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High performance gas-phase ethylene polymerization metallocene catalyst investigation in a pilot-plant fluidized bed reactor (1) experimental analysis

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ABSTRACT

This work aims to explore the scaling up process of lab developed heterogeneous metallocene catalyst in a pilot-plant scale fluidized bed reactor in comparison of benchmark catalyst producing polyethylene. The catalyst performance has been evaluated through copolymerization behaviors and polymerization kinetics. The produced polymers are analyzed in revealing the scale up effect of the catalyst. It was found that the catalyst particle size distribution shows very similar size distribution compared to the industrial catalyst and good particle morphology, which will benefit the gas phase fluidized bed operation. Compared to the benchmark HP-100, PME-18 shows better catalytic parameters in the ethylene/1-hexene polymerization behavior and reaction kinetics. The final product demonstrates very similar particle size distribution and polymer properties, which will obviously influence the product quality and production state.

1. Introduction

Heterogeneous catalyst systems provide numerous advantages on the polyolefin production, especially for better size and morphology controlling, where catalyst active centers are supported on the inorganic matrix [1]. The most widely commercialized two industrial heterogeneous polyolefin catalytic systems are Ziegler-Natta catalyst and Phillips catalyst, which have been intensively explored in co-catalyst, multi-active sites nature, polymerization process, polymer properties and commercialization [2,3], but the polymer structures can be adjusted only to a limited degree. Metallocene catalysts own one type of active site and produce polymers with much narrower molecular weight distribution (MWD), herein polymer structure can be easily controlled [4]. Meanwhile, in industrial polyolefin production, the heterogeneous catalyst will be conveniently expanded to the existing production process or the traditional catalysts.

The metallocene catalysts have been applied to a powdery and insoluble substrate, and the most widely used supports are inorganic solids [5]. There are three methods for the metallocene catalyst heterogenization [4,6,7]: direct heterogenization (physisorption or chemisorption onto support), the species covalent bonding to the support and adsorption/simultaneous activation of the metallocene onto the support (indirect way). The third method makes the polymer own the properties similar to those produced by the homogeneous catalyst. Each metallocene on the support generates an active center and starts a polymer chain growth. Because active sites on the surface of each catalyst grain are identical, all polymer chains grow uniformly leading to the narrow MWDs polymers. In that respect, supported metallocene catalyst commercialization is very essential for new polyolefin material research and development.

As three of mainly applied industrial polyolefin production processes, gas phase polymerization holds the distinguishing features, no liquid phase involving in the reaction system, reaction occurring at the interface between the solid catalyst and the polymer matrix. Furthermore, gas phase processes can reduce the construction costs up to 30% and operating costs of 35% than the liquid slurry and solution production processes [8,9]. Fluidized bed reactors are hereby used in gas-phase polyolefin industry due to their huge potential capability in moving out the chemical reaction heat and uniformly particle mixing behaviors [10,11]. A large number of publications increasingly appeared

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in literatures dealing with the metallocene catalyst development. Though metallocenes have been known since 1951, it was not widely studied until the work of Kaminsky, Sinn and coworkers in 1970s when lots of potential metallocene catalyst were developed and realized [12,13], the critical discovery was the dramatic increase of the catalytic activity resulting from the use of methylaluminoxanes(MAO). However, the commercial use of metallocene catalyst began in the early of 1990s. ExxonMobil Chemical Company developed single-site metallocene catalysts (e.g. XCAT series catalysts) and successfully applied in Univation Company UNIPOL™ gas-phase polyethylene (PE) process, which provided an environmentally friendly and low-pressure process and also created platform for metallocene technology. Since then, the metallocene catalyst commercialization has made a great progress, especially in new metallocene catalyst development and expanded to the specific applications, such as special film and medium-density PE. When a new catalyst comes to commercialization phase, the earliest stage catalyst research includes structure design, lab synthesis, catalyst/polymer characterization, reaction kinetics and polymer capacity testing, which is such that there is limited capability to extrapolate performance-scoping data to evaluate the catalyst performance. When moving to development stage, the performance studies go to pilot plant reactor for trial run. It enables fine-tuning of the catalyst structure and formulation, large scale testing of prototype products and process assessment of catalyst responses to scale up factors, such as residence time distribution (RTD) and operation conditions, as well as product particle morphology and process transitioning. Polymer morphology is closely related to the morphology of the original catalyst particle, both in terms of shape and porosity. In addition, the process conditions have an especially important effect on particle morphology during the initial stages of polymerization.

