

POISONING OF ACTIVE SITES ON ZIEGLER-NATTA CATALYST FOR PROPYLENE POLYMERIZATION

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Abstract The effects of poisoning materials on catalytic activity and isospecificity of the supported Ziegler-Natta catalyst were investigated. A minor amount of simple structure of Lewis base, *i.e.*, methanol, acetone, ethyl acetate, was introduced into the catalyst slurry for partial poisoning catalytic active centers. It was found that the variations in deactivation power were in the order of methanol > acetone > ethyl acetate. The kinetic investigation *via* stopped-flow polymerization showed that poisoning compounds caused a decrease in activity through the reduction of the number of active sites whereas no effect on the degree of isotacticity was observed.

Keywords: Poisoning material; Ziegler-Natta catalyst; Stopped-flow propylene polymerization.

INTRODUCTION

Electron donor is a crucial component in the Ziegler-Natta heterogeneous catalytic system to achieve polymer with high activity and isotacticity^[1]. The function of such donors in the MgCl_2 -supported catalysts has been known to provide electronic and steric effects on active species. Its coordination on the catalyst surface in the surrounding of the active sites leads to a dramatic increase of the catalyst stereospecificity. A selective poisoning of nonstereospecific sites or transformation of aspecific sites to isospecific ones has been proposed by several authors^[2–5]. In general, the former leads to a lowering in the number of active centers while the latter can improve the propagation rate constant. We also have reported that this kinetic parameter of isospecific sites was several times higher than that of aspecific sites^[6, 7]. Thus, the coordination of the electron donors can be regarded to influence the catalyst activity on both the directions of activation and deactivation but the addition of electron donor often causes a decrease in overall productivity rather than provide the activity enhancement. However, up to now, these fundamental matters concerning the activation/deactivation behaviors of the active sites have not yet been fully elucidated and still open for discussion as a consequence of the complexities of the catalytic system. No detailed studies have so far been carried out to investigate the precise kinetic parameters relating to the number of the active sites and their chain propagation rate constants.

Recently, the stopped-flow technique has turned out to be one of the most powerful methods for studying the kinetic and stereospecific natures of the active sites on the heterogeneous Ziegler-Natta catalysts for propylene polymerization^[8]. Interestingly, polymerization reaction proceeded within an extremely short period (*ca.* 0.2 s) exhibits a quasi-living characteristic, where the states of the active sites are kept constant without time-dependent changes, and any side reactions including chain transfer and deactivation after the initiation of polymerization are negligible. Because of this outstanding advantage, direct information corresponding to the

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nature of active sites and polymerization mechanism can be obtained^[6, 9–11].

In the present study, a catalyst of type TiCl_4 /ethyl benzoate/ MgCl_2 was prepared via a chemical route by using magnesium ethoxide as a support precursor. The catalyst was pretreated with several chemically different poisoning materials such as alcohol, ketone and ester with the aim at deactivating active Ti species. Poisoning compounds with simple structure and small molecules were selected in order to directly clarify the mechanism of the site deactivation and in the mean time avoiding their steric effect, which may have a beneficial influence on generating isospecific sites or even transforming aspecific sites into isospecific ones. A precise kinetic study for the effect of the poisoning materials was conducted using the stopped-flow polymerization combined with gel permeation chromatography (GPC) analysis.

EXPERIMENTAL

Chemicals

Propylene of research grade (donated by Chisso Corp.) was used without further purification. Methanol, acetone and ethyl acetate were used as representatives of alcohol, ketone and ester, respectively, which have the least steric hindrance structure in order to minimize steric effects from the poisoning materials. Ethyl benzoate (EB) as an internal donor, and anhydrous grade of methanol, acetone and ethyl acetate as the poisoning materials (purchased from Wako Pure Chemical Industries Ltd.) were used after dehydration with molecular sieves. Anhydrous magnesium ethoxide ($\text{Mg}(\text{OEt})_2$), titanium tetrachloride (TiCl_4) (both donated by Toho Titanium Co. Ltd.), triisobutylaluminium (TIBA, donated by Tosoh Akzo Corp.) and nitrogen (purchased from Uno Sanso Co.) were used without further purification. Heptane and toluene as solvents were purified by passing through molecular sieves 13X column.

