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Improved Catalytic Capabilities of Vanadium Complexes bearing Tridentate Constrained Cyclic β-Enaminoketonato Ligands towards Ethylene (Co) polymerization

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ABSTRACT

Non-metallocene catalysts for polymerization of olefin have experienced the development for years, and a huge number of late and early transition metal catalyst precursors were successfully pllaned and synthesized to copolymerize olefins. Amongst those non-metallocene catalysts, vanadium catalysts exhibit excessive catalytic activities for generating (co)polymers owning excessive molecular weight (MW) and comonomer contents. But, the energetic species can be reduced to low-valent inactive vanadium species and decompose in the course of the polymerizations, which result in decrease of catalytic activities and the formation of producing polymers with multimodal or bimodal distribution.

Establishing tridentate Schiff ligands having pendant donors, either the, steric environment, electronic character or both of the complexes can be tuned properly. This process is proved to be an efficient approach to improve the stabilities of the catalysts, as well as other transition metal catalysts. Tang and his colleagues invented tridentate a Schiff-based titanium catalyst which shows desirable catalytic properties, even in copolymerizations of ethylene with water comonomers. Gibson and his coworkers evaluated that the catalytic properties of chromium catalyst bearing [O, N, N] type tridentate ligands in ethylene polymerization were about one order of magnitude higher than the analogues of bidentate. When both of them was compared, our group reported that the tridentate complexes showed much improved performances in ethylene polymerization. Even though, the side arm donor showed pronounced stabilization reactions on active species obtained from the corresponding catalysts, the catalytic activity of the catalysts decreased due to their influences on the steric environment and electronic character of the active species.

A chain of vanadium complexes having tridentate constrained cyclic β-enaminoketonato ligands were prepared and characterized, and the structures of complexes 2b and 2c were further evaluated by X-ray crystal analysis. In the presence of reactivating agent such as ethyl trichloroacetate, Et2AlCl activated vanadium units produced polyethylene’s with unimodal distribution. Complex 2a without bulky R group showed lesser catalytic activity than 2b Complex having phenyl group at R position, and the catalytic activity of these catalysts could be easily tuned by differing the polymerization conditions and ligand structure. These complexes of tridentate vanadium exhibit promising thermal stabilities and is not deactivate within 30 minutes. The ethylene copolymerization with exo 1,4,4a,9,9a,10-hexahy-dro-9,10(1′,2′)-benzeno-1,4-methanoanthracene (HBM) and norbornene (NBE) were also effectively catalyzed by these vanadium catalysts, and copolymers possessing high comonomer incorporations and high glass transition temperature were obtained. Different kinds of vanadium complexes having tridentate constrained cyclic β-enaminoketonato ligands were prepared and the shapes in solid state of complexes 2b and 2c were evaluated by single crystal X-ray diffraction. In these complexes, R functional group had been restrained by way of cyclic skeletons near the hydroxyl donor

Keywords: Coordination polymerization, Polyethylene; Copolymer, Vanadium catalysts