

# Novel SiO<sub>2</sub>-supported chromium catalyst bearing new organo-siloxane ligand for ethylene polymerization

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## Abstract

Nowadays, SiO<sub>2</sub>-supported Cr-based catalysts mainly including oxo chromium (Phillips catalyst) and silyl chromate (UCC catalyst) systems are still important industrial catalysts for ethylene polymerization. It was found that the addition of triphenylsilanol could transform Phillips catalyst into silyl chromate catalyst. In this work, a new chiral organo-silanol was synthesized and subsequently introduced to modify the Phillips catalysts in order to develop a new SiO<sub>2</sub>-support Cr-based catalyst with a chiral organo-siloxane ligand for ethylene polymerization. The new catalyst was characterized by X-ray photoelectron spectroscopy (XPS) and solid-state NMR methods. The new Cr-based catalysts with chiral organo-siloxane ligand presented as an active catalyst for ethylene polymerization, and their kinetic characteristic is found to be similar with that of calcined Phillips catalyst combined with TEA cocatalyst. It was very interesting to find the existence of short chain branches (SCBs) in these ethylene homo-polymers. The introduction of the new chiral organo-siloxane ligand was also found to produce polyethylene with bimodal molecular weight distribution and to enhance the amount of SCBs, which might be due to the steric and/or electronic effect of such chiral ligand, indicating a new method to improve the performance of Cr-based catalyst for polyethylene production.

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**Keywords:** Phillips catalyst; Ethylene polymerization; Chiral organo-siloxane ligand; Bimodal molecular weight distribution; Short chain branches (SCBs)

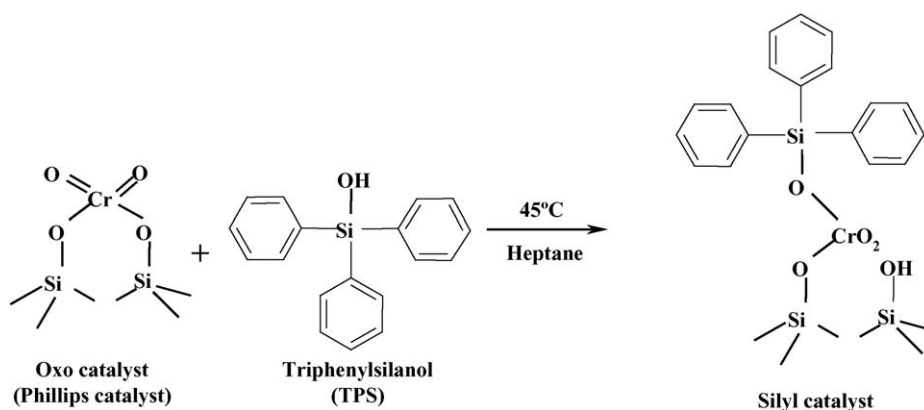
## 1. Introduction

Phillips CrO<sub>x</sub>/SiO<sub>2</sub> catalysts, patented in 1958 by Hogan and Banks, are still responsible for more than one-third of the worldwide commercial high-density polyethylene (HDPE) production. The most unique performance of Phillips catalyst is contributed to production of HDPE with ultra-broad molecular weight distribution and chain branches including short and long chain branches, which is especially applied for blow-molding process. Until now, most work of the chromium-based catalyst for polyolefin has been focused on Phillips catalyst, commonly referred as oxo chromium supported on silica with high surface area [1,2]. However, a number of organo-chromium systems like chromocene and organo-silyl chromate, which are mainly synthesized by chemisorption of organo-chromium on dehydrated silica support, also show high activity for ethylene polymerization [3–6]. Of the organo-

chrome-based systems, silyl chromate derived catalysts are used extensively for commercial PE production according to some specific performances of silyl chromate catalyst. In comparison, Phillips catalyst shows much higher productivity than silyl chromate catalyst; however, silyl chromate catalyst shows not only less activity but also prolonged induction period. However, silyl chromate catalyst can produce polyethylene with broader molecular weight distribution (MWD) on both high and low molecular weight ends meeting different market demanding.

Recently, Cann et al. [6] found that the Phillips catalyst can be transformed into the silyl chromate catalyst through introduction of silyl ligand from triphenylsilanol (TPS) as shown in Scheme 1 [6,7]. It was further confirmed that the polymerization performance observed with oxo chromium-based catalysts could be converted to that observed with silyl chromate type catalysts by the addition of TPS into the former. In our opinion, this report also indicates a general method for developing various new SiO<sub>2</sub>-supported Cr-based catalysts for olefin polymerization through modification of the Phillips catalyst using various organo-silanol compounds. Since the

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Scheme 1. Conversion of Phillips catalyst to silyl chromate catalyst.

catalyst structures are similar in nature, it is also possible to synthesize another type silyl chromate catalyst by direct conversion of the chromium oxide catalyst through the introduction of a novel chiral organo-siloxane ligand. Such chiral organo-siloxane bonded on chromium site via an oxygen atom was expected to result in a novel Cr catalyst with some specific performances.