Catalyst Preparation

In the current study, a monoester-type catalyst TiCl_4 /EB/ MgCl_2 was prepared by a chemical reaction method without mechanical treatment (ball milling). TiCl_4 was reacted with a mixture of $\text{Mg}(\text{OEt})_2$ and EB in the following procedure: $\text{Mg}(\text{OEt})_2$ (40 g) and TiCl_4 (80 mL) in toluene (320 mL) were heated up to 90°C, mixed with EB (12 mL) and reacted at 90°C for 2 h. The mixture was washed with toluene and treated again with TiCl_4 (80 mL) in toluene (320 mL) at 90°C for 2 h. Finally, the catalyst obtained was washed with heptane for several times, and then used as heptane slurry. Ti content was 3 wt% determined by the titration method.

Slurry Propylene Polymerization

Slurry polymerization was conducted to obtain preliminary information for the deactivating effect of the poisoning materials. It was performed in a 300 mL round-bottom glass reactor equipped with a magnetic stirrer. The required amounts of heptane (200 mL) and catalyst (0.095 mmol) were added into the reactor and then heated up to 30°C along with saturation of propylene at atmospheric pressure. A desired amount of the poisoning materials was introduced into the reactor and reacted with the catalyst for 1 min followed by the injection of TIBA (Al/Ti molar ratio: 30) to start polymerization. After 10 min, the reaction was terminated by venting the reactor and by adding acidic ethanol. The product was washed with water for several times, and then evaporated and dried under vacuum at 60°C for 6 h.

Stopped-Flow Polymerization

The stopped-flow polymerization of propylene and determination of the kinetic parameters were carried out according to the method reported previously^[6, 8, 12–15]. The propylene polymerization was typically performed with catalyst (ca. 1.0 g) and TIBA (14 mmol, Al/Ti molar ratio: 30) in heptane at 30°C for 0.1, 0.15 and 0.18 s. The heptane slurry (100 mL) of the catalyst and a solution of TIBA in heptane (100 mL) saturated with propylene at 101.325 kPa were placed into two vessels. Methanol as a poisoning material was introduced into the catalyst vessel for 1 min before starting polymerization (poisoning material/Ti molar ratio = 0.1).

The propagation rate constant k_p and active sites concentration $[C^*]$ were determined according to the following equations^[15],

$$M_n = M_0 \cdot \frac{k_p \cdot [M] \cdot t}{1 + k_{tr} \cdot t} \quad (1)$$

$$Y = k_p \cdot [M] \cdot [C^*] \cdot t \quad (2)$$

Where M_n , M_0 , $[M]$, t , k_{tr} and Y are the number-average molecular weight of the polymer, the molecular weight of the monomer, monomer concentration, polymerization time, chain-transfer rate constant and polymer yield, respectively.

GPC Characterization

The molecular weight and molecular weight distribution of the polypropylene obtained in this study were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140°C using *o*-dichlorobenzene (ODCB) as a solvent.

¹³C-NMR Spectroscopy

¹³C-NMR spectra were recorded on a Varian Gemini 300 spectrometer at 120°C using 200 g/L solutions in 1,2,4-trichlorobenzene. 10 vol% benzene-*d*₆ was added for the internal lock, and hexamethyldisiloxane was used as the reference (internal chemical shift).

