Immobilized Polyolefin Catalysts: Organic Versus Inorganic Supports

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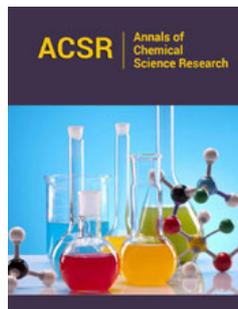
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Abstract

The polyolefins are the most widely used synthetic resin and greatly influence nearly every walks of life. About 70% polyolefin production is made from the immobilized polyolefin catalysts in gas-phase, slurry or bulk process equipment. Although the inorganic supports have been successfully industrialized, some inconvenient drawbacks calls for a new type of support to solve those problems. Porous organic polymers (POPs) have proved to be an excellent choice and have been considered as a versatile platform for the deployment of catalysts. The flexible design and synthesis approach provides POPs with high surface area and bulk density, excellent flowability, and various functionalities for desired catalysts performance. The POPs-based polyolefin catalysts obtained high polymerization activity and tailored molecule structure including molecular weight, molecular weight distribution, chemical composition distribution, stereoregularity, etc. due to the nature of the organic support.

Keywords: Porous organic polymers (POPs); Olefin polymerization; Metallocene catalyst; Ziegler-Natta catalyst

Introduction

Since the discovery of Ziegler-Natta and Phillips catalysts, polyolefins have witnessed continuous and tremendous growth of production and consumption combined with polymerization process innovation. By far, about 70% of total commercial polyolefins are based on the supported catalysts and inorganic supports have been widely used in the immobilized polyolefin catalysts. The supported high yield catalysts are compulsorily used in gas-phase, bulk or slurry phase industrial polyolefin equipment, to avoid reactor fouling by the particle morphology control of catalysts without further atactic removal and purification [1,2].

A great deal of researches focusing on inorganic supports such as silica gel, magnesium dichloride, molecular sieves, aluminium oxide, zeolite and clays have been reported [3-7] for olefin polymerization. The inorganic $MgCl_2$ and SiO_2 have been successfully applied in the conventional Ziegler-Natta or metallocene catalysts. The prepared polymers obtained excellent particle morphology and flowability by replication effect of the inorganic supports especially with sphere or granule shape, which is suitable for gas phase or slurry process. Furthermore, the inorganic supports typically tend to be highly porous with active sites dispersed more or less evenly throughout them, thus benefiting the diffusion of monomer(s) to the surface of the active sites around the supports and helping the immobilized Z-N catalysts or metallocene catalysts to achieve high polymerization activity.

Despite obvious physical advantage and the tremendous success, these inorganic supports based polyolefin catalysts undergo several deficiencies. The excess of surface acidic groups, such as the silanol or -SiOH on the silica surface, could cause catalyst deactivation and need

tedious pre-treatment before immobilization of active metal on their surface [8,9]. Due to inorganic residuals within the prepared polymer matrix during the process of catalysts fragmentation, the properties of the produced polyolefins could be harmed. For example, the mLLDPE film produced from a silica supported metallocene catalyst, more often than not, suffer from observable fisheyes which mainly caused by the inorganic SiO_2 impurities and the inhomogeneous insertion of comonomer (1-hexene) in both high molecular weight and low molecular weight PE with significantly different melting temperature. Although the supports are generally considered as an inert composition during the polymerization, the high ash content of inorganic support-based catalysts restrict their application in high-end and cleaner areas, such as electrical film and medical appliance.

The search for green and environmentally friendly alternative is a major motivation for scientists or researchers, especially in electrical and medical industries. As a replacement, porous organic polymers (POPs) provide a much similar polymerization environment with homogeneous polymerization and incorporate into the polymer no extra impurities which would dramatically affect the properties of the final product [9,10], except for the active components. It's very facile and feasible to design and synthesize functionalized POPs with desired polymer frameworks and surface chemistry, by a selection of suitable solvent and monomer and/ or functional monomers especially by radical polymerization, and the post-modification approaches also provide versatile routes for various functionality of the porous materials [11]. A schematic illustration of how the supports can influence the polymer molecular structure is presented in Figure 1.
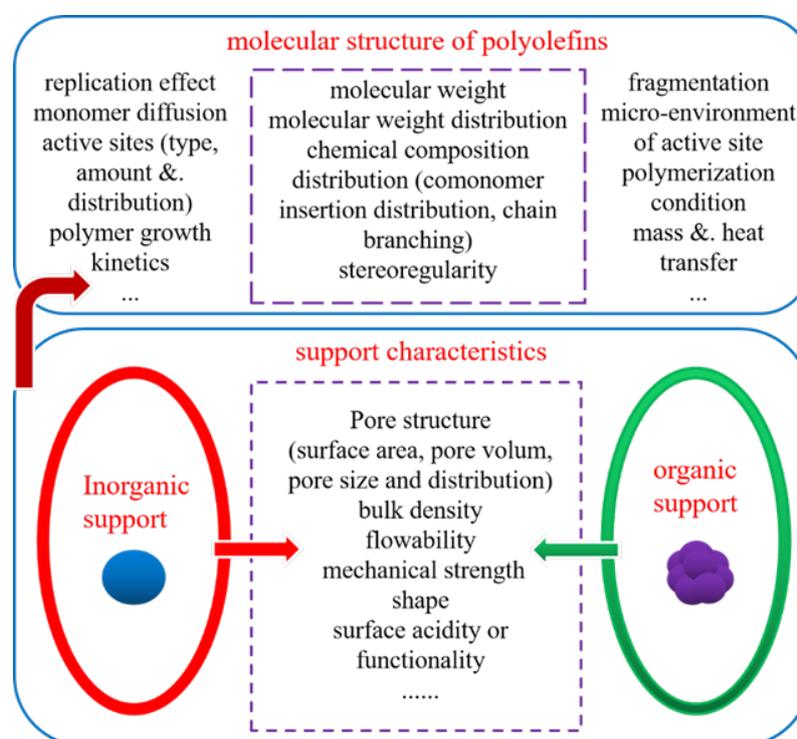
Figure 1: Schematic illustration of how the supports can influence the polymer molecular structure.

