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Supported hybrid early and late transition metal catalysts for the synthesis of polyethylene with tailored molecular weight and chemical composition distributions

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Supported hybrid catalysts using metallocenes and a nickel diimine catalyst were synthesized and used for ethylene slurry polymerization and ethylene/1-hexene copolymerization. Two types of metallocenes, together with a nickel diimine catalyst were supported onto SiO_2 through chemical bonding, and a borate compound was physisorbed for the activation of the catalysts. These supported hybrid catalysts had high catalyst activities and made free-flowing polymer particles. The chemical composition distribution, molecular weight averages and distributions of resultant polymers were controlled by catalyst structure and polymerization conditions such as reaction temperature and the use of α-olefin. According to GPC-IR, ^{13}C NMR and CEF characterization results of some polymers, more 1-hexene was incorporated in the high molecular weight region, short chain branches were generated by the chain walking mechanism in low molecular weight region. The morphologies of the resulting particles were investigated by SEM.

1. Introduction

Metallocenes have been considered as a possible replacement for Ziegler–Natta catalysts for production of linear low-density polyethylene (LLDPE) due to their remarkable α-olefin reactivity. Although LLDPE made with metallocenes offers superior mechanical properties such as excellent toughness, impact strength and clarity, it suffers from poor processability. To overcome this disadvantage, LLDPE may be produced with a bimodal molecular weight distribution (MWD). The advantages of bimodal resins are in the control of the chemical composition distribution (CCD) as well as the MWD. The presence of more short chain branches (SCB) in the higher molecular weight region improves the strength properties and reduces brittleness. This fraction has been linked to the formation of tie molecules between the crystalline lamellae, resulting in improved stress crack resistance, for instance. For the typical industrial production of LLDPE with tailored MWD and SCB distribution (SCBD), serial or cascade reactors are involved, where each reactor produces a polymer with desired properties controlled by the polymerization conditions [1–3].

Alternatively, in order to take advantage of commonly available polymerization plant infrastructure using a single reactor, the use of hybrid catalyst systems, where each catalyst makes a polymer with its own unique properties, has considerable value [3,4]. Obviously, hybrid metallocene catalysts can be selected to make bimodal MWD resins. Because metallocene catalysts produce polymers with narrow MWD and constant SCB averages across the MWD, combining a metallocene that makes high molecular weight polymer with higher co-monomer content and another metallocene that produces low molecular weight polymer with low co-monomer content is an evident way to produce a bimodal product. For example, $Me_2Si(C_5Me_4)(N\text{-}t\text{Bu})TiCl_2$ (a constrained geometry catalyst, CGC) has an open structure around the active sites, resulting in olefin copolymer production with high α-olefin content. On the other hand, $(n\text{BuCp})_2ZrCl_2$ makes low molecular polymer with low α-olefin content [3]. Therefore, a hybrid catalyst using CGC/$(n\text{BuCp})_2ZrCl_2$ could make polyethylene with bimodal MWD and reverse co-monomer incorporation. Nevertheless, “optimal” hybrid catalysts are hard to accomplish because each catalyst has its own characteristics, such as life time, activity, co-monomer response, and hydrogen sensitivity. Thus, chemical and kinetic compatibilities must be taken into account to create a well-balanced catalyst useful for industrial plant operation.

Olefin polymerization processes in slurry and gas-phase reactors require the use of solid-supported catalysts. The catalyst should not leach from the support during polymerization, and the catalyst structure, activity, and co-monomer reactivity must be maintained after supporting. For continuous operation of processes with single-site catalysts, this requires fixing soluble catalysts such as early and late

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transition metal complexes onto insoluble carriers [5–9]. Physical-adsorption supporting methods are commonly used for metallocene supporting due to its simplicity [10]. However, metallocenes supported through physical-adsorption can be extracted by diluents during polymerization in slurry reactors. These solubilized sites make polymer particles with poor morphology and may form or cause polymer chunks that lead reactor fouling. In addition, the catalyst active sites may react with impurities on the inorganic carrier or hydroxyl groups on the SiO_2-support surface, producing inactive sites and significantly decreasing catalyst activity. Alternatively, chemical supporting methods create covalent chemical bonds between the catalyst and the support [11–13]. In this method, a functionalized metallocene is synthesized first and then the functional groups on the metallocene ligand are allowed to react with other functional groups present on the support surface. Chemically tethered groups, which are strongly connected between metallocene and support, can reduce catalyst leaching from the support surface, thus minimizing reactor fouling.

Dubois et al. used SiO_2 surface hydroxyl groups to anchor functionalized metallocene complexes [13]. Unfortunately, side reactions may also take place during the supporting process (for example, between other metallocene ligands such as chlorine and SiO_2), forming inactive sites and other byproducts, such as water and hydrochloride acid, that act as catalyst poisons. Repsol introduced a metallocene supporting method where siloxane groups on the SiO_2 surface react with functional groups on the metallocene ligands to create a supported metallocene [14]. This method is attractive because byproducts such as water are not formed during catalyst supporting. Introducing a spacer group between the support surface and the catalyst is considered by some researchers the best method to improve catalyst activity. The spacer group reduces not only electronic, but also steric effects between support and catalyst [15]. LG Chem developed hybrid SiO_2-supported metallocene systems, where a metallocene with functionalized spacer groups led to high catalyst activity and to the production of bimodal ethylene copolymers with controlled microstructures [16]. For supported late transition metal catalysts, SiO_2-supported nickel diimine catalysts, where the catalyst sites had been covalently bonded to the support, are also very active and produce polyethylenes having SCBs without the use of any co-monomer due to the chain walking mechanism. The use of internal borate activators with these systems helps reducing reactor fouling, and obtains spherical polymer particles with good morphology [17].