RESULTS AND DISCUSSION

In the first series of propylene polymerization, slurry polymerizations were conducted after a pretreatment of the catalyst with the poisoning materials for 1 min. The polymers obtained were characterized and the results are illustrated in Fig. 1, consisting of the yield and *mmmm* pentad. At a poisoning materials/Ti molar ratio of 0.1, the catalyst activity decreased substantially in the following order: ethyl acetate > acetone > methanol, while there was no significant change in the *mmmm* pentad. The results obviously demonstrated that the catalytic activity was greatly influenced by the chemical nature of the poisoning materials, and that all the materials independently poisoned the active sites regardless of their stereoregulating ability.

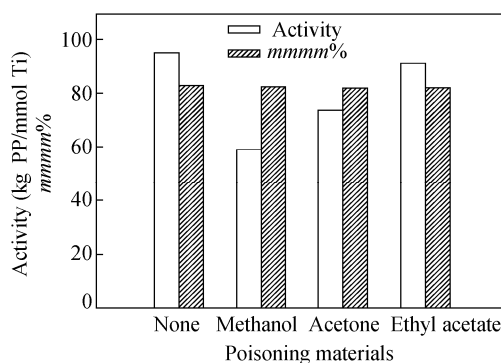


Fig. 1 Characterization of polypropylene obtained with different poisoning materials
Slurry propylene polymerization was carried out with TIBA (Al/Ti = 30) in heptane at 30°C after the pretreatment of the catalyst with the poisoning materials for 1 min (poisoning material/Ti = 0.1).

In the case of methanol, it is generally accepted that TiCl_4 is readily reacted with alcohol to produce alkoxide complexes inactive for propylene polymerization^[16] and HCl. In consequence, HCl must react with TIBA to reduce its activation power and the titanium chloride alkoxides produced on the catalyst surface might have some negative effects on the catalyst activity^[16]. In the case of ethyl acetate, the donor likely trend to coordinate on the MgCl_2 supports though their oxygen atom. Therefore, the catalyst activity was found to have little effect. In contrast, acetone might interact with the catalyst surface in a similar fashion as ethyl acetate while

it could further react with the Ti-alkyl or Ti-polymer to form bulky alkoxy-Ti chlorides^[17] resulted in an apparent decrease in catalytic activity.

In the second series of polymerization, kinetic studies were carried out using a combination of the stopped-flow technique and GPC analysis with the aim to quantify the effect of the poisoning materials in terms of the number of the active sites and the chain propagation rate constant. Similar to the slurry polymerization, methanol was chosen to poison the catalysts for 1 min before starting the polymerization owing to its prominent deactivation effect, which supposed to exhibit the clear evidence of active site destruction. Figure 2 represents the dependence of the polymer yields on the polymerization time in the presence and absence of methanol. The linear correlation was observed within 0.2 s indicating that the catalyst possessed a constant activity without deactivation and late activation even after adding methanol. This behavior suggested that the reaction between methanol and the catalyst was completed within 1 min pretreatment. From Fig. 3, the two molecular weights were proportional to the polymerization time. This appeared to confirm a quasi-living nature of the polymerization with or without methanol. Furthermore, the molecular weight was unchanged after the pretreatment by methanol.

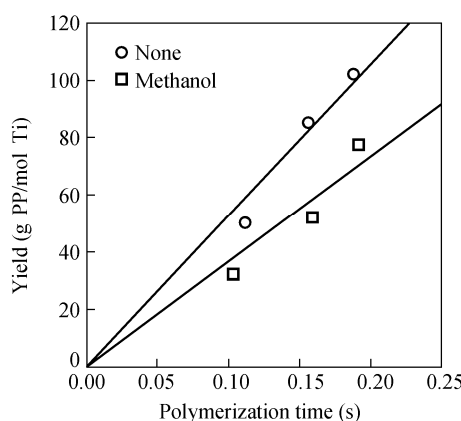


Fig. 2 The relationship between polymer yield and polymerization time

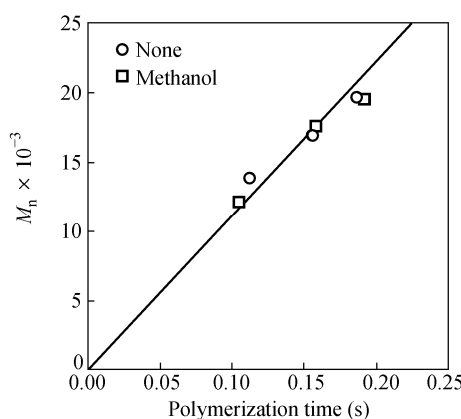


Fig. 3 Dependence of number-average molecular weight (M_n) on polymerization time

