

TiCl₄ hybridization with modified Ni(II) α -diimine catalyst complex for ethylene polymerization

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Abstract—A hybrid Ni(II) α -diimine and conventional TiCl₄-based Ziegler-Natta catalyst was synthesized to study the effect of hybridization on the properties of the produced polymer. As the Ti/Ni ratio increased, the catalytic activity decreased due to the steric hindrance of the Ni site, but the deactivation was not severe. The molecular weight distribution showed bimodality in the higher Ti/Ni ratio due to the combined effects of the polymerization of low molecular weight polymers from the Ti-based active sites and the increase in polymer molecular weight from the Ni-based active sites. The polydispersity index (PDI) of the produced PE increased as high as 76, which was 22 times higher than that of the PE polymerized by the pure Ni(II) α -diimine catalyst. The melting points of PEs also increased as the Ti/Ni ratio increased due to the contribution of the TiCl₄ catalyst.

Key words: Ni(II) α -Diimine, Ziegler-Natta Catalyst, Ethylene, Polymerization, Hybridization

INTRODUCTION

Ni(II) α -diimine-based catalysts with bis(imino)pyridyl ligands developed by Brookhart et al. have been widely studied as promising alternatives to both Ziegler-Natta and metallocene catalysts for olefin polymerization due to their tunable polymer properties by simple modification of the ligand structures [1-3]. For instance, these catalysts can produce controlled short-chain branched polyethylene (PE) as well as high molecular weight PE [4]. However, one major drawback for commercialization of these catalysts is the rapid and quantitative deactivation of Ni(II) species during polymerization, and many attempts have been made to improve the stability and control the polymer properties by modifying the ligands through such processes as the incorporation of bidentate diimine, salicyl imine, iminocarboxamide or tridentate 2,6-bis(imino)-pyridyl [5-9]. Recently, we have synthesized a series of very stable Ni(II) α -diimine catalysts with remote push-pull substituents and reported their performance related to the steric bulkiness and electronic environment [10-12]. The bulky ligands in the Ni(II) α -diimine catalysts preferred insertion to chain transfer, which resulted in high molecular weight PE. On the other hand, the less sterically hindered ligands increased the chain-transfer rate, which resulted in low molecular weight PE.

In this paper, we further modified the Ni(II) α -diimine-based catalysts with titanium tetrachloride (TiCl₄) to control the molecular weight distribution (MWD) of PE. The effects of the Ti/Ni mole ratio were also investigated in view of polymerization activity and polymer properties. We believe that the hybridization of new and multi-functional Ni(II) α -diimine-based catalysts with a conventional TiCl₄-based Ziegler-Natta type catalyst, which is widely used

in industry, can promote further applications of the late transition metal-based catalysts [13].

MATERIALS AND METHODS

1. Materials and Equipment

All reactions were performed using a standard glove box system under a purified argon atmosphere. Toluene (Duksan Chem) was purified by distillation over sodium metal. Methylaluminoxane (MAO) was purchased from Albermal (4.4 wt% Al in toluene), and all the other reagents used in this study were purchased from Aldrich Chemical and used without further purification.

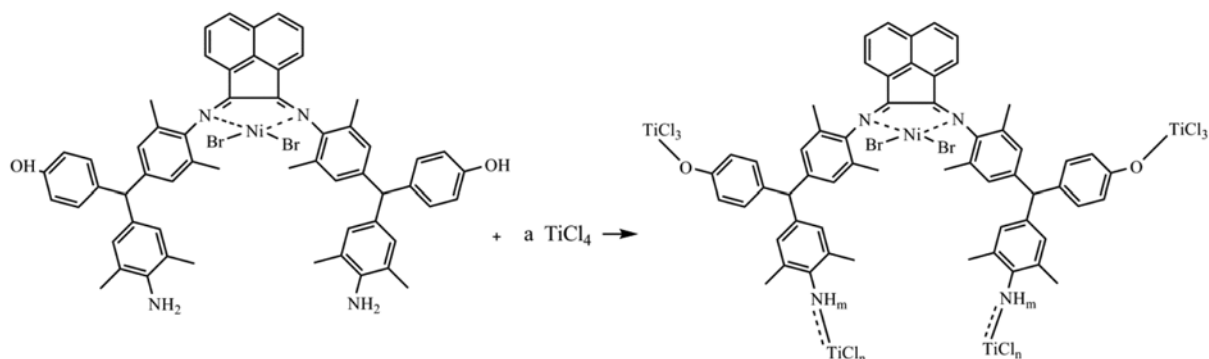
The molecular weight (MW) and PDI were determined by gel permeation chromatography (GPC, Waters GPC V2000) in 1,2,4-trichlorobenzene after standard calibration. The melting point (T_m) was measured with a differential scanning calorimeter (DSC, TA instrument Q20) with a 10 °C/min scan rate.

