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Author(s)	Poonpong, Supawadee
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氏　　名	Supawadee POONPONG			
学　位　の　種　類	博士（マテリアルサイエンス）			
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論　文　題　目	Structure-performance relationship of alkoxysilanes as external donors in various propylene polymerizations using Ziegler-Natta catalyst			
論文審査委員	主査	寺野　稔	北陸先端科学技術大学院大学	教授
		江　東林	同	教授
		金子達雄	同	教授
		谷池俊明	同	准教授
		新田晃平	金沢大学	教授

論文の内容の要旨

The structure-performance relationship of alkoxysilane external donors was explored in terms of catalyst activity, stereospecificity, comonomer incorporation and hydrogen response. Both di- and trialkoxysilanes were used in propylene polymerization.

The introduction of external donor gave lower polymer yield with higher stereoregularity due to the poisoning of the aspecific active sites. The effects of alkoxysilanes depend on the number and size of alkoxy groups as well as those of alkyl groups. The structure-performance relationship of dimethoxysilane was investigated in Chapter 2. It was found that catalyst activity was related to the coadsorption energy of the donors onto $MgCl_2$. Dicyclopentyldimethoxysilane gave not only the highest catalyst activity but also the best stereospecificity from the sterically hindered structure. It can be assumed that structure of alkoxysilanes gives the different ability to prevent deactivation of $TiCl_4$ by alkylaluminum. As results, it was found that an alkoxysilane which adsorbed more strongly on $MgCl_2$ surfaces in DFT calculations tended to give a higher polymer yield. Though the branching at the C_α carbons was a prerequisite for higher isospecificity, the conformation detail around active sites was also important.

To generalize the structure-performance relationship, effects of triethoxysilane structure on the catalyst performance was also determined and discussed in Chapter 3. It was also found that Similar as dimethoxysilane, an alkoxysilane adsorbed stronger on the $MgCl_2$ surface based on coadsorption model tends to give a higher polymer yield in SF and slurry polymerization while no tendency was found in pressurized polymerization. Moreover, the relationship between insoluble fraction and stereospecificity calculated based on coadsorption model remained valid with the addition of triethoxysilane structures as shown in Figure 1.

From the propylene copolymerization results in Chapter 4, it was found that the presence of ethylene and 1-octene enhanced the polymer yield for all alkoxysilane structures. This can be explained by the enhanced diffusion rate to less-crystalline copolymer. The tendencies of comonomer content in the presence of different types of alkoxysilane were found to be similar for both ethylene and 1-octene, in which alkoxysilane that produced polypropylene with higher isotacticity gives copolymer with less comonomer content. This result indicated that the incorporation of comonomer was largely governed by the comonomer diffusion. A polypropylene with less tacticity permits better diffusion of comonomer to give a higher incorporation.

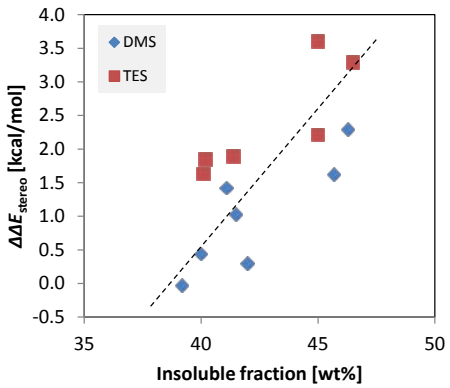

Figure 1. Correlation between experimental insoluble fractions from SF polymerization and calculated stereospecificity of active sites ($\Delta\Delta E_{stereo}$)

To investigate the effect of hydrogen response, propylene polymerization in the presence of hydrogen was conducted using different types of alkoxysilane in Chapter 5. In the absence of hydrogen, molecular weight of the obtained polymer was found to correlate with the stereospecificity. Molecular weight tends to increase with the increase of stereospecificity, probably due to increase of propagation rate. However, this tendency became unclear in the presence of hydrogen. In the presence of hydrogen, triethoxysilanes provided the better hydrogen response compared to dimethoxysilanes. Comparing among dimethoxysilane structures, cyclic alkyl substituents tended to provide better hydrogen response.

The results obtained in this study have provided the information for the developments of new donor system. This study is expected to open the door for the further detailed study of the SPR of other donors in heterogeneous ZN propylene polymerization.

Keywords: Alkoxysilane; Structure-performance relationship; Ziegler-Natta catalyst; propylene polymerization

論文審査の結果の要旨

Due to the excellent basic properties and low production cost, polypropylene (PP) has been the most widely used plastic and the development of new application has been a great target for the world PP producers. The improvement of alkoxysilane external donor used in Ziegler-Natta (ZN)

catalyst system is one of the most effective approaches for the purpose. The catalyst performance greatly depends on the type and the structure of the donor. There have been several studies reported about the effects of alkoxysilane structure on catalyst performance. Although some level of relationship was already explored, the quantitative structure-performance relationship of alkoxysilane is still unknown.

So, the objective of this study is to systematically clarify the effects of alkoxysilane structures on catalytic properties in ZN propylene polymerization, aiming at the establishment of the design of new donor system. In this study, internal donor-free catalyst was used in stopped-flow polymerization to determine the effects of alkoxysilane at the level of active sites without the unfavorable reaction from internal donor. The catalyst performances, such as catalyst activity, stereospecificity, hydrogen response and comonomer incorporation, were employed to evaluate the effects of alkoxysilane The introduction of external donor gave lower polymer yield with higher stereospecificity due to the poisoning of the aspecific active sites. The effects of alkoxysilane depend on the number and size of alkoxy and alkyl groups. Moreover, it was also found that an alkoxysilane adsorbed more strongly on $MgCl_2$ surfaces in DFT calculations tended to give a higher polymer yield. After structure-performance relationship of triethoxysilane was explored to generalize the other types of alkoxysilane, it was found that the relationship between insoluble fraction and stereospecificity calculated based on coadsorption model remained valid for the various structures. In the case of copolymerization, the presence of ethylene and 1-octene enhanced the polymer yield for all alkoxysilane structures. The efficiency of comonomer incorporation depended on the stereoregularity of polymer which can be explained from the different k_p depending on the alkoxysilane structures. In the presence of hydrogen, triethoxysilanes provided the better response. The results obtained in this study have provided the information to open the new door for the development of new donor system which can be applied for heterogeneous ZN propylene polymerization catalysts.

As mentioned above, this dissertation greatly contributes to the understanding of the most important industrial olefin polymerization catalyst. Therefore, this dissertation can be recommended for the doctor degree of JAIST in the field of materials science.