Although fluidized bed reactors (FBRs) were intensively investigated in the open publications from the condensed mode, modeling and simulation, and operation condition, the pilot-plant FBR owns the limited research due to more complicated structures and chemical engineering principles. The pilot-plant reactor experiment plays a critical role in the process from lab formulation screening and commercial production in chemical plant. Shamiri et al. analyzed the propylene polymerization in a pilot-scale FBR through experiment and modeling simulation. A two-phase model was established and validated with the pilot-plant polymerization data, and the reactor hydrodynamics was integrated with polymerization kinetics model to explore the reactor performance and polypropylene property. The comprehensive model can be used to predict the temperature, monomer concentration, and polypropylene production rate [14]. Che et al. explored a pilot-plant FBR temperature profile along the radial/axial direction and reactor hydrodynamics under the ethylene polymerization, the PE particle size distributions (PSDs) and flow mode have been presented [10,11,15]. The related work can be helpful in guiding the scale up of new catalysts; however, the Ziegler-Natta catalysts were only used in the series of studies.

Lanzhou Petrochemical Research Center (LPRC), a branch of the Petrochemical Research Institute of PetroChina Company, has developed series of novel supported metallocene catalysts, such as PME-18 for high performance PE production. The laboratory-scale catalyst experiment and polymer performance shows very positive results, especially in catalyst/co-catalyst evaluation, active center immobilization and the process optimization. More than fifty patents have been issued in the area of new catalyst formulation, MAO investigation and innovation, catalyst support silicon research and commercialization, and so on. How to commercialize novel catalyst plays an important role in the polyolefin industry. Unfortunately, there are no published data for the heterogeneous metallocene catalyst scaling up in pilot-plant fluidized bed reactor. This work aims to investigate a novel heterogeneous metallocene catalyst scale up process in a pilot-plant reactor and the catalyst performance and morphology have been explored. The produced polymer particles also have been studied to evaluate the scaling up process and operation stability.

2. Experimental section

2.1. Raw materials

In this pilot-plant trial run, the raw materials include the monomers (ethylene and 1-hexene), hydrogen and nitrogen. The below table lists the specification of raw materials' composition and purity (Table 1). Because it is a pilot-plant reactor trial run, ethylene and 1-hexene are both polymerization grade, which can be easily moved forward to the manufacturing production when all of the specifications meet the final product production requirement.

2.2. Catalyst preparation

Supported metallocene catalyst enables the producing polymer powders with good morphology and high bulk density. To explore the novel catalyst, the benchmark catalyst, HP-100 (Univation Technology), has been used to compare the catalyst and polymer properties. The heterogeneous new catalysts (PME-18) were prepared and produced by LPRC and shipped to Daqing Petrochemical Research Center (DPRC), where the gas-phase pilot-plant scale FBR was equipped and installed. PME-18 catalyst combines the inherent advantages of homogeneous metallocene catalyst (high activity and PE structure controlling) with the contribution of support (good PE particle morphology, high bulk density powder, and gas phase operation). Catalyst preparation methodology is of great commercial interest, because it can strongly affect the catalyst activity/kinetics/morphology and polymer properties, such as the support type and treatment method, immobilization approach.

Supported metallocene catalyst can be described by the following schematic including macroparticles (macro scale) and microparticles (micro-scale) [16]. In industrial production, it requires the precisely control of the morphology along the polymerization process to avoid the reactor fouling.

2.3. Pilot-plant FBR experimental system

Fig. 1 presented a simplified gas phase ethylene polymerization process schematic of the pilot-plant FBR, which is similar to the UNIPOL gas phase process. Fresh monomer and co-monomer are fed into the unit where trace quantities of impurities are removed through a separate series of purifiers. After then, the raw materials are introduced into the reaction system, consisted of a body of FBR, a cycle gas compressor and cooler, and the product discharging tanks. The FBR is operated and run continuously, so the fresh raw materials and recycled stream (unreacted monomer and co-monomer) from the vent recovery system are fed continuously into the bed. The final product, PE, is drained from the bed body by the discharging tank and transported to a purge tank where unreacted monomer and dissolved hydrocarbons are stripped from the resin and back to the vent recovery system. The purged resin is sent to the pelleting system. The condensed components are returned directly to the reaction system and the light is used as a conveying gas to reduce nitrogen consumption. The solid and liquid additives are metered and sent to the pelleting system, where the resin and additives are well mixed, melted and pelleted. The polymer pellets are finically dried, cooled and sent to product blending and storage [17].

Table 1
The specification of raw materials in the pilot-plant FBR trial run.

Items	Ethylene	1-hexene	Hydrogen	Nitrogen	Unit
–	≥99	≥97	≥99	≥99	%
O_2	≤1	≤2	≤1	≤1	ppm
H_2O	≤1	≤2	≤1	≤1	ppm
CO	≤0.03	–	≤0.03	≤0.03	ppm
CO_2	≤0.03	–	≤0.03	≤0.03	ppm