2. Synthesis of Catalysts

The overall procedure for the catalyst synthesis is shown in Scheme 1 [14,15]. All ligand precursors were prepared based on the previous reports with proper modifications [16,17]. The bidentate ligands, prepared by the Schiff-base condensation of two equivalents of the desired 2,6-dialkyl substituted anilines with acenaphthenequinone, were dissolved into dichloromethane, followed by the addition of 1 : 1 equivalent of (DME)NiBr₂ (DME=dimethoxyethane) and were stirred overnight at 30 °C. After the complete dissolution of the (DME)NiBr₂, the solution was precipitated and then titrated in ether. The final product was dried under vacuum at 60 °C after filtering and washing. Hybrid catalysts were prepared in-situ before the polymerization reaction. Toluene (80 mL) and the calculated amounts of Ni(II) α -diimine and TiCl₄ were added to the glass reactor, followed by stirring for 30 min at 50 °C. Before the polymerization, the reactor was vented to remove gaseous byproducts.

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Scheme 1. Synthesis of a hybrid Ni(II) α -diimine and conventional TiCl_4 -based Ziegler-Natta catalyst.

3. Polymerization

Predetermined amounts of toluene, catalyst and MAO were charged into the reactor in the glove box to avoid oxygen contamination. The polymerization was carried out in a 12 oz. glass reactor equipped with a two-blade folding impeller for 60 min under a constant ethylene pressure and temperature of 2.65 bar and 30 °C, respectively. The final product was washed with an excess amount of 5% HCl/methanol solution, followed by drying in a vacuum oven for 24 hrs at 50 °C.

RESULTS AND DISCUSSION

1. Selection of Co-catalyst for the Hybrid Catalyst

The co-catalysts, i.e., alkylating agents, have significant effects on the ethylene polymerization reactions for both TiCl_4 and Ni(II) α -diimine catalysts especially in view of catalytic activity. Even though the effect of co-catalysts still remains unclear, it has been reported that the type of alkyl aluminum or aluminoxane could significantly affect the MW and MWD of polymers [18,19].

Recently, we reported that the catalytic activity of the late transition metal catalysts in combination with ethylaluminum sesquichloride (EAS) as a co-catalyst was better than that of any other alkyl aluminum for ethylene polymerizations because it generated more active sites [12,20]. In the meantime, the co-catalyst for hybrid catalysts should be selected by focusing on the activity of homogeneous TiCl_4 , as it showed one-order lower activity than that of Ni(II) α -diimine catalysts. As shown in Table 1, the homogeneous TiCl_4 catalyst with MAO showed a six times higher catalytic activity than that of TiCl_4 with EAS for ethylene polymerization. Even though TEA showed the highest activity with homogeneous TiCl_4 , only trace amounts of polymer were obtained when TEA was used with a hybrid catalyst due to its low activity toward Ni(II) α -diimine catalyst [12]. In this report, we selected MAO as a co-catalyst for the TiCl_4 /

