

Title	固体NMRおよびXPSによるPhillipsエチレン重合触媒の評価
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Citation	
Issue Date	2003-03
Type	Thesis or Dissertation
Text version	none
URL	<a href="http://hdl.handle.net/10119/3028">http://hdl.handle.net/10119/3028</a>
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Description	Supervisor:寺野 稔, 材料科学研究科, 修士

### C17p3 Characterization of Phillips Catalysts for Ethylene Polymerization by Solid-State NMR and XPS

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**[Introduction]** As one of the most important members in the family of commercial polyolefin catalysts, Phillips catalyst is still responsible for several million tons of commercial production of polyolefins including HDPE and LLDPE, etc. Because of many unique properties and applications of produced HDPE such as long chain branching and broad molecular weight distribution, etc., Phillips catalyst cannot be substituted by Ziegler-Natta catalyst and metallocene catalyst until now. Although almost 50 years have passed since discovery of Phillips catalyst, the polymerization mechanism and the nature of the active sites still remain controversial. Under such background, this research about traditional Phillips catalyst was studied in order to obtain further understanding on reaction mechanisms from catalyst preparation to polymerization.

In this paper, the following three aspects of the Phillips catalyst are studied: a) effects of calcination conditions during preparation process, b) effects of organometallic cocatalysts and c) initiation mechanism of ethylene polymerization.

**[Experiments]** The precursor of Phillips catalyst and silica were calcined under a series of temperature to prepare the catalysts, which were characterized by solid-state NMR and XPS in order to study the effects of calcination temperature. The calcined catalysts donated from company were treated by different organometallic cocatalysts and used to study the effects of cocatalyst through solid-state NMR and XPS methods. Solid-state NMR was also used to characterize a Phillips catalyst reacted with ethylene at 100°C for 30min during the induction period in order to study the initiation mechanism of the first chain propagation on Phillips catalyst.

**[Results and discussion]** During calcination procedure, the following aspects had been found from  $^{29}\text{Si}$  CP/MAS NMR study (Fig.1): i) Cr compound has reacted with the geminal and single silanol groups on silica gel even at 120 °C; ii) reaction of the geminal silanol groups has completely finished up to 300 °C and iii) existence of the catalytic species obstructs the removal of the single silanol groups at high calcination temperature. The results of Cr 2p XPS study indicate that the bulk  $\text{Cr}^{6+}$  species changes to the chromate species directly or in some case there are some transitional species as  $\text{Cr}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{4+}$  or  $\text{Cr}^{5+}$  exist between bulk  $\text{Cr}^{6+}$  and chromate species coexist on the surface. At high temperature, the chromate species anchored on the silica surface partly change to  $\text{Cr}_2\text{O}_3$  crystal. In the results of activation procedure by organometallic cocatalysts, a new peak assigned to proton in B-H or Li-H was found in the samples treated by TEB or BuLi; Al species with different coordination number were observed in  $^{27}\text{Al}$  NMR spectra; and the reaction ability of TEA, TNOA and DEAE is TEA > TNOA > DEAE for this Phillips catalyst system. In the study on initiation mechanism, the peaks assigned to Cr-alkylidene species in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra suggest an ethylene metathesis initiation mechanism during the induction period of ethylene polymerization.

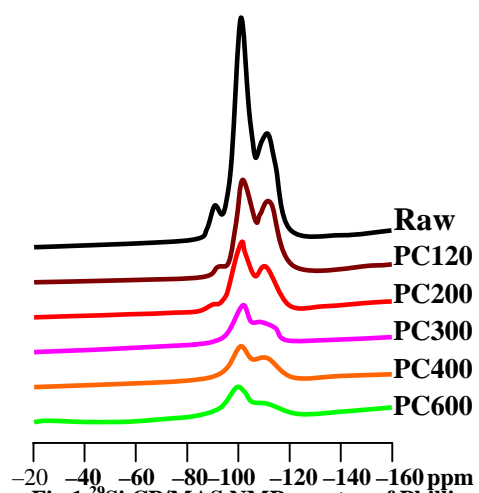


Fig.1  $^{29}\text{Si}$  CP/MAS NMR spectra of Phillips catalysts calcined under different temperature

Keyword: Phillips catalyst, organometallic cocatalyst, metathesis, ethylene polymerization