AIIM

Association for Information and Image Management

1100 Wayne Avenue, Suite 1100
Silver Spring, Maryland 20910
301/587-8202

Centimeter

Inches

MANUFACTURED TO AIIM STANDARDS
BY APPLIED IMAGE, INC.

1 of 1

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE COBALT DICARBOLLIDE CONTAINING POLYMER RESINS FOR CESIUM AND STRONTIUM UPTAKE

AUTHOR(S) W. P. Steckle, Jr., MTL-7
J. R. Duke, Jr., MTL-7
B. S. Jorgensen, MTL-7

SUBMITTED TO POLYMER MATERIALS SCIENCE AND ENGINEERING, AMERICAN CHEMICAL SOCIETY, VOL. 71
FALL MEETING 1994
WASHINGTON, D.C. (AUGUST 21-25, 1994)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

COBALT DICARBOLLIDE CONTAINING POLYMER RESINS FOR CESIUM AND
STRONTIUM UPTAKE W.P. Steckle, Jr., J.R. Duke, Jr., and B.S. Jorgensen;

Los Alamos National Laboratory, MST-7, MS E549, Los Alamos, NM 87504

Large amounts of high level radioactive waste has been generated by the atomic industry over the past several decades. These wastes exist as a mixture of radioactive elements and flocculants that makes processing difficult. A majority of the thermal energy produced in these wastes arises from $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$. Cobalt(III) dicarbollide $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}]^-$ has been found to selectively extract these cations from solution. Unfortunately the current technology employs extracting these metals into nitrobenzene. In order to avoid the use of organic solvents in processing these wastes it is our goal to attach these dicarbollide moieties to a base resin in a manner where they can be utilized as a quasi-ion exchange resin. Once these metals have been removed from the waste streams it is hoped that they can be washed off the resins then vitrified into glass logs. The base resins that have successfully derivitized include polystyrene and polybenzimidazole. A series of derivatives was prepared starting with carborane ($\text{C}_2\text{B}_{10}\text{H}_{12}$), lithium carbollide $[(\text{C}_2\text{B}_9\text{H}_{11})^- \text{Li}^+]$, and finally cobalt dicarbollide. The reaction proceeds by anionically grafting the carborane derivatives onto a chloromethylated resin. The synthesis and subsequent characterization of these materials will be investigated.

COBALT DICARBOLLIDE CONTAINING POLYMER RESINS FOR CESIUM AND STRONTIUM UPTAKE

W.P. Steckle, Jr., J.R. Duke, Jr., and B.S. Jorgensen
Los Alamos National Laboratory, Polymer and Coatings Group
MST-7, MS E549, Los Alamos, NM 87504

Introduction

Over the past several decades large quantities of high level radioactive waste have been generated by the atomic industry. $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ occur in nuclear waste as the result of fission in reactor fuels. One of the major problems presented by these particular isotopes present in storage is that they contribute upwards of 97% of the thermal energy to the storage tanks.¹ Wastes have been generated in such a manner that they contain a wide variety of metals and isotopes along with a variety of flocculating agents. Prior treatment methods have employed the use of phosphotungstic acid, ferro- and ferricyanides and tetraphenylborate to precipitate these metals. In multi-element streams this leads to a long tedious process where many precipitates are formed adding to the quantity of waste being processed.

Macrocyclic crown ethers have also been employed for removal of Cs and Sr. Selectivity can be achieved by selecting the size of the cavity of the crown ether in which the metal cation fits. The drawbacks to crown ethers are their cost and the inability to remove the metal from the crown ether once it has been extracted.²

Although cobalt(III) dicarbollide $[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{Co}]^-$ (CB_2), Fig. 1, was first made in the 1960's³ it was not until the 1970's that its use for Cs and Sr extraction was investigated by Russians and Czech researchers⁴⁻⁵. CB_2 showed high levels of selectivity and extraction in an organic phase. Nitrobenzene exhibited the highest distribution coefficient of the solvents investigated, three time greater than that of ethyl acetate.⁴ Due to the carcinogenic and toxic nature of this solvent coupled with more stringent environmental regulations the use of nitrobenzene, and in general, any organic solvent, should be avoided.

