ABSTRACT

Two trinuclear oxo-centered chromium(III) carboxylate complexes have been synthesized by reacting commercial $Cr(NO_3).9H_2O$ and $CrCl_3.6H_2O$ with F_3CCO_2H and Cl_3CCO_2H respectively. The elemental and thermogravimetric analyses of the green resulting products as well as, FTIR spectroscopy, magnetic susceptibility measurements and single crystal X-ray structure analysis, all revealed that the complexes structure are $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ (A) and $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ (B). Both compounds have a central μ_3-O atom, with a planar triangular arrangement of the 3d trivalent chromium atoms, bonded to the central oxygen and six acetate ligands, each doubly bridging across the metal center using both oxygen atoms of the carboxylate group.

Both complexes, in combination with $AlEt_2Cl$, form highly active heterogeneous Ziegler-Natta catalysts for ethylene polymerization. The effects of varying the monomer pressure and Al / