Synthesis of Ni complexes bearing a Lewis basic functional group and its application to the copolymerization in the presence of Lewis acidic supports

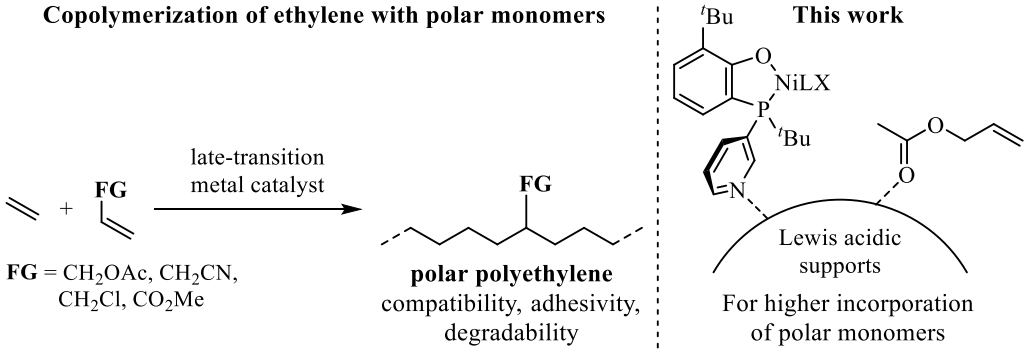
(*Graduate School of Engineering, The University of Tokyo*) ○Go Yonezaki, Falk William Seidel, Kyoko Nozaki

Keywords: Copolymerization; Supramolecular Catalysts; Lewis Acidic Supports

Solid supports play essential roles in olefin polymerization catalyzed by group 4 metal compounds represented by the Ziegler-Natta or metallocene catalysts. It is often proposed that the Lewis acidic sites of the solid supports, such as aluminoxane or magnesium chloride, abstract halogen atoms from the active center providing vacant site available for olefin monomers.

Unlike the homopolymerization of olefins, late-transition metal catalysts are the major players for the coordination-insertion copolymerization of ethylene with polar monomers, owing to their high tolerance against the polar functional groups. There are several reports in which Ni or Pd complexes were heterogenized on solid supports towards slurry- and gas-phase polymerization. These studies are rather focused on controlling the morphology of the obtained polymers.[1–4] In this study, we aim to control the incorporation ratio of the polar monomers using a combination of nickel complex and Lewis acidic supports.

We synthesized a nickel phosphine-phenolate complex bearing Lewis basic pyridyl moiety and applied it to the copolymerization of ethylene with polar monomers in the presence of a Lewis acidic support. As a result, the catalyst increased the incorporation ratio by 3.7 times compared to that without the support. The improvement of the incorporation ratio may be attributable to the Lewis acidic support interacting with both the Lewis basic moiety of the nickel complex and polar monomers to assist the efficient approach of the polar monomer to the active site.



1) H. Tafazolian, D. B. Culver, M. P. Conley, *Organometallics* **2017**, *36*, 2385. 2) D. B. Culver, H. Tafazolian, M. P. Conley, *Organometallics* **2018**, *37*, 1001. 3) X. Fu, L. Zhang, R. Tanaka, T. Shiono, Z. Cai, *Macromolecules* **2017**, *50*, 9216. 4) H. Zhang, C. Zou, H. Zhao, Z. Cai, C. Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 17446.

© The Chemical Society of Japan