In this work, we report the synthesis of supported hybrid early and late transition metal catalysts to polymerize ethylene in a slurry reactor. The metallocene is supported on SiO_2 to make high molecular weight polymer with controlled SCBs by addition of 1-hexene. The nickel diimine catalyst is supported on the same SiO_2-support to produce low molecular weight polymer with controllable SCB frequency by the chain walking mechanism. These hybrid catalysts can make polymers with precisely tailored SCBs frequencies, especially inverse SCBDs, as well as broad MWD. The resultant polyethylene particles were spherical and free-flowing, ideally suited for slurry and gas-phase processes. The polymer microstructure was analyzed by high-temperature gel permeation chromatography with infrared spectroscopy detector (GPC-IR), crystallization elution fractionation (CEF), and nuclear magnetic resonance (^{13}C NMR). The polymer particle morphology was characterized by scanning electron microscopy (SEM).

2. Experimental

2.1. Materials

All operations were carried out under high purity nitrogen (99.999%, Praxair) using standard Schlenk techniques or inside a glove box (Vacuum Atmosphere Company, Nexus). Polymer grade ethylene (99.9%, Praxair) and nitrogen were purified by passing through columns packed with R3-11 copper catalyst, activated alumina and 3A/4A mixed molecular sieves. Materials for bis(4-amino-2,3,5,6-tetramethylimino)acenaphtene nickel(II) dibromide (named **N**) synthesis [18] were purchased from Aldrich and used without further purification. The metallocenes, Bis(6-t-butoxyhexylcyclopentadienylide)zirconium dichloride (named **Z**), and methyl (6-t-Butoxyhexyl)silyl(η^5-tetramethylcyclopentadienyl)(t-butylamido)titanium dichloride (named **T**) were provided by LG Chem [16]. The trimethyl aluminums (TMA, 2 M in toluene and in hexane) were purchased from Aldrich. SiO_2 (Sylopol 948, Grace Davison: average particle size 55 μm, total volatiles 10.0%, surface area 280–355 m^2/g, pore volume 1.55 cc/g) was used as the catalyst support after drying under vacuum overnight at 150 °C. Solvents for catalyst synthesis and polymerization were purified by passing through columns packed with activated alumina and molecular sieves (Zeolum Type F-9, Tosoh Co.). The borate activator, dimethylanilium tetrakis(pentafluorophenyl)borate (named **B**) was purchased from Strem Chemicals. The structure of the used catalysts and the borate activator are shown in Fig. 1.

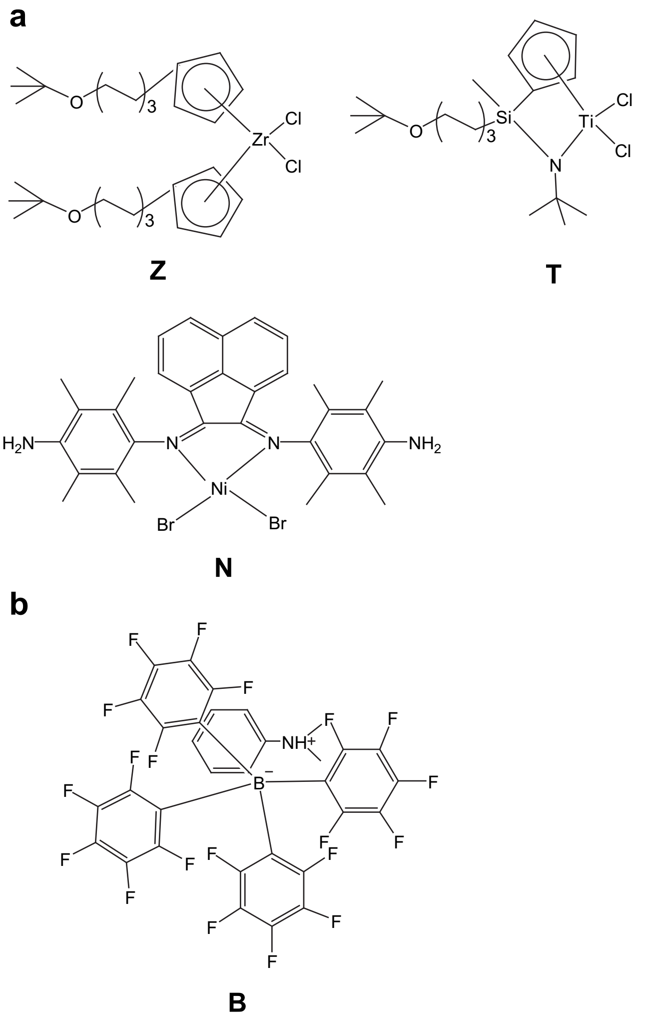

Fig. 1. a) Catalysts: Bis(6-t-butoxyhexylcyclopentadienylide)zirconium dichloride (**Z**), methyl(6-t-Butoxyhexyl)silyl(η^5-tetramethylcyclopentadienyl)(t-butylamido)titanium dichloride (**T**), and bis(4-amino-2,3,5,6-tetramethylimino)acenaphtene nickel(II) dibromide (**N**); and b) Activator: dimethylanilium tetrakis(pentafluorophenyl)borate (**B**).