Olefin shape-controlled polymerization with single-site catalyst inside the nanospace of metal-organic frameworks

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Abstract: Ethylene-1-hexene were copolymerized using metallocene catalyst inside nanostructure of metal-organic framework (MOFs) with different window sizes and pore structures. Catalytic characteristics and, copolymer properties were studied. It was determined that the nanostructure of the MOFs affects the properties of the copolymers produced.

Keywords: metal-organic Frameworks, metallocene, olefin copolymerization, shape-selective

1. Introduction

Metal-organic frameworks (MOFs) are gaining attention as new porous crystalline materials having wide surface area and open pore structure, which allow migration of large number of molecules or solvents compared to known porous materials. It has the advantage that it can change the frame or constituents of the formed center metal and organic ligand and can control the size of the pore[1]. Ravon and Farrusseng studied the selectivity of MOFs (IRMOF-1, IRMOF-8, and H-BEA), with different cage and window sizes, in the alkylation of polyaromatic compounds[2]. IRMOF-1 and IRMOF-8, which has large pore sizes and similar pore structures, show similar shape selectivity because most of the bulky products do not have diffusion hindrance. However, H-BEA with small cages and windows showed steric hindrance of bulky product. In this study, ethylene/1-hexene was copolymerized using metallocene catalyst supported on MOFs with different window sizes and pore structures. The properties of the resulting polymer were studied.

2. Experimental

MOFs and amorphous silica were suspended in dried toluene then metallocene ($(n\text{-BuCp})_2ZrCl_2$) and MAO mixed solution were added. After stirring at 70 ^{0}C for 3 hours, the reaction product was washed with toluene several times and vacuum dried.

The ethylene polymerization was performed in a 500 mL steel high-pressure reactor. Following the addition of 280 mL of hexane, comonomer, and triethylealuminum (TEAL) into the reactor, the temperature was increased to the designated polymerization temperature (70^{0}C). A certain amount of catalyst in hexane and a 10 wt% hexane solution of TEAL, used as a scavenger, was then injected into the reactor with a syringe. Polymerization started with feeding and saturating the reactor with monomer and the total polymerization pressure was 7 bars. After polymerization, the polymer was vacuum filtered, washed with ethanol, and vacuum dried.

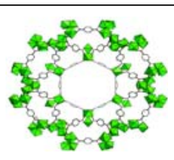
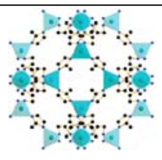
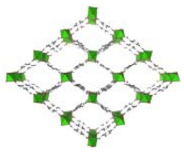
3. Results and discussion

Based on BET analysis of the supports, MIL-101 has the largest surface area, average pore diameter, and pore volume; followed ZIF-8, then the smallest, MIL-53. Table 1 includes the ICP analysis and copolymerization results of supported metallocene catalysts while Table 2 shows the structure and window size of the MOFs. MIL-101 with larger windows than MIL-53 and ZIF-8 has higher amount of catalyst loaded. Window size of MOFs affects the migration and diffusion of the metallocene and MAO molecules into the support. Since metallocene molecules are limited when they are diffused into MOFs with small window sizes, it is difficult to carry them in the pores of MIL-53 and ZIF-8, which are small in window size, and are expected to be mainly supported on the particle surface. However, in the case of MIL-101, which has a relatively large window size, the metallocene diffuses freely into the pores, so that the amount of metallocene catalyst is high. From Table 1 it could also be seen that the copolymerization characteristics of copolymers produced using MOFs MIL-53, ZIF-8, and amorphous silica exhibited similar characteristics and changes with C_6/C_2 mole ratio in feed. As the content of comonomer in all three catalysts increased, the melting point decreased. Furthermore, Figure 1 shows that comonomer content of the copolymers produced using the three catalyst increases at higher C_6/C_2 mole ratio in feed. It is believed that similar copolymerization characteristics are exhibited because there is no significant difference in the steric environment of the metallocene catalyst supported on MIL-53, ZIF-8, and SiO_2. On the other hand, copolymers produced using MIL-101 showed little change regardless of the C_6/C_2 mole ratio in feed. Since the catalysts supported on MIL-101 are loaded with metallocene and MAO in the cage, the space inside the cages and windows are greatly reduced. This resulted to the difficulty in diffusion of ethylene and 1-hexene into the catalytic active sites. The diffusion rate of 1-hexene, with a large kinetic diameter, becomes so small that diffusion into the pores is difficult, so shape-selective polymerization takes place. Consequently, 1-hexene content in the resulting copolymer was hardly measured and the melting point remained unchanged.

Table 1. Results of ethylene-1-hexene copolymerization with $(n\text{-}BuCp)_2ZrCl_2$ supported on metal-organic frameworks(MOFs)

Catalysts	Zr content (μmol/g-cat)	Al content (mmol/g-cat)	C_6/C_2 molar ratio in feed (mol/mol)	PE (g)	T_m (°C)
MIL-101/MAO/ $(n\text{-}BuCp)_2ZrCl_2$	151	1.3	0.0	6.5	129.0
			4.4	6.6	127.0
MIL-53/MAO/ (n-BuCp)2ZrCl2	130	1.5	0.0	7.9	133.6
			4.4	1.5	112.4
ZIF-8/MAO/(n-BuCp)$_2$ZrCl$_2$	87	1.6	0.0	9.8	134.5
			4.4	0.95	118.4
SiO2/MAO/ (n-BuCp)2ZrCl2	195	0.9	0.0	41.0	132.1
			4.1	25.0	111.6

Table 2. Characteristics of the Metal-Organic Frameworks

	MIL-101	ZIF-8	MIL-53
Window size (nm)	1.2/1.6	0.34	0.85
Structure			

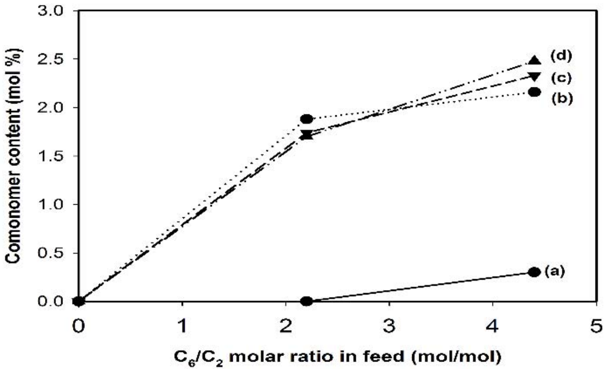


Figure 1. Comonomer content in ethylene-1-hexene copolymers produced by (a) MIL-101/MAO/$(n\text{-}BuCp)_2ZrCl_2$, (b) MIL-53/MAO/$(n\text{-}BuCp)_2ZrCl_2$, (c) ZIF-8/MAO/$(n\text{-}BuCp)_2ZrCl_2$ and (d) SiO_2/MAO/$(n\text{-}BuCp)_2ZrCl_2$ with respect to the C_6/C_2 molar ratio in feed.

4. Conclusions

It was confirmed that the nanostructure of metal-organic framework used as a support to the metallocene catalyst affects the properties of the catalyst and copolymers.

References

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