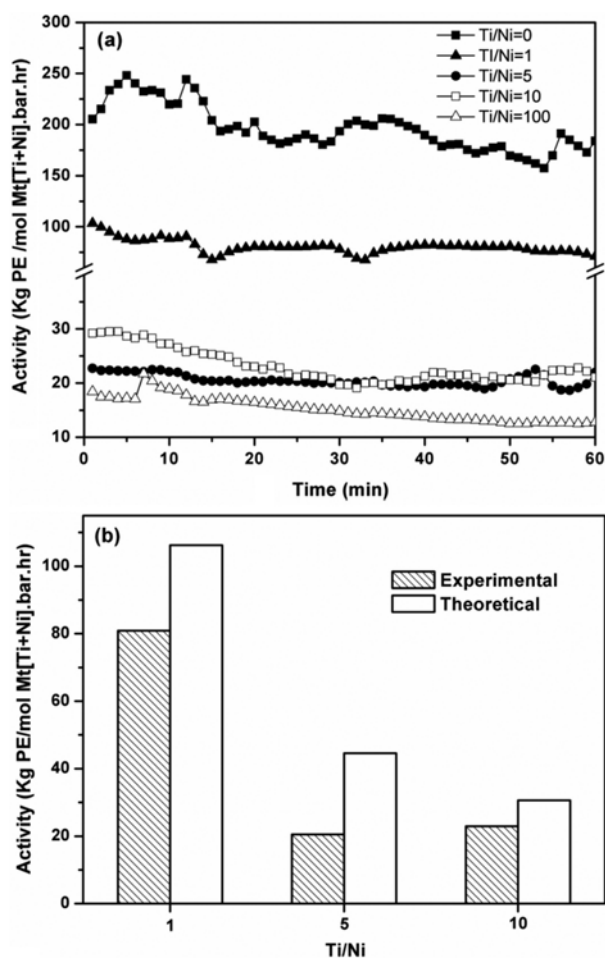


Fig. 1. (a) Activity profiles of ethylene polymerization catalyzed Ni(II) α -diimine/ TiCl_4 /MAO with various Ti/Ni ratios. (b) Comparison of theoretical and experimental activities.

Table 1. Catalytic activity of the homogeneous TiCl_4 catalyst for the ethylene polymerization with respect to the type of co-catalyst

Catalyst loading (μmol)			Co-catalyst	Mol ratio (Al/Ti)	Rp (* 10^{-4} g PE/mol Ti \cdot bar \cdot hr)	Yield (g)	T (°C)
Ni catalyst	Z-N catalyst	Total					
0	20	20	EAS	200	0.192	0.134	30
0	20	20	TEA	200	7.289	1.434	30
0	20	20	TEA	200	9.260	1.625	50
0	20	20	MAO	200	1.150	0.484	30

Table 2. The effect of Ni/Ti ratio on the catalytic activity of Ni(II) α -diimine/TiCl₄/MAO*

Ni diimine catalyst loading (μ mol)	Al/Ni*	Ti/Ni	Reaction time (min)	Yield (g)	Activity (Kg PE/mol Mt(Ti+Ni)·bar·hr)
5	300	0	60	2.60	196
5	300	1	60	2.14	80.8
5	300	5	60	1.63	20.5
5	300	10	60	3.35	22.9
5	300	100	60	8.11	15.1

*Polymerization conditions: co-catalyst=MAO, temperature=30 °C, P_{C₂H₄}=2.65 bar

Ni(II) α -diimine hybrid catalysts to balance the catalytic activities between the two catalysts.

2. The Effect of Ti/Ni Ratio on Ethylene Polymerization

The polymerization results of hybrid catalysts are shown in Fig. 1 and Table 2. The amount of Ni(II) α -diimine catalyst and the Al/Ni ratio were fixed to 5 μ mol and 300, respectively. As shown, there was no severe deactivation observed during the polymerization, but the catalytic activity decreased as the Ti/Ni ratio increased. To determine the activity change of each component in the hybrid catalyst, we calculated the theoretical activity of each component and compared them with experimental results by using Eq. (1). The catalytic activity of TiCl₄ alone was estimated at highly excess Ti conditions (Ti/Ni=100).

