Polymer Attached Catalysts

FINAL REPORT
2 Mar-31 Aug 79

Robert H. Grubbs

7 January 1980

U. S. Army Research Office

Contract Number DAAG-29-79-C-0051

California Institute of Technology
Pasadena, California 91125

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.
Monomers containing two ligand groups separated by either flat aromatic groups or long alkyl chains were prepared. These materials were use to make polymers in with nickel(II) or rhodium(I) halides were used to link the monomer units. The major part of the study used 1,12-bis(diphenylphosphino)-dodecane as the monomer unit. Polymethylmethacrylate-Pt.
ABSTRACT (contd)

Composites were evaluated as oxidation catalysts and as electrode coatings.

PUBLICATIONS (from DOD support)


SCIENTIFIC PERSONNEL

Gwen Goretsas - M.S. student

AREAS OF ADVANCEMENT

Preparation of Ligating Monomers

Monomers containing two ligating groups separated by distances greater than that favorable for chelation on one metal center were prepared. These included the following:

\[
\begin{align*}
\text{CH}_3 & - C - \text{CH}_2 & C & - O & - (\text{CH}_2)_\{12\} & - O & - C - \text{CH}_2 & - C - \text{CH}_3 \\
\phi_2 P & - (\text{CH}_2)_\{12\} & - P\phi_2 \\
\phi_2 P & - \bigcirc & - \bigcirc & - P\phi_2
\end{align*}
\]

Attempts were made to prepare the following cyclopentadienyl monomer from the norbornadienyl precursors:

\[
\begin{align*}
\text{Li} & - \bigcirc - \text{Li} & + & \bigcirc & \quad 1) \text{ether} \\
& & & & \quad 2) \text{Me}_2\text{SO}_4
\end{align*}
\]
Good preparations of the ethers were developed, however, clean conversion to the monomer were not achieved due to the lack of time.

**Polymer Formation**

Polymers were prepared from the bisphosphine and nickel and rhodium halide salts. These insoluble polymers showed the appropriate analysis and were of the proper color for the desired polymers.

\[
\phi_2 P-(CH_2)_2P\phi_2 + NiCl_2 \rightarrow
\]

\[
\left\{ \begin{array}{c}
\phi \mid (CH_2)_2P \mid Cl \\
\phi \mid (CH_2)_2P \mid Cl \\
\end{array} \right\} _n
\]

\[
\phi_2 P-(CH_2)_2P\phi_2 + [(COE)_2 Rh-C1]_2 \rightarrow
\]

\[
\left\{ \begin{array}{c}
Cl \mid Rh \mid _n \mid P \mid (CH_2)_2P \mid _m \\
\end{array} \right\}
\]

n = 1, 2 or 3; m = large

Further characterization and the development of these materials as catalysts must await further support.

**Polymer Imbeded Metals**

Materials can be prepared containing mixed valent metal salts in a variety of polymeric matrices. The most stable of these, polymethylmethacrylate-Pt, was evaluated for the oxidation of sulfides and as an electrode coating.

**Oxidations**

The ethanol insoluble material produced from polymethylmethacrylate and PtCl_2/MeOH was tested for the oxidation of various sulfides at one atmosphere of O_2 and temperatures up to 60°C. None of the sulfides showed any enhanced oxidation rates.
Electrochemistry of Polymer Coated Electrodes

A preliminary examination of these materials as coatings on graphite electrodes was carried out. These studies suggest that the polymer containing platinum can change the characteristics of a carbon electrode toward those of a standard platinum electrode.