Fig. 1. Cobalt dicarbollide. Protons attached to borons and carbons omitted for the sake of clarity.

Dicarbollides are useful in this application in that they are highly stable to redox, thermal, chemical, and radiolytic attack. Of the metals (Co, Fe, or Ni) that can be placed between the carbollide cages, cobalt is essentially insoluble in water and creates the complex with the greatest stability.⁶ Initial efforts to modify a resin was to simply adsorb the CB_2 onto the surface of the resins. Although there is limited solubility in water, there was noticeable desorption of the CB_2 under acidic conditions. This led to the need for covalently bonding the CB_2 to a resin substrate.

Synthesis of Resins with Grafted Cobalt Dicarbollide

Previous work in the area of polymer supported metal catalysts has led to the

Macrocyclic crown ethers have also been employed for removal of Cs and Sr. Selectivity can be achieved by selecting the size of the cavity of the crown ether in which the metal cation fits. The drawbacks to crown ethers are their cost and the inability to remove the metal from the crown ether once it has been extracted.²

Although cobalt(III) dicarbollide $[(C_2B_9H_{11})_2Co]^-(CB_2)$, Fig. 1, was first made in the 1960's³ it was not until the 1970's that its use for Cs and Sr extraction was investigated by Russians and Czech researchers⁴⁻⁵. CB_2 showed high levels of selectivity and extraction in an organic phase. Nitrobenzene exhibited the highest distribution coefficient of the solvents investigated, three time greater than that of ethyl acetate.⁴ Due to the carcinogenic and toxic nature of this solvent coupled with more stringent environmental regulations the use of nitrobenzene, and in general, any organic solvent, should be avoided.

Fig. 1. Cobalt dicarbollide. Protons attached to borons and carbons omitted for the sake of clarity.

Dicarbollides are useful in this application in that they are highly stable to redox, thermal, chemical, and radiolytic attack. Of the metals (Co, Fe, or Ni) that can be placed between the carbollide cages, cobalt is essentially insoluble in water and creates the complex with the greatest stability.⁶ Initial efforts to modify a resin was to simply adsorb the CB_2 onto the surface of the resins. Although there is limited solubility in water, there was noticeable desorption of the CB_2 under acidic conditions. This led to the need for covalently bonding the CB_2 to a resin substrate.

Synthesis of Resins with Grafted Cobalt Dicarbollide

Prior research in the area of polymer supported metal catalysts has led to the attachment of 1,2-dicarbado-decaborane, a precursor of CB_2 , to polystyrene (PS). Chandrasekaran et al.⁷ prepared a rhodium complex for use as a hydrogenation catalyst in this manner. An anion of the carborane cage was prepared by the reaction of the decaborane with $n\text{-BuLi}$ and was then subsequently reacted with a chloromethylated PS.

In this study a series of cross linked resins was used. Different solvents were investigated in order to determine the rate of reaction and whether or not the degree of swelling effected the substitution. Once it was determined

that the carborane cage was actually grafted onto the resin and not merely adsorbed onto the surface, a series was prepared incorporating lithium carbollide $[(C_2B_9H_{11}) \cdot Li^+]$ and cobalt dicarbollide onto a resin.

Another resin investigated was polybenzimidazole (PBI). Since PBI does not contain a reactive chlorine site, epichlorohydrin was grafted on as reported by Chanda et al.⁸ The resulting hydroxyl group from the opening of the epoxide was then protected by hexamethyldisilazane. The reaction scheme for the grafting of CB_2 onto PBI is given below:

Experimental

Some of the chloromethyl polystyrene (CMPS) resins that were used are

Experimental

Some of the chloromethyl polystyrene (CMPS) resins that were used are commercially available from Polysciences and some were made in house. The PBI resin was Aureoz microporous resin beads made by Hoechst-Celanese and was used as supplied. Cyclohexane, toluene, and tetrahydrofuran (THF) used during grafting reactions were freshly distilled from sodium under an argon purge. *n*-buLi, hexamethyldisilazane, methanol, and ethanol was purchased from Aldrich and used as received. Carborane was purchased from Alfa was purified by sublimation prior to use. Lithium carbolide and CB_2 was prepared at Los Alamos National Laboratory, CST-12.

