Title	新しいタイプのチーグラー-ナッタ触媒の合成とそれらのオレフィン重合への応用
Author(s)	加地，栄一
Citation	
Issue Date	1998-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/2053
Rights	
Description	Supervisor:曽我 和雄 教授，材料科学研究科，博士

Syntheses of novel type of Ziegler-Natta catalysts and their application to olefin polymerizations

Eiichi Kaji

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

(Supervised by Kazuo Soga)

Keywords: Ziegler-Natta catalyst, Propene polymerization, Non-metallocene complex, $MgCl_2$-supported titanium β-diketonate catalyst, Electron donor, Ethene - α-olefin copolymerization, Overreduction of titanium species

Abstract :

Since the discovery of the Ziegler-Natta catalysts, many researchers have been paid much efforts to improve the catalyst performance. As a result, the Ziegler-Natta catalysts show the adequate performance even in the industrial fields. However, it is difficult to design the catalyst to produce the tailor-made polyolefins because of the complicated catalyst systems, i.e., $MgCl_2$, $TiCl_4$, internal donor, external donor, alkylaluminum, chlorinating reagent and so on. On the other, metallocene compounds have distinct structures. Although metallocene catalysts offer numerous advantages for olefin polymerization, there still remain some unsolved problems. For examples, the difficulty in controlling the polymer morphology, the improvement of thermal stability, a large amount of methylalumoxane used, etc. To overcome those problems, heterogenization of metallocene catalysts is one effective method and give many advantage. However, in comparison to the corresponding homogeneous metallocene catalysts, the supported-type metallocene catalysts show the very low polymerization activities.

Recently, some non-metallocene complexes have been claimed as the catalysts for olefin polymerizations. However, the performance of non-metallocene catalysts is usually very poor as compared to the metallocene catalysts, Moreover, there are only a few reports on the supported-type non-metallocene catalysts.

From such viewpoints, in this study, we aim at the development of the new supported-type transition metal β-diketonate catalysts to olefin po lymerization.

In Chapter 2, synthesis and characterization of a series of Ti(β-di ketonato)$_2$Cl$_2$ is summarized, i.e., Ti(acetylacetonato)$_2$Cl$_2$; Ti-AA, Ti(1-benzoylacetonato)$_2$Cl$_2$; Ti-BA, Ti(2,2,6,6-tetramethyl-3,5-heptanedionato)$_2$Cl$_2$; Ti-DPM, Ti(4,4,4-trifluoro-1-phenyl-1,3-

butanedionato)$_2$Cl$_2$; Ti-BFA, and Zr(acetylacetonato)$_2$Cl$_2$; Zr-AA. As a result, those complexes can be easily synthesized in high yields.

In Chapter 3 were prepared the $MgCl_2$-supported Ti-AA, Ti-BA, Ti-DPM and Ti-BFA catalysts by impregnation method and tested to propene polymerization. It was found that those catalysts were activated by MAO as well as ordinary alkylaluminums to give PP in fairly high yields. Especially, the $MgCl_2$-supported Ti-BFA catalysts showed the highest activity among the catalysts prepared. The catalyst isospecificity was comparable to the conventional Ziegler-Natta catalyst without the addition of any electron donor. For reference, the corresponding homogeneous catalysts were almost inactive for propene polymerization.

In Chapter 4 deals with the effect of typical Lewis bases [ethyl benzoate, di-n-butyl phthalate, dicyclopentyldimethoxysilane, di-i-propyldimethoxysilane(DIPDMS), phenyltriethoxysilane] on performance of the catalysts described above in some detail, which indicated that organic silane compounds are most effective for the improvement of isospecificity of those catalysts.

In Chapter 5, the $MgCl_2$-supported Ti-BFA catalysts with different Ti contents (0.017-0.002 mmol/g) were synthesized and applied to propene polymerization using triethylaluminum and DIPDMS as the cocatalyst and external donor, respectively. When polymerization was conducted in the absence of DIPDMS, neither the activity nor the isospecificity of catalyst were dependent upon the Ti content. However, the effect of DIPDMS on the catalyst performance was found to be markedly dependent upon the Ti content, i.e., the addition of DIPDMS to the catalyst with a less Ti content caused a more prominent increase in the activity for isotactic polymerization. As a result, the present catalyst with a less Ti content gave a highly isotactic polypropene having Tm = 169.3 ℃ and [mmmm] $>$ 99 in high selectivity (I.I. = 97.7 %).

In Chapter 6 describe the results of ethene - propene and ethene - 1-hexene copolymerization to obtain the information on the titanium active species of the novel catalyst. As a results, the catalyst especially showed the high activity to ethene. And, it became clear by the Cross Fraction Chromatography analysis of the copolymers obtained that the copolymers were composed of the two groups with different comonomer contents. That is, the active species of the novel catalysts were almost homogeneous, but slightly showed the heterogeneity raised from the overreduction of the active species, Ti(III).

Finally, in Chapter 7 were summarized the results obtained above together with some comments for the future study in the field.

Key Words :

Ziegler-Natta catalyst, Propene polymerization, Non-metallocene complex, $MgCl_2$-supported titanium β-diketonate catalyst, Electron donor, Ethene - α-olefin copolymerization, Overreduction of titanium species

List of Publications :

1) K. Soga, E. Kaji, T. Uozumi, Polymerization of Propene with the $MgCl_2$-Supported Dichlorobis(β-diketonato)titanium Catalysts Combined with M ethylaluminoxane or an Ordinary Alkylaluminum, J. Polym. Sci.; part A, Polym. Chem. 35, 823-826(1997)
2) K. Soga, E. Kaji, T. Uozumi, Propene Polymerization with the $MgCl_2$-Supported Dichlorobis(β-diketonato)titanium Catalysts Activated by Or dinary Alkylaluminums, J. Polym. Sci.: part A, Polym. Chem., in printing.
3) E. Kaji, T. Uozumi, J. Jin, T. Sano and K. Soga, Synthesis of the $MgCl_2$-supported dichlorobis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)titanium catalysts with different titanium contents and their application to propene polymerization, Macromol. Chem. Phys., submitted.
4) K. Soga, J. Jin, E. Kaji, T. Uozumi and Y. Suzuki, Amalgamation of Ziegler-Natta and Metallocene Catalysts, Macromol. Symp. 118, 55-60(1997)

Other related papers :

1) K. Soga, Y. Suzuki, T. Uozumi, E. Kaji, Polymerization of Propene with the $XTiCl_3/MgCl_2$-$Al(i\text{-}Bu)_3$ Catalyst System (X = Cyclopentadienyl, Pentamethyl-cyclopentadienyl, Indenyl, and Heptamethylindenyl) in the Absence and Presence of a Lewis Base, J. Polym. Sci.: part A, Polym. Chem. 35, 291-297(1997)
2) M. J. Schneider, E. Kaji, T. Uozumi, K. Soga, Influence of propene pressure on the isotacticity of polypropene produced with typical C1-symmetric metallocene and Ziegler-Natta catalysts, Macromol. Chem. Phys. 198, 2899-2904(1997).

Note: the thesis is written in Japanese.

February 20, 1998