For those reasons, porous organic polymers have attracted lots of interests from academic and industrial researchers over the past several decades [12-18]. The high surface area combined with the well-defined pore structure and functionalities offer POPs as a versatile platform for the deployment of heterogeneous polyolefin catalysts. A series of studies on organic polymer-supported polyolefin catalysts were reported with functional group on the surface, and most of the synthesized porous organic polymer are based on styrene or divinylbenzene monomer. In order to anchor the active sites of Ziegler-Natta catalysts or metallocene catalysts, Functional comonomer(s) are involved in these polymers with acrylic acids, hydroxyl, amino, esters, chloromethyl, sulfonate groups, etc. For the POPs-based metallocene catalysts, they exhibits excellent ethylene homo-polymerization and ethylene/α-

olefin copolymerization abilities and much higher polymerization activity than silica-based metallocene catalysts could be obtained. However, the polymer morphology and bulk density didn't manifest to be as good as that of silica-based catalysts. Similar predicaments appeared in the POPs-based Ziegler-Natta catalysts, in addition, the polymerization activity was a little lower than the $MgCl_2$-based counterparts, but acceptable for industrialization. It seemed that it is still a long time to go before successful commercialization for the organic polymer supported catalysts.

Given that the bad polymer morphology and low bulk density straits could be solved, the POPs-based polyolefin catalysts are promising. The feasibility of design and synthesis of POPs with high surface area, controllable pore structure, surface morphology and

bulk density has been investigated by our group [19]. By selection of appropriate solvent(s) with matched thermodynamic solubility with used comonomer and the prepared polymer, template agent, functional monomer and cross ling agent content, the synthesis of eligible POPs which meet the requirement as the commercial polyolefin catalysts supports would be practicable, and POPs with high surface area, good surface morphology and high bulk density were prepared. In another attempt, highly flowable nano TiO_2/POPs hybrid supports with reasonable pore structure and surface morphology were synthesized and the prepared metallocene catalysts exhibited higher ethylene polymerization activity than inorganic silica supports with no obvious activity decay for 2 hours [20]. This inorganic-organic hybrid approach proved to be an efficient way to overcome the drawbacks, and will surely benefit to facilitate the industrialization of POPs in olefin catalysis.

Besides the importance of the support on activity, the POP support also can profoundly influence on the prepared catalysts and polymer properties. The organic support can remarkably change the surface hydrophilicity and modify the micro chemical environment of active sites on the catalyst, which would reflect in molecular weight, molecular weight distribution (MWD), chemical composition distribution (CCD) and stereoregularity (when propylene polymerization were conducted). As reported the sulfonated POPs-supported Ziegler-Natta catalysts for propylene polymerization by our group, the immobilized catalysts exhibited particular properties with broad molecular weight distribution and high stereoselectivity with common internal electron donor of diisobutyl phthalate (DIBP) adopted [21].

Klapper and co-workers [12] have revealed that the inorganic and organic supports based metallocene catalysts can impose substantial inconsistency in the incorporation of comonomer and short chain branching (SCB) [22]. The SCB distribution of the prepared PE copolymer from silica gel-supported metallocene is inhomogeneous, while by comparison, 1-hexene insertion is quite uniform in all the PE chains from the organic PS-based metallocene. Thus, homogeneous CCD of the copolymers are obtained and phase separation with different melting temperature due to branching distribution is limited, which is beneficial to the development of high-end mPE materials. The main explanation was proposed from a series of analysis that the monomer diffusion process plays a critical role in the incorporation of higher α-olefin. The rigid or flexible surface nature between the silica and organic supports cause different monomer diffusion behavior at the active sites on the surface and inside the silica pores. The formed crystalline polymer layer around the rigid surface of silica affects, in particular, the diffusion of 1-hexene with the bigger size, resulting in a broadening MWD and heterogeneous CCD. In contrast, the filtering effect of monomer diffusion is negligible due to the different fragmentation behavior for organic supports-based catalysts, and the ethylene/comonomer ratio is similar at all active sites around the micro-grain surface and the broadening phenomenon is suppressed [23].

Conclusion

In conclusion, Porous organic polymers (POPs) have showcased their enormous potential for industrial application as a new type of polyolefin catalyst supports. The high surface area, modifiable pore structure and functionalities, cleaner and greener chemical composition will endow the porous organic polymers with a versatile platform for various olefin polymerization catalysis. The change of support from inorganic to organic offers us a powerful and practical tool to tailoring the polymer properties along with varying catalyst types and polymerization process conditions. The unique aggregation and fragmentation modes of POPs occurring in the synthesis of the organic particles and polymerization process, respectively, facilitate homogeneous insertion of comonomers and uniform distribution of CCD and short chain branching, etc. Porous organic polymers present a new route to solve the emerging obstacles or drawbacks in the inorganic supports-based polyolefin catalysts.

Acknowledgement

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