ANOTHER LOOK AT SITE HETEROGENEITY IN ZIEGLER-NATTA CATALYSTS FOR POLYOLEFIN PRODUCTION

John McCoy[1] and Randhir Rawatlal[1]

[1]Department of Chemical Engineering, University of Cape Town, Rondebosch, 7700, South Africa

ABSTRACT

Ziegler Natta (ZN) catalysts are often used to produce a wide range of polyolefins on an industrial scale. It has long been known that polymer produced on these catalysts consists of a relatively wide distribution in chain lengths; values for the Poly-Dispersity Index (PDI) are generally well above 2, the value that would be expected if a single catalyst site type were active. The prevailing view of site heterogeneity in ZN catalysts is reflected in their name: multi-site catalysts. ZN catalysts are conceptualised as containing a number of different active sites, which produce polymer with different average molecular weights [1]. Different molecular weights can result from differing propagation rates. More rapid chain propagation reactions produce longer polymer molecules; a variety of propagation rates will produce a range of chain lengths, leading to a broad chain length distribution.

No physical explanation for the existence of different site types has been offered, except for some studies which have investigated different crystal face attachments for Ti active sites on $MgCl_2$ supports [2-4]; these studies do not explain why different propagation rates should exist.

In this work, we propose that sites differ not in propagation rate but in the rate at which chain growth is terminated by a range of terminating agents, including hydrogen, monomer and co-monomer. This interpretation is described in the context of experimental and simulation results in the literature [1,5-7], and then used to investigate experimentally-determined chain length distribution data for ethylene-1-butene copolymer produced in lab reactors. It is shown that this new view of the heterogeneity of ZN active sites can successfully reproduce key polymer properties, including PDI and mean chain lengths.

References:

1 Floyd, S.; Heiskanen, T.; Taylor, T.; Mann, G. & Ray, W. *Journal of Applied Polymer Science*, **1987**, *33*, 1021-1065
2 Lin, J. & Catlow, C. *Journal of Catalysis*, **1995**, *157*, 145-152
3 Boero, M.; Terakura, K. & Parrinello, M. *International Journal of Molecular Sciences*, **2002**, *3*, 395-406
4 Brambilla, L.; Zerbi, G.; Piemontesi, F.; Nascetti, S. & Morini, G. *Journal of Molecular Catalysis A: Chemical*, **2007**, *263*, 103-111
5 Zakharov, V.; Matsko, M.; Echevskaya, L. & Mikenas, T. Macromolecular Symposia, 2007, 260, 184-188
6 Dompazis, G.; Kanellopoulos, V.; Touloupides, V. & Kiparissides, C. *Chemical Engineering Science*, **2008**, *63*, 4735-4753
7 Touloupides, V.; Kanellopoulos, V.; Pladis, P.; Kiparissides, C.; Mignon, D. & Van-Grambezen, P. *Chemical Engineering Science*, **2010**, *65*, 3208-3222