Activity_{th}

$$= \frac{(\text{mol of Ni}) \times (\text{Activity of Ni cat.}) + (\text{mol of Ti}) \times (\text{Activity of Ti cat.})}{(\text{mol of Ni} + \text{mol of Ti})} \quad (1)$$

As shown in Fig. 1(b), the experimental activity was 76% of the theoretical activity at Ti/Ni=1, 46% at Ti/Ni=5 and 75% at Ti/Ni=10. The initial decrease in experimental activity can be attributed to the increased steric hindrance of Ni(II) α -diimine caused by the bonded TiCl₄ [6]. As there are two moles of amine groups and two moles of hydroxyl groups in the Ni(II) α -diimine catalyst, four moles of TiCl₄ can react with them, which might explain the further decrease in experimental activity at Ti/Ni=5. The recovery of activity ratio at Ti/Ni=10 may be due to the contribution of large amounts of TiCl₄ compared to that in Ni(II) α -diimine catalysts.

3. The Effects of Ti/Ni Ratio on Polymer Properties

Molecular weight and PDI are shown in Fig. 2 and Table 3. The MW and MWD at relatively low Ti/Ni ratios (i.e., Ti/Ni=0 and Ti/Ni=1) were almost the same due to the low catalytic activity of the unsupported TiCl₄ catalyst [12]. The increase in weight average MW (\bar{M}_w) and z-average MW (\bar{M}_z) at Ti/Ni=1 can be attributed to the bulky substituent effect of the Ni(II) α -diimine catalyst [3,12]. Spe-

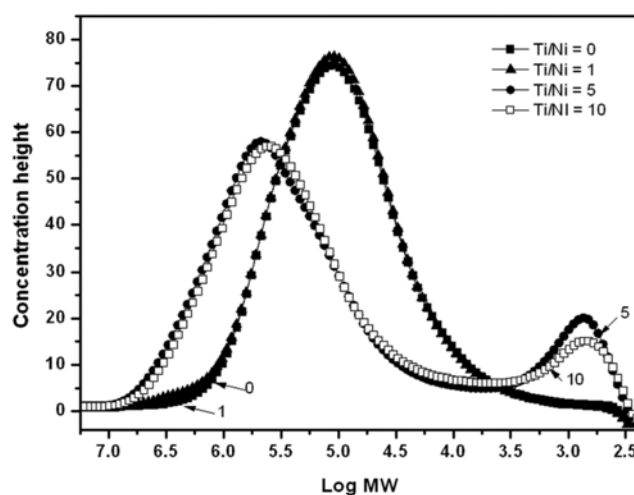


Fig. 2. GPC diagrams of polyethylene produced by Ni(II) α -diimine/TiCl₄/MAO hybrid catalyst with various Ti/Ni ratios.

cifically, the bulky groups in the axial position of the metal center caused a decrease in the chain transfer rate relative to the propagation rate, resulting in the formation of high molecular weight polymers. The reaction of TiCl₄ with amine groups in the ligand of the Ni catalyst also increased the bulkiness, which resulted in the production of high molecular weight PE. Another interesting observation was the changes in the molecular weight distribution of the produced PE. As the Ti/Ni ratio increased, the shape of the molecular weight distribution became bimodal due to the combined effects of i) production of low molecular weight polymers from the Ti sites, and ii) the further increase in polymer molecular weight from the sterically hindered Ni sites. The PDI increased 22-fold by using the hybrid catalyst, as shown in Table 3. Note that Al/Ti decreased as Ti/Ni increased, as we fixed the amount of Ni(II) α -diimine catalyst. As Badin reported, the lower Al/Ti ratio of homogeneous TiCl₄ catalysts at the higher Ti/Ni conditions caused the lower catalytic activ-

Table 3. The effect of Ni/Ti ratio on the polymer properties with Ni(II) α -diimine/TiCl₄ hybrid catalyst*