From the kinetic parameters as reported in Table 1, the value of k_p was hardly changed while the number of $[C^*]$ drastically decreased from 0.40 mol% to 0.28 mol%, which was accounted for 30% reduction comparing to the reference polymerization. It is well recognized that heterogeneous Ziegler-Natta catalysts contain a great variety of active sites and the chain propagation rate constant of different types of active sites significantly increases as the isospecificity of the active sites increases^[18, 19]. In this regard, the value of k_p could be changed

only in the case that there was some selective poisoning on the different types of the active sites. For example, a selective poisoning of aspecific sites or isospecific sites must lead to higher or lower k_p , respectively. In this sense, the constant k_p was indicative of a non-selective poisoning, which was supported by the nearly constant *mmmm* pentad in the slurry polymerization in Fig. 1. With the stopped-flow polymerization, we could attribute the poisoning effect of methanol on the catalyst performance only to the decrease of the number of active centers.

Table 1. Kinetic parameters for propylene polymerization^a

Poisoning material	k_p (l/(mol·s)) ^b	$[C^*]$ (mol%) ^b
None	4800	0.40
Methanol	4600	0.28

^a Stopped-flow propylene polymerization was performed with TIBA (Al/Ti = 30) in heptane at 30°C after the pretreatment of the catalyst with methanol for 1 min (methanol/Ti = 0.1);

^b k_p and $[C^*]$ were calculated based on Eqs. (1) and (2).

Finally, the stopped-flow result suggested that the active site concentration was quite sensitive to the methanol. The reaction taking place at methanol/Ti molar ratio of 0.1 would result in the reduction of the activity by 10% if the reaction had undergone stoichiometrically ($\text{CH}_3\text{OH} + \text{TiCl}_4 \rightarrow \text{inert TiCl}_3\text{OCH}_3 + \text{HCl}$). However, the actual observation of the decrease in catalytic activity reached as large as 30%. This might be explained by the spatial distribution of the TiCl_4 species. It is well known that the heterogeneous Ziegler-Natta catalyst particles are composed of numerous aggregated primary particles (5–8 μm)^[20]. In the pretreatment, TiCl_4 species exposed on the outermost surface of the secondary particles should be easily accessed and therefore dominantly killed by methanol rather than the TiCl_4 species hidden inside. Namely, the deactivated TiCl_4 species on the outermost surface of the secondary particles must largely exceed 10%. Furthermore, the polymers conducted by the stopped-flow method should originate from such the outermost TiCl_4 species, since the short-time polymerization hardly causes the breakage of the secondary particles as proved by the absence of any further activation. In this regard, the number of the active centers derived from the stopped-flow method is directly related to the activated outermost TiCl_4 on the surface of the secondary particles, which were dominantly damaged by the methanol pretreatment.

CONCLUSIONS

We examined the effects of poisoning materials on the catalytic performances of a MgCl_2 -based Ziegler-Natta catalyst. Methanol, acetone, and ethyl acetate were used as the least bulky structure poisoning agents. The polymerization results showed that methanol exhibited the strongest deactivation power among three types of employed poisoning compounds. This was attributed to its highest reactivity to form titanium chloride alkoxide species, which was inactive for polymerization. A precise kinetic study with the stopped-flow method for the effect of the methanol pretreatment revealed that the catalytic reduction came mainly from the decrease of the active site concentration. The constant of the propagation rate constant along with consistency in the degree of isotacticity reflected the unselective poisoning on the catalytic sites.

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