiber-catalyst to be used in a fixed-bed flow system similar to the microfiltration cartridge (Sterapore-PKO) developed by the Mitsubishi Rayon Co.

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