Enhanced Ethylene Polymerization Activity in Union Carbide Catalysts

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Chromocene on silica was discovered in the early 1970's as commercial ethylene polymerization catalyst.[1] The Union Carbide Catalyst displays high activity in ethylene polymerization at low pressure and temperature in absence of co-catalysts and activators.[2] Linear, high density polyethylene featuring narrow molecular weight distribution is characteristic for metallocene based systems. Substituted cyclopentadienyl (Cp) rings as well as mixed silica/alumina supports are known to diminish catalytic activity. However, preparation of silica surface itself seems crucial in controlling both activity and stability. For example, OH-groups in closed proximity to active sites are believed to act as catalyst inhibitors.
The predominant proportion of chromium on silica surface is present in the divalent state. Due to remarkably high transfer respond to hydrogen it is believed that active sites contain one Cp ligand during polymerization. Moreover, solid state NMR based studies have assigned half sandwich Cr(II) dimers to be the predominant surface sites.[3] However, in homogeneous phase only few half sandwich Cr(III) complexes show activity in ethylene polymerization.[4]
Greater insight in molecular level understanding is appropriate to evaluate actives sites and polymerization mechanism. The enhanced catalytic performance of chromocene on silica prepared by applying principles of surface organometallic chemistry will be discussed.

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