In this work, a new chiral organo-silanol species, methyl (1-naphthyl) phenylsilanol, was synthesized and subsequently used to react with calcined Phillips  $\text{CrO}_x/\text{SiO}_2$  catalyst in order to develop a novel  $\text{SiO}_2$ -supported Cr-based catalyst. The physico-chemical states of the new synthesized chromium catalyst were characterized by solid-state NMR and X-ray photoelectron spectroscopy (XPS) methods. The ethylene homo-polymerization was carried out using the new catalyst in the presence of triethylaluminum (TEA) cocatalyst. The microstructures of the obtained polymers were investigated by solution NMR method. A general method for developing new  $\text{SiO}_2$ -supported Cr-based catalyst with improved performance for ethylene polymerization has been demonstrated.

## 2. Experimental

### 2.1. Raw materials

$\alpha$ -Bromonaphthalene, sodium sulfate, lithium aluminum hydride, methanol, benzene, diethyl ether ( $\text{Et}_2\text{O}$ ) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co. Industries. Phenylmethyldimethoxysilane was obtained from Shin-Etsu Chemical. (–)-Menthol was obtained from Nacalai Tesque Inc. Solid potassium hydroxide, cyclohexane and pentane were purchased from Wako Pure Chemical Industries. Di-*n*-butyl ether was obtained from TCI. THF,  $\text{Et}_2\text{O}$ , hexane and benzene were purified by distillation after drying over sodium metal prior to use. Such materials were used for the preparation of the chiral organo-silanol compound.

Nitrogen of G3-grade (total impurity < 5 ppm) and pure air of G1-grade (total impurity < 1 ppm) were purchased from Uno Sanso Corp. Molecular sieves 4A and molecular sieves 13X, which were purchased from Wako Pure Chemical Industries Ltd., were used as moisture scavengers for gas purification. Q-

5 reactant catalyst (Aldrich) was used as oxygen scavenger for gas purification. A Phillips catalyst precursor (Crosfield ES370X donated from Asahi Kasei Corp.) with 1.0 wt.% of Cr loading (surface area: 280–350  $\text{m}^2/\text{g}$ , pore volume: 1.45  $\text{cm}^3/\text{g}$ ) was used for preparation of Phillips  $\text{CrO}_x/\text{SiO}_2$  catalysts.

### 2.2. Preparation of novel chiral organo-silanol compound

#### 2.2.1. Preparation of racemic $\alpha$ -naphthylphenylmethylmethoxysilane

The Grignard reagent was prepared from 0.10 mole of  $\alpha$ -bromonaphthalene in a solvent mixture containing benzene (100 ml), and tetrahydrofuran (100 ml). It is important to avoid the presence of  $\beta$ -bromonaphthalene in more than trace amounts. Substantial contamination by  $\beta$ -naphthylsilanes may cause great difficulty in the subsequent separation of diastereoisomers. And then the Grignard reagent was added dropwise to the solution of phenylmethyldimethoxysilane (0.10 mole, obtained from Shin-Etsu Chemical) in  $\text{Et}_2\text{O}$  (50 ml) for 1 h. This solution was stirred overnight at 55 °C and followed by treatment with cold aqueous ammonium chloride, washing with water, drying over sodium sulfate, and subsequent removal of solvents. Distillation gave 22.3 g (80% yield) of  $\alpha$ -naphthylphenylmethylmethoxysilane, b.p. 143–146 °C (0.15 mmHg) and m.p. 62.5–63.5 °C (after recrystallization from hexane).

#### 2.2.2. Preparation of diastereomeric $\alpha$ -naphthylphenylmethyl-(–)-menthoxysilanes

Distillation flask were placed 13.9 g (0.05 mole) of  $\alpha$ -naphthylphenylmethylmethoxysilane, 7.8 g (0.05 mole) of (–)-menthol, 0.093 g of solid potassium hydroxide, and 100 ml of toluene. The reaction mixture was maintained at 145–155 °C for 10 h, while the methanol–toluene azeotrope (69% methanol, b.p. 63.8 °C) was distilled through a fractionating column. After removal of the basic catalyst by passing the product through a short column of silica gel, fractional distillation gave a 90.5% yield (18.2 g) of the diastereomeric  $\alpha$ -naphthylphenylmethyl-(–)-menthoxysilane as a viscous syrup having b.p. 173–177 °C (0.07 mmHg). This material had an infrared spectrum virtually identical with that of the crystalline, separated diastereoisomers described below.

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