RESEARCH ARTICLE | FEBRUARY 05 2019

Synthesis of uniform rod-like polymer particles via propylene polymerization using metallocene catalysts supported on Stober silica FREE

Kuo-Tseng Li; Cheng-Ni Yang

AIP Conf. Proc. 2065, 030017 (2019)
https://doi.org/10.1063/1.5088275

Synthesis of Uniform Rod-like Polymer Particles Via Propylene Polymerization Using Metallocene Catalysts Supported on Stober Silica

Kuo-Tseng Li*, Cheng-Ni Yang

Department of Chemical Engineering, Tunghai University, Taichung, 40704, Taiwan

**email: ktli@thu.edu.tw*

Abstract. Monodispersed silica particles were synthesized via Stober method and were used to support $Me_2Si(Ind)_2ZrCl_2$)/MAO for studying the effects of silica size and MAO concentration on propylene polymerization activity, polypropylene particle shape / size and polymer properties. 5nm catalyst exhibited significantly better polymerization activity and produced much more uniform polymer particles than 700nm catalyst did, which was ascribed to their differences in local mass and heat transfer coefficients. With the increase of external MAO concentration, polymer yield, particle size, molecular weight and melting point increased but molecular weight distribution decreased. Uniform rod-shaped PP particles were fabricated at an intermediate MAO concentration, which packed with numerous polymer nanofibrils and had a smooth exterior surface.

Keywords: polypropylene particles, propylene polymerization, nano-scale catalyst.
PACS: 82.35.Np

INTRODUCTION

Isotatic polypropylene (PP) accounts for about 25% of the world plastics made today. PP has a wide range of application. Metallocene catalyst has tended to replace Ziegler-Natta catalyst for PP production because the former has much higher activity and can produce PP with different kinds of microstructures and of a purity that cannot be obtained by the latter. Metallocene/MAO catalysts immobilized on siica can overcome reactor fouling problems and can have a better particle morphology control. Commercially applied porous silica is made by neutralization of aqueous alkali metal silica with acid. The fragmentation of silica particles and the change of polymer morphology during polymerization make it quite difficult to reproduce polymer particle morphologies consistently. Stober method is one of the most important methods for forming monodispersed silica particles. In this study, the effects of Stober silica size (700 nm and 5 nm) and external MAO concentration on PP particle size/shape and properties were studied using $Me_2Si(Ind)_2ZrCl_2$ metallocene catalyst. We found that 5nm catalyst exhibited significantly higher polymerization activity and produced PP particles with much more uniform size and better properties than 700 nm catalyst did. In addition, the increase of external MAO concentration significantly changed catalyst activity, polymer particle size/shape and properties.

EXPERIMENTAL

Two monodispersed silica particles were prepared according to the procedure of Shimura and Ogawa [1]. Procedures for immobilizing metallocene/MAO catalyst on Stober silica were similar to those we reported before [2]. Catalysts were characterized with ICP-AES, BET, SEM and TEM. Propylene polymerization was carried out in a 100 mL agitated autoclave reactor. Polymers produced were characterized with SEM, XRD, DSC, FTIR and GPC.

RESULTS AND DISCUSSION

Figure 1 and Figure 2 show that two Stober silica particles have the sizes of around 5 nm and 700 nm, respectively, which are significantly smaller than those obtained (10 nm and 1290 nm, respectively) by Shimura and Ogawa[1] at the same methanol /TEOS molar ratio. It might be due to the difference of aqueous ammonia solution (NH_4OH) amount added and the temperature used.

Proceedings of PPS-34
AIP Conf. Proc. 2065, 030017-1–030017-4; https://doi.org/10.1063/1.5088275
Published by AIP Publishing. 978-0-7354-1793-9/$30.00

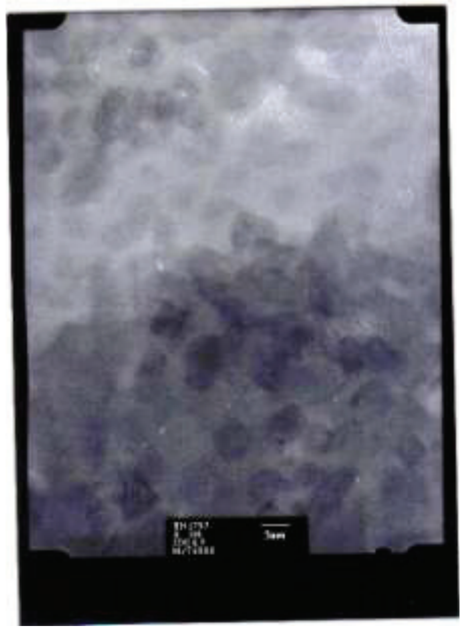

FIGURE 1. TEM micrograph of the 5nm silica particles.

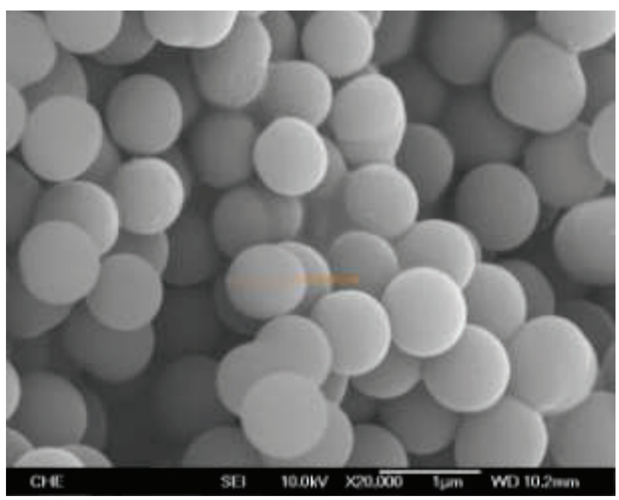

FIGURE 2.FE-SEM image of the 700nm silica particles.