Reaction conditions for both the grafting of the carborane series as well as the preparation of the PBI prior to the CB₂ reaction were as previously cited.^{7,8} In order to insure that the carboranes were not merely adsorbed to the surface of the resins all samples were washed three times with methanol before soxhlet extraction for 48-72 hours in ethanol. Samples with adsorbed carborane or CB₂ that were subjected to similar work up were found to be free of either the carborane or CB₂.

Samples were analyzed using a Perkin Elmer 1600 FTIR and a Nicolet 730 FTIR equipped with a Nic-Plan IR microscope. Diamond windows were used in order to compress the resin beads. Beads were looked at both in transmission as well as reflectance modes. Solid state ¹³C and ¹¹B NMR of these resins was done using a Bruker ASX 300.

Elemental analysis is currently be done in order to quantify the extent of reaction.

Results and Discussion

Two reaction routes were first envisioned for obtaining CB₂ grafted onto a resin. One involved directly grafting CB₂ to the CMPS if that were possible. This route would be easier on the resin than having to expose the resin to the harsh conditions under which a B-H is extracted from the carborane cage. Steric hindrance and the fact that each cage on CB₂ itself is a dianion needed to be taken into consideration. Since carborane had previously been shown to react with CMPS⁷, this reaction was optimized before trying to graft the carbollides. This reaction can be followed using IR spectroscopy by monitoring the disappearance of the CH₂-Cl stretch, ca. 1265 cm⁻¹, and the growth of the strong B-H absorbance ca. 2580 cm⁻¹ as seen in Fig. 2. Not only is the B-H absorbance dependent on the type of cage, it can be seen to shift 5 - 10 cm⁻¹ upon grafting. The second cage in the series to be attached was the lithium carbollide. Somewhat less sterically hindered than CB₂ this too could be readily attached to CMPS. Being an anionic species apparently did not prevent the formation of the carbanion. Surprisingly the CB₂ reaction also proceeded smoothly.

Fig. 2 FTIR spectra of carborane and the starting CMPS resin along with the grafted carborane resin.

Elemental analysis is currently be done in order to quantify the extent of reaction.

Results and Discussion

Two reaction routes were first envisioned for obtaining CB_2 grafted onto a resin. One involved directly grafting CB_2 to the CMPS if that were possible. This route would be easier on the resin than having to expose the resin to the harsh conditions under which a B-H is extracted from the carborane cage. Steric hindrance and the fact that each cage on CB_2 itself is a dianion needed to be taken into consideration. Since carborane had previously been shown to react with CMPS⁷, this reaction was optimized before trying to graft the carbollides. This reaction can be followed using IR spectroscopy by monitoring the disappearance of the $\text{CH}_2\text{-Cl}$ stretch, ca. 1265 cm^{-1} , and the growth of the strong B-H absorbance ca. 2580 cm^{-1} as seen in Fig. 2. Not only is the B-H absorbance dependent on the type of cage, it can be seen to shift $5 - 10\text{ cm}^{-1}$ upon grafting. The second cage in the series to be attached was the lithium carbollide. Somewhat less sterically hindered than CB_2 this too could be readily attached to CMPS. Being an anionic species apparently did not prevent the formation of the carbanion. Surprisingly the CB_2 reaction also proceeded smoothly.

Fig. 2 FTIR spectra of carborane and the starting CMPS resin along with the grafted carborane resin.

Another consideration was whether or not the extent of swelling effected the reaction rate and whether the carborane was reacting uniformly throughout the resin. THF and toluene were chosen as swelling solvents and cyclohexane as the non-swelling solvent. Samples were taken off via syringe and quenched with methanol. They were then washed several times with methanol to insure the removal of any unreacted carborane. Fig. 3 shows the rate of reaction as a function of the normalized intensity of the B-H stretch. Values of the absorbance were normalized against a $\text{C}=\text{C}$ aromatic stretch @ 1600 cm^{-1} . There is a corresponding decrease in the absorbance of the $\text{CH}_2\text{-Cl}$ stretch. The reaction in THF goes to completion

in under 15 minutes whereas it takes over 4 hours in toluene. After 72 hours in cyclohexane the reaction had considerably slowed down at a conversion of approximately 60%. This is due to better solvation of both the n-buLi and carborane carbanion ion pairs in THF. This coupled with the inability of the reactants to swell into the pores of the resin the cyclohexane was the least effective solvent.

Fig. 3 Reaction rate of CB2 as a function of the normalized intensity of the B-H absorbance.

^{13}C and ^{11}B solids NMR has been used to confirm the presence of carborane and CB₂ on both the PS and PBI resins. Unfortunately quadrupolar relaxations of ^{11}B leads to a significant amount of broadening of the peaks. Fortunately carborane and CB₂ are the only sources of boron in the system.

Conclusions

CB₂ has been successfully covalently bonded to both PS and PBI resins. THF was found to be the most efficient solvent for the grafting reaction. Further analysis is currently being performed in order to quantify the extent of these reactions. Separation coefficients are also being determined for these resins in order to see whether or not these materials perform as well as the non-grafted CB₂.

Acknowledgments

Funding was provided by the DOE. We would also like to thank P. Hurlburt, R. Miller, T. Foreman, K. Abney, and S. Kinkead of CST for providing all the carborane derivatives for this work.

1. U.S. Dept. of Energy, "Department of Energy Plan for Recovery and Utilization of Nuclear Byproducts from Defense Wastes", DOE/DP-0013, Vol.2, August 1983.
2. W. Schulz and L. Bray, *Sep. Sci. Tech.*, **22**, 191, 1987.
3. M. Hawthorne and T. Andrews, *Chem. Commun.*, 443, 1965.
4. J. Rais, P. Selucky, and M. Kyras, *J. Inorg. Nucl. Chem.*, **38**, 1376, 1976.
5. M. Saeed and M. Kanada, *Radiation Induced Polymerization*, 24, 22

Fig. 3 Reaction rate of CB2 as a function of the normalized intensity of the B-H absorbance.

^{13}C and ^{11}B solids NMR has been used to confirm the presence of carborane and CB_2 on both the PS and PBI resins. Unfortunately quadrupolar relaxations of ^{11}B leads to a significant amount of broadening of the peaks. Fortunately carborane and CB_2 are the only sources of boron in the system.

Conclusions

CB_2 has been successfully covalently bonded to both PS and PBI resins. THF was found to be the most efficient solvent for the grafting reaction. Further analysis is currently being performed in order to quantify the extent of these reactions. Separation coefficients are also being determined for these resins in order to see whether or not these materials perform as well as the non-grafted CB_2 .

Acknowledgments

Funding was provided by the DOE. We would also like to thank P. Hurlburt, R. Miller, T. Foreman, K. Abney, and S. Kinkead of CST for providing all the carborane derivatives for this work.

1. U.S. Dept. of Energy, "Department of Energy Plan for Recovery and Utilization of Nuclear Byproducts from Defense Wastes", DOE/DP-0013, Vol.2, August 1983.
2. W. Schulz and L. Bray, *Sep. Sci. Tech.*, **22**, 191, 1987.
3. M. Hawthorne and T. Andrews, *Chem. Commun.*, 443, 1965.
4. J. Rais, P. Selucky, and M. Kyrš, *J. Inorg. Nucl. Chem.*, **38**, 1376, 1976.
5. V. Scasnar and V. Koprda, *Radiochem. Radioanal. Letters*, **34**, 23, 1978.
6. J. Plešek, K. Base, F. Mares, F. Hanousek, B. Stbir; and S. Hermanek, *Collect. Czech. Chem. Commun.*, **49**, 2776, 1984.
7. E.S. Chandrasekaran; D.A. Thompson; and R.W. Rudolph, *Inorg. Chem.*, **17**, 760, 1978.
8. M. Chanda, K.F. O'Driscoll, and G.L. Rempel, *Reactive Polymers*, **9**, 277, 1988.

DATE

FILMED

7 / 8 / 94

END

I