Ni diimine catalyst loading (μ mol)	Al/Ni	Ti/Ni	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	PDI	T _m (°C)
5	300	0	40,000	165,000	481,000	4.1	128.98
5	300	1	39,000	197,000	997,000	5.1	128.97
5	300	5	5,600	509,000	1,940,000	91	130.24
5	300	10	6,200	474,000	1,750,000	76	133.54
5	300	100	5,700	290,000	2,690,000	51	132.58

*Polymerization conditions: co-catalyst=MAO, temperature=30 °C, P_{C₂H₄}=2.65 bar

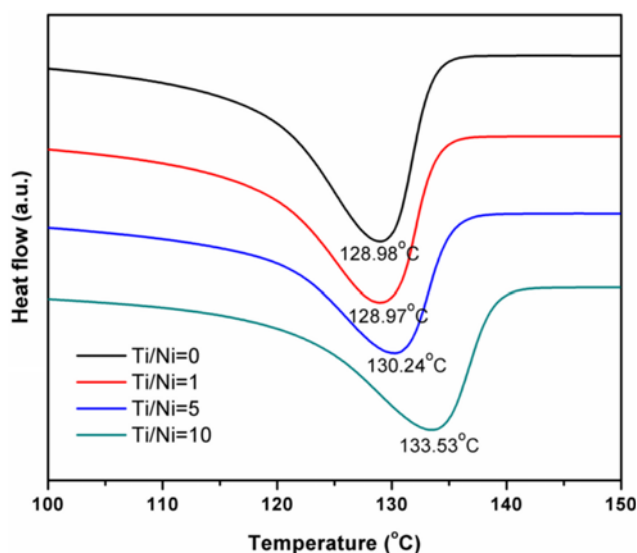


Fig. 3. DSC profiles of polyethylene produced by Ni(II) α -diimine/ TiCl_4 /MAO hybrid catalyst with various Ti/Ni ratios.

ity of TiCl_4 catalyst and production of the low molecular weight PE, which resulted in the formation of a low MW peak in the MWD, as shown in Fig. 2 [21].

The DSC thermograms and the melting points of each polymer are shown in Fig. 3 and Table 2. The melting points of the polymers did not change at $\text{Ti/Ni}=1$ compared to Ni(II) α -diimine catalyst alone ($\text{Ti/Ni}=0$); however, as the Ti/Ni increased, the melting points also increased and broadened. It is well known that PE polymerized by Ni(II) α -diimine catalysts exhibits a controlled level of short-chain branching, but PE produced by the TiCl_4 type Ziegler-Natta catalysts does not. The unique short-chain branching observed with Ni(II) α -diimine catalysts is proposed to occur via an alkyl chain isomerization process [1]. Firstly, β -hydride elimination yields a putative hydride olefin π -complex. Then, rotation of the π -coordinated olefin moiety about its coordination axis followed by reinsertion produces a secondary carbon unit and a branching point. The consecutive repetition of this process allows the metal center to migrate down the polymer chain, resulting in production of longer chain branches. The increase in melting point in this study shows the same trend as that of molecular weight distribution, which means that, as the Ti/Ni ratio increases, high melting point polymers increase due to the contribution of TiCl_4 , which results in increased melting points and a broadened melting range.

CONCLUSIONS

Ethylene polymerization was performed using a hybrid Ni(II) α -diimine and conventional TiCl_4 -based Ziegler-Natta type catalyst. As the Ti/Ni ratio increased, a certain degree of catalytic activity loss was observed due to the steric hindrance of the Ni site, but no severe deactivations were observed. As the Ti/Ni ratio increased, the shape of the molecular weight distribution showed bimodality

due to the combined effects of the polymerization of low molecular weight polymers from the Ti sites and the further increase of polymer molecular weight from the sterically hindered Ni sites. The PDI of the produced PE increased as high as 76, which was 22 times higher than that of the PE polymerized by the pure Ni(II) α -diimine catalyst. Melting points of PEs also increased as the Ti/Ni ratio increased due to the contribution of the TiCl_4 catalysts.

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