Under identical MAO concentration, polymer yields obtained with 5 nm catalyst are significantly greater than those obtained with 700 nm catalyst, as shown in Figure 3, which also indicates that polymer yields increase continuously with increasing external MAO concentration .

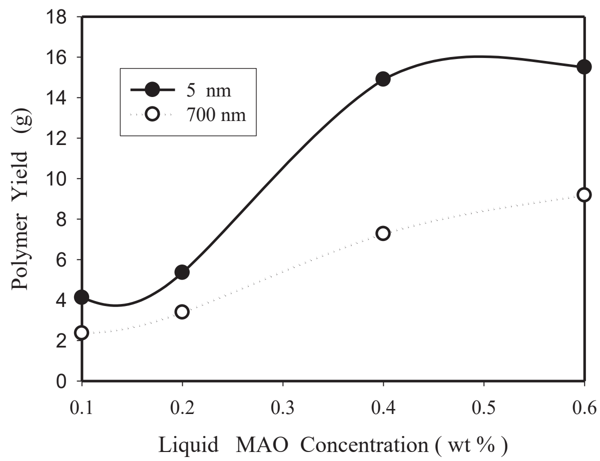

FIGURE 3. Polymer yields as a function of MAO concentration and silica size.

PP particles produced with 5 nm and 700 nm catalysts have significant different morphology. The former (shown in Figure 4) exhibits rod-like shape (different from the flaxseed shape we obtained before using a commercial nanosized silica [2]) with smooth exterior surface and uniform size (around 6 μm length and 2.5 μm width), while the latter (shown in Figure 5) exhibits irregular shape and non-uniform size. In addition, the former has greater dimension than the latter, which should be due to its better polymer yield, as shown in Figure 3. These differences of polymer yield (shown in Figure 3) and particle morphology should be mainly due to the difference of mass and energy transfer coefficients.

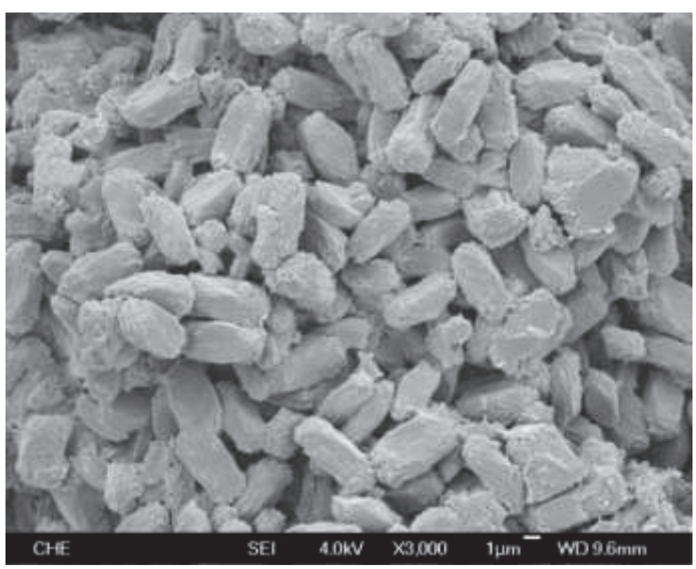

FIGURE 4. SEM micrograph of PP particles produced by 5nm catalyst.

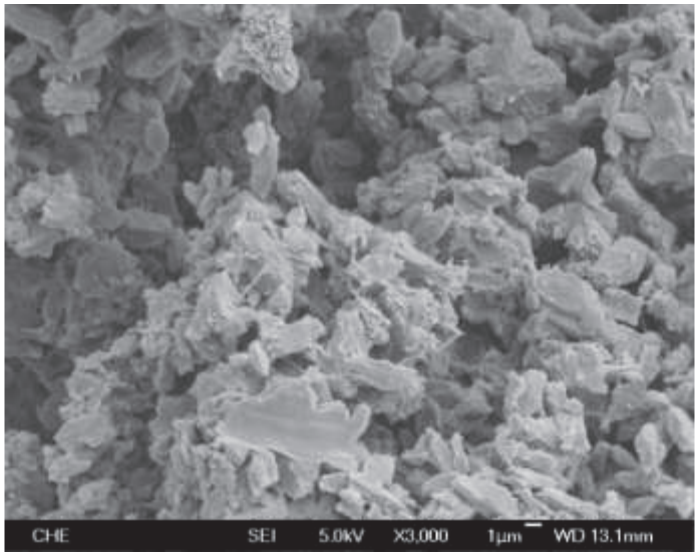

FIGURE 5. SEM micrograph of PP particles produced by 700nm catalyst.

CONCLUSIONS

5nm catalyst exhibited greater activity and produced PP particles with much more uniform shape/size and properties than 700 nm catalyst, which were ascribed to their differences in local mass and heat transfer coefficients. The increase of external MAO concentration significantly changed catalyst activity, polymer particle size/shape and properties.

ACKNOWLEDGMENTS

The authors are grateful to National Science Council of ROC for financial support (NSC-97-2221-E029-028).

REFERENCES

1. N. Shimura, M. Ogawa, J. Mater. Sci. **42,**5299-5306(2007).
2. K.T. Li, F.S. Ko, J. Appl. Polym. Sci. **107,**1387-1394(2008).