Asian Journal of Chemistry;   Vol. 23, No. 1 (2011), 471-472

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

NOTE

Ethylene Polymerization with Silica Support *Bis*(butylcyclopentadienyl)zirconium Dichloride as Catalyst

IRAJ KOHSARI[1], FARIDEH AZIMFAR[2] and SAEED BABAEE[1,*]

[1]Faculty of Material and Manufacturing Technologies, Malek Ashtar University of Technology, Lavizan Avenue, P.O. Box 16765/3454, Tehran, Iran
[2]National Petrochemical Company, Research & Technology Company, Tehran, Iran

*Corresponding author: Tel: +98 2122970231, Fax: +98 2122936578, E-mail: safnba@gmail.com

(*Received*: 26 June 2010; *Accepted*: 4 September 2010) AJC-9088

In this work, a catalyst of *bis*(butylcyclopentadienyl)zirconium dichloride was prepared. The heterogeneous catalyst was prepared by immobilization of *bis*(butylcyclopentadienyl)zirconium dichloride, (n-But Cp)$_2$ZrCl$_2$, on silica support. Metal content (Zr %) was determined by inductively coupled plasma technique. Then ethylene polymerization was performed in the temperature range between 313 and 343 K. Metallocene catalyst system was active for ethylene polymerization in presence of methylaluminoxane by different Al/Zr ratio. The conditions for achieving of the highest polymerization yield were studied.

Key Words: Heterogeneous catalyst, Polymerization, Support, Silica.

A great deal of academic research is directed towards the study of metallocene systems activated by methylaluminoxane (MAO). Among the various metallocene complexes, homogeneous and supported *bis*(butylcyclopentadienyl)zirconium dichloride (n-BuCp)$_2$ZrCl$_2$ have had their catalytic activity reported in the literature[1]. SiO$_2$ has even been used as a support for metallocene and Ziegler-Natta catalysts[2-7]. This paper presents the comparative behaviour of (n-BuCp)$_2$ZrCl$_2$ supported on silica and activated by methylaluminoxane, in ethylene homopolymerization.

Silica (Aldrich grade 643) was activated for 16 h at 723 K. Methylaluminoxane (supplied by Aldrich, 10.0 wt. % toluene solution). *Bis*(butylcyclopentadienyl)zirconium dichloride (n-BuCp)$_2$ZrCl$_2$ was synthesized. Ethylene and nitrogen were deoxygenated and dried through columns of activated molecular sieve prior to use. Toluene and tetrahydrofuran were deoxygenated and dried by standard techniques before use.

Synthesis of (n-BuCp)$_2$ZrCl$_2$: Cyclopentadiene was prepared from cracking dicyclopentadiene. Then cyclopentadieneylsodium was synthesized by adding dropwise with stirring freshly cyclopentadiene to sodium in dry tetrahydrofuran in the flask. BuBr and THF were charged to flask. NaCp was added slowly from 22-40 ºC. The volume of the mixture was reduced under vacuum to 25 % of its original volume. Afterward THF was added and further deprotonation of BuCp was performed with sodium. Then ZrCl$_4$ powder was directly added to NaBuCp with stirring. Finally the product (BuCp)$_2$ZrCl$_2$ was filtered and dried.

Preparation of supported catalyst: All experiments were performed under inert atmosphere. Toluene was added to (n-BuCp)$_2$ZrCl$_2$ and pretreated silica in concentration corresponding to 1.5 wt. % of Zr/SiO$_2$ and the mixture was stirred for 6 h at 350 K. The slurry was filtered, washed with toluene and then dried. Metal content (Zr %) was determined by inductively coupled plasma (ICP) technique. Zr per cent in the catalyst was 2.3 %.

Polymerization reactions: Ethylene homopolymerizations were performed in 1 L reactor. Methylaluminoxane was used as cocatalyst in different Al/Zr molar ratios. The polymerizations were performed at atmospheric pressure at temperature range between 343 and 313 K. The products were washed with ethanol and finally dried. The molecular weight of the polyethylene was 197637 that obtained by gel permeation chromatography system. The morphology of polymer was also characterized by scan electron micrography.

Polymerization reactions were conducted with supported catalyst at various Al/Zr molar ratios and at a constant zirconium concentration for the establishment of the optimum activity. Slurry polymerizations were carried out in 400 mL of dry toluene at 60 ºC, at a zirconium concentration of 0.025 mmol/L, with one bar pressure of the ethylene.

Fig. 1 shows that increase the Al/Zr molar ratio increased the productivity of the catalyst, whereas a further increase in the ratio reduced the productivity. Methylaluminoxane alkylates active centers of the catalyst. When the concentration of methylaluminoxane was increased above the optimum value, side-product complexs were formed.

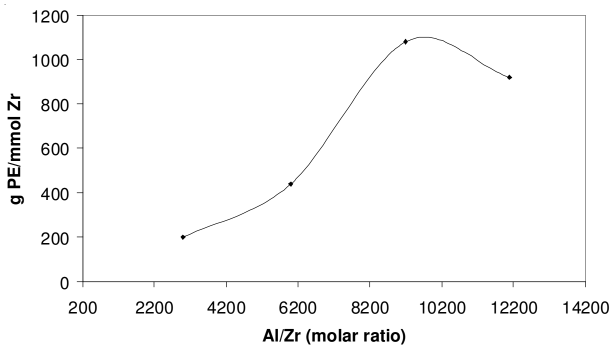

Fig. 1. Effect of Al/Zr ratios on the polymer yield

The increase of polymerization observed by rising the temperature due to an increase of the active sites as well as to the obvious increase of propagation rate (Fig. 2). However, further increasing the temperature causes the formation of side products inactive.

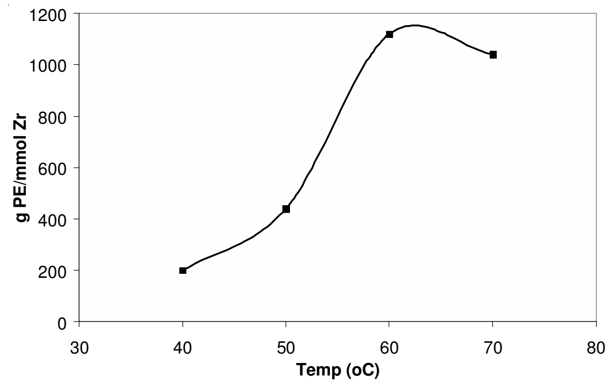

Fig. 2. Effect of temperature on the polymer yield

Figs. 3-5 show the morphologies of support, catalyst and polyethylene prepared by the corresponding catalyst. The presence of a supporting matrix, such as silica, was used to produce polymer particles with a more acceptable morphology. Polyethylene duplicates the morphology of the catalyst.

Conclusion

In this study, after the polymerization process and the conditions optimization the important points were as followed: (i) There was an optimum Al/Zr molar ratio with respect to the yield of polymer. (ii) Highest productivity was obtained at 60 ºC. (iii) Silica support improved morphology of polymer. (iv) The catalyst activity was very high, producing close to 1.1×10^6 g PE (mol Zr).

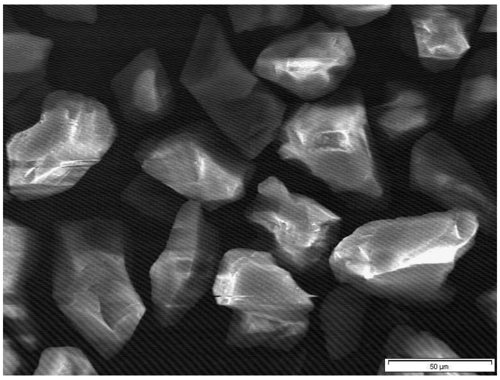

Fig. 3. SEM image of SiO_2 support

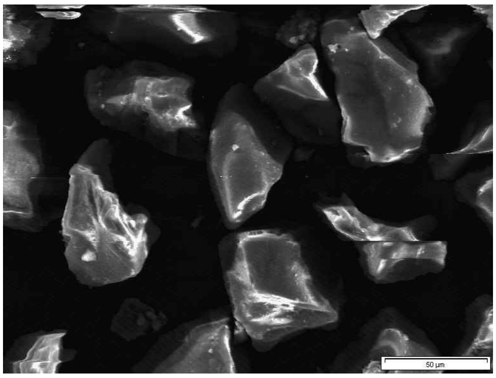

Fig. 4. SEM image of catalyst

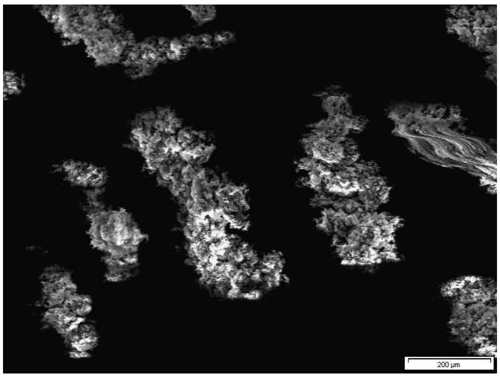

Fig. 5. SEM image of polyethylene

REFERENCES

1. J. Santos, A. Larentis, M. Rosa and C. Krug, *Macromol. Chem. Phys.*, **200**, 751 (1999).
2. H. Lu and S. Xiao, *Makromol. Chem.*, **194**, 421 (1993).
3. L.K. Johnson, C. Killian and M. Brookhart, *J. Am. Chem. Soc.*, **117**, 6414 (1995).
4. B.L. Small, M. Brookhart and A.M. Bennet, *J. Am. Chem. Soc.*, **120**, 4049 (1998).
5. G.M. Benedikt, Metallocene Technology in Commercial Applications, Plastics Design Library, New York (1999).
6. G.H. Zohuri, F. Azimfar, R. Jamjah and S. Ahmadjo, *J. Appl. Polym. Sci.*, **89**, 1177 (2003).
7. T. Jiang, W. Chen, F. Zhao, Y. Liu, R. Wang, H. Du and T. Zhang, *J. Appl. Polym. Sci.*, **98**, 1296 (2005).