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Mangala
PREFACE

The development of polymer supported catalysts can be considered as an advancement for attaining one of the major goals of ‘green chemistry’, i.e., to facilitate efficient recovery of the catalyst from the reaction products, thereby reducing inorganic waste.

Polycarbosilanes (PCS) a rather neglected class of polymers has attained considerable interest recently. This class of polymers can be compared to the existing classes of inorganic and organic polymers, they possess a combination of low $T_g$’s and high synthetic versatility similar to polyphosphazenes and polysiloxanes and with good chemical backbone stability similar to that of polyolefins. Polycarbosilanes can represent structural hybrid between polysilanes and polyolefines, which have found applications as liquid crystals, SiC-precursor and catalyst support.

By introducing transition metal ions to polycarbosilanes, we can create functional polymer with properties such as catalytic activity. The immobilization of transition metal ions on polymer supports offers a number of advantages over solution phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they also do not contaminate the product solution, they can be recycled, and they can help in increasing the selectivity.

Relatively few examples of metal-functionalized polycarbosilanes have been reported. In a reaction, the functionalized macromolecules with bound catalytic centers surrounded by solvents fulfil the function of isolated micro reactors. The high surface area of the polycarbosilane increases the rate of the reaction.
Dendrimers are monodispersed nanosized polymeric molecules composed of two or more tree like dendrons. Dendritic molecules are repeatedly branched species that are characterized by their structure perfection. Dendrimers are mainly used in the area of catalysis and in biotechnology and medicine. Dendrimers are considered to fill the gap between homogeneous and heterogeneous catalysts. The dendrimer functionalized polymers can be used as heterogeneous catalyst.

**Objectives of the present study**

1. Synthesis and characterization of polycarbosilanes.
2. Incorporation of metal ions on polycarbosilanes and their characterization.
3. Study of the catalytic activity of metal ion incorporated polycarbosilanes.
5. Study of the catalytic activity of PPI dendrimer immobilized polysilane.

Thesis comprises of six chapters

In the first chapter, literature review about polymer supported metal catalysts is presented. This chapter also includes a thorough review of silicon polymers, particularly polycarbosilanes.

The second chapter mainly discusses about polycarbosilanes and their synthesis. Polycarbosilanes are organic-inorganic hybrid polymers which have both Si and C in their back bone structure; they have been of exacting significance as potential precursor to SiC. Polycarbosilanes have variety of possible applications that are opening up for these hybrid polymers in the areas
such as nanotechnology, surface science, bio-medicine, catalysis, electrochemistry, liquid crystals, new ceramic materials, organic hybrid materials and nanocomposites. Many of these play dominant roles in the development of science in the twenty first century, and we have no doubt that silicon will occupy a prominent position in all of them as well. Five polycarbosilanes were synthesized from corresponding monomers, trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane. Homopolymers with trichloromethylsilane, diethoxymethylvinylsilane and copolymers with trichloromethylsilane in combination with chlorodimethylvinylsilane, diethoxymethylvinylsilane, trimethoxyvinylsilane were prepared. The preparation involved the Wurtz-type coupling reaction of monomer molecules in the presence of metallic sodium. Characterization of the prepared polycarbosilanes by various spectroscopic techniques such as UV-Vis DRS, FT-IR, $^{29}$Si-CP-MAS NMR, solid state- $^{13}$C NMR spectroscopy, TG-DTA, BET surface area analysis and X-ray diffraction analysis is also presented. Halogen estimation was done by Volhard method. From the results of analytical data the structure of polycarbosilanes were established. All the prepared polycarbosilanes are of highly cross-linked structure and amorphous in nature. All of them possess high temperature stability and high surface area. The polycarbosilanes, except PCS 5, are capable of further functionalization since they have at least one chlorine substituent.

The third chapter deals with the synthesis and characterization of metal ion immobilized polycarbosilanes. The nucleophilic substitution reaction has been used to add side chains or to modify the structure of initially obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer back bone. Polycarbosilanes formed by the polymerization of monomers such
as trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane were used for the incorporation of metal ions. The metal ions selected were Ti(IV), Mn(II), Co(II), Ni(II), Cu(II) and Pd(II). Metal ion incorporated polycarbosilanes were characterized using various analytical methods. The spectroscopic techniques used are FT-IR, UV-Vis DRS, $^{29}$Si-CP-MAS NMR, $^{13}$C CP-MAS NMR and EPR spectroscopy. Thermal behaviour was analysed by TG/DTA. Magnetic susceptibility measurements, BET surface area analysis were used to analyse the properties of metal ion incorporated polycarbosilanes. Metal ions were estimated with AAS/ICP-AES. Factors influencing metal incorporation were studied in detail.

Chapter four deals with the detailed study of the catalytic activity of polycarbosilane supported transition metal ions. Transition metals have important role as catalysts in organic synthesis. Metal ion incorporated polycarbosilanes were used as catalysts for different organic reactions. Four different types of reactions were taken into consideration viz, Mannich reaction, Knoevenagel Condensation Reaction, Biginelli reaction and Heck reaction. Reaction conditions were optimized. The purity of the reaction products was checked by means of HPLC and characterized with $^1$H NMR, LC-MS and FT IR spectroscopic techniques and melting point.

Fifth chapter includes the discussion about dendrimers and polymer supported dendrimers and their preparation. This chapter discusses about the preparation of dendrimer functionalized polysilane. Polysilane was synthesized from the monomer, trichloromethylsilane. The polysilane was characterized by GPC, FT-IR, $^{29}$Si-CP-MAS NMR and $^{13}$C CP-MAS NMR spectroscopy. The polysilane supported PPI dendrimer was prepared by divergent method and dendrimer upto the third generation was prepared.
Michael addition and reduction were used to synthesize PPI dendrimer. The polysilane functionalized with dendrimer was characterized by FT-IR, $^{29}\text{Si}$-CP-MAS NMR, $^{13}\text{C}$ NMR spectroscopy and amino group estimations were carried out in each generation. The catalytic activity of PPI dendrimer immobilized polysilane was studied. Knoevenagel Condensation Reaction was selected to study the catalytic activity. Reaction conditions were optimized.

The final chapter presents the summary and important conclusions of the thesis.