

**Kinetic features of ethylene polymerization over postmetallocene catalysts involving Co, V, Cr and Zr complexes on the base of data on the number of active centers, propagation rate constants and molecular mass distribution of polymers**

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Last years a great amount of the new homogeneous (nonmetallocene) catalyst for olefin polymerization has been developed. The great variety of the transition metals complexes with different metals and ligands are used as precursors for these catalytic systems. The most of these catalysts are nonstable and show the decay type of kinetic profile at polymerization. The data on the number of active centers and their reactivity (propagation rate constants) as well the data on the molecular mass and molecular mass distribution (MMD) of polymers produced are needed for the more detail kinetic study of these catalysts. Recently we have used this approach for study of ethylene polymerization over catalysts  $\text{LFeCl}_2/\text{MAO}$  ( $\text{L}=\text{bis}(\text{imino})\text{pyridine}$ ) /1/.

The new data on the number of active centers (the quenching of polymerization by  $^{14}\text{CO}$ ), propagation rate constants ( $K_p$ ) and MMD of polymers produced at ethylene polymerization with different nonmetallocene catalysts are presented and discussed in this contribution. Two groups of the homogeneous catalysts with decay type kinetic have been studied:

(i) bis(imino)pyridine complexes with composition  $\text{R}_n\text{-LMtCl}_x$  and MAO as activator ( $\text{Mt}=\text{Co, V, Cr}$ ;  $\text{R}=\text{Me, i-Pr, i-Bu}$  for  $2,6\text{R}_2\text{-LCoCl}_2$ ,  $\text{R}=\text{Me, Et}$  for  $2,6\text{R}_2\text{-LVCl}_3$ ,  $\text{R}=\text{Me}$  for  $2,4,6\text{R}_3\text{-LCrCl}_3$ )

(ii) bis(phenoxy-imine) $\text{ZrCl}_2/\text{MAO}$  catalyst.

It was found the maximal number of active centers depends on the composition of  $\text{LMtCl}_x$  complexes and polymerization temperatures and varies from 0.76 mol/mol Cr ( $\text{LCrCl}_3$ ) to 0.11 mol/mol Zr ( $\text{L}_2\text{ZrCl}_2$ ).  $K_p$  values vary from  $5.4 \cdot 10^4$  L/mol·s ( $\text{L}_2\text{ZrCl}_2$ ) to  $1.4 \cdot 10^3$  L/mol·s ( $\text{LCrCl}_3$ ). The number of active centers decreases with polymerization time for all catalysts studied. The catalysts  $\text{R}_2\text{-LCoCl}_2$  and  $\text{R}_3\text{-LCrCl}_3$  keep the single site character at polymerization. Activation energy for propagation reaction over single site catalyst  $(\text{t-Bu})_2\text{-LCoCl}_2$  has been measured ( $E_p=4.5$  kkal/mol) that is much lower than effective activation energy ( $E_{\text{eff}}=9.4$  kkal/mol).

Catalyst  $\text{t-Bu}_2\text{-LCoCl}_2$  is more active in comparison with  $\text{Me}_2\text{-LCoCl}_2$  catalyst because the higher number of active centers at the same  $K_p$  value and it produces polyethylene with much higher molecular mass (ca. in 160 times). It was found substitution of Me groups on t-Bu groups in ligand L decreases the transfer reaction constant with monomer greatly.

$R_3\text{-LCrCl}_3$  catalyst exhibits the decrease of PDI value from 1.5 to 1.3 at decrease of polymerization temperature and increase of Mw value at increase of polymerization temperature. These unusual kinetic features and data on  $C_p$  and  $K_p$  values are discussed on the base of the dormant sites formation at polymerization over these catalytic system.

Catalysts bis(phenoxy-imine) $ZrCl_2$ /MAO and  $LVCl_3$ /MAO produce PE with narrow MMD at the initial stage of polymerization ( $\tau_p < 5$  min), but we have found polydispersity of polymers increases with increase of polymerization time and depends on polymerization temperature as well because formation of the new high molecular fraction (formation of the new active centers).

The possible correlations between obtained kinetic data, data on the MMD of polymers and structures of intermediates formed in these catalysts are discussed.

1. A.A.Barabanov, V.A/Zakharov, M.A.Matsko, et.al., *Macromol.Chem.Phys.*, 206 (2005) 2292.