

Title	含ケイ素ポリマー担持型新規メタロセン触媒の調製とオレフィン重合への応用
Author(s)	HOANG, THE BAN
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Description	Supervisor: 曾我 和雄 教授, 材料科学研究科, 博士

Synthesis of Novel Metallocene Catalysts Supported on Silicon Containing Polymers for the Application to Olefin Polymerizations

Hoang The Ban

*School of Materials Science,
Japan Advanced Institute of Science and Technology*

(Supervised by Professor Kazuo Soga)

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ABSTRACT

This dissertation describes a new route to synthesize new types of supported metallocene catalysts using silicon-containing polymers such as polysiloxanes, poly[*p*-(silylene)phenylenes] as carriers. The performance of these supported catalysts toward olefin polymerizations, especially the influences of silicon-polymer structures on the catalytic activity, stereospecificity and thermal stability have been rationally investigated in detail under a wide range of polymerization conditions. The syntheses of silicon-containing polymer supported metallocene catalysts cost a lot of effort and play an important role in this study. In fact, they were prepared according to the following three-step procedure:

- Synthesis of organochlorosilanes having cyclopentadienyl (Cp), indenyl (Ind), and fluorenyl (Flu) substituted groups by interactions between RMgBr (R = Cp, Ind, Flu) and Me_xSiCl_{4-x} .
- Synthesis of catalyst precursors via condensation reactions between these functional organochlorosilanes and water or dilithio salts of benzene to form polysiloxanes and poly[*p*-(silylene)phenylenes], respectively.
- Synthesis of supported catalysts via interactions between lithiated catalyst precursors with transition-metal salts.

This dissertation consists of an introduction and five experimental chapters. In chapter 2 are shown the method to synthesize and isolate 11 new organochlorosilanes having Cp, Ind, and Flu-substituted groups. These compounds were further utilized as primary building blocks for preparing the corresponding polysiloxanes and poly[*p*-(silylene)phenylenes]. The special features of these polymers result from their well-defined surface structures,

highly thermal stability and high potential of loading transition-metal ions via typical π -coordination. These methodologies can be expanded to synthesize any kind of functional organochlorosilanes with different type of substituted groups and the ligand's numbers.

In chapter 3 are described the synthetic method of a series of metallocene catalysts supported on both linear and cross-linked polysiloxane precursors and their catalytic performances to ethene and propene polymerizations. It was interesting to found that the contents of zirconium in these polymer supported catalysts are drastically increased as compared to that of conventional supported metallocene catalysts using inorganic compounds as carrier. This is considered as one of the first important conditions in order to obtained a highly active supported metallocene catalyst. From the results of ethene and propene polymerizations, it was demonstrated that the behaviors of these supported catalysts depend remarkably on the structures of polymer backbones as well as their modes of supporting. In fact, while catalysts with bisindenyl substituted groups showed the highest activities, catalysts with fluorenyl substituted groups gave polymers with the highest molecular weights. In all cases, the activities of polysiloxane supported catalysts were found drastically improved as compared to that of silica supported ones. The increase of activity in these catalyst systems is attributed to the increase of concentration of the active species. On the contrary to the homogeneous metallocene catalysts, that can not be activated by common AlR_3 , polysiloxane supported ones were able to be activated even by common alkylaluminums such as TIBA or TEA to give polyethene with very high molecular weights and melting points. The effect of siloxane backbones on the stereospecific polymerization of propene is considered as one of the most important aspects of these catalyst systems. Actually, highly isotactic-PP can be obtained not only with a well-known C_2 -symmetric metallocene (catalyst II, IV, and VI) but also even by a C_{2v} -symmetric (catalyst III) and a C_1 -symmetric ones (catalyst VII). It is more surprisingly that a supported version of $[Me_2Si(Cp)(Flu)]ZrCl_2$, which usually yields completely a-PP in homogeneous phase, was able to produce highly syndiotactic-PP. The presence of siloxane backbones are considered to give driving force for the formation of isotactic and syndiotactic polypropene from the aspecific active sites. The results obtained in this study provide us valuable information involved to the influence of silica surface on the activity and stereospecificity of silica supported metallocene catalysts, which are not well-understood so far.

In chapter 4 are shown a new route for synthesis of novel dinuclear ansa-zirconocene catalysts having a biphenyl bridge via condensation reaction between p-dilithiobiphenyl and bisindenyl phenylchlorosilane in diethylether, followed by reacting with a solution of $ZrCl_4 \cdot 2THF$. The special feature of the dinuclear catalyst is that two active metal centers are conjugated through a biphenyl bridge having π -electron system alternating arrangement on the whole catalyst structure. It was proved that such a ligand framework has remarkable effects on both the catalytic activity and the thermal stability. In fact, the activity and thermal stability of dinuclear catalyst were drastically increased as compared to that of corresponding mononuclear catalyst. Synthesis of separated rac- and

meso-dinuclear catalysts was carried out via a diastereoselective method e.g., rac-catalyst was prepared from rac-precursor, and meso-catalyst from meso-precursor. Both catalysts, especially the meso-isomer, show an extremely high activity for ethene polymerization to give polyethene with high Mw even at 150°C. From the results of rate-time profiles conducted with ethene polymerization at 70°C, it was demonstrated that the deactivation process of rac- and meso-dinuclear catalysts is slower than that of with mononuclear analogue, indicating that the active species formed in the dinuclear catalysts are much more stable.

In chapter 5 are described the syntheses of poly[*p*-(silylene)phenylene] supported metallocene catalysts as well as their catalytic behavior to olefin polymerizations. The replacement of flexible and polarized siloxane backbones by more rigid and covalent *p*-(silylene)phenylene backbones is strongly expected to improve the catalytic performance. In fact, thermal stability of the active species formed in these catalysts was found to be drastically enhanced as compared to those of the corresponding mononuclear, dinuclear and polysiloxane supported catalysts. This conclusion was further supported by the results of rate-time profile and ethene consumption during polymerization. It was surprisingly to us that these polymer supported catalysts could be easily activated even by common alkylaluminums to give polyethenes with higher activities as compared to that of previously obtained with silica and polysiloxane supported analogues. Contrary to ethene polymerization, these catalysts show poor activities for propene polymerization. It is considered that phenyl-substituted groups on the silicon bridge and their alternating π -electron systems arranged throughout the polymer backbones are responsible for such an enhancement. A systematic investigation of the variety of catalytic behavior from mononuclear, dinuclear and polymer supported catalyst carried out in this study represents as one of the first examples for a rational model approach corresponding to heterogeneous metallocene catalysts which is hardly achievable so far.

In chapter 6 are shown the results of copolymerization between ethene and 1-octene with silicon containing polymer supported metallocene catalysts under practical polymerization conditions. Polystyrene-beads was selected as the carrier in preparing heterogeneous catalyst. These catalysts showed high activities to give copolymer with high molecular weight in range of industrial acceptance. While the homogeneous catalysts yield polymer with higher activity, the heterogeneous analogues were able to produce copolymers with higher molecular weights. The contents of comonomer in feed, polymerization temperature as well as polymerization solvent were found to have strong effect on the activity, molecular weight, and morphology of copolymer produced. Under identical polymerization conditions, copolymers with good morphology and high bulk density can be obtained.

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Note: the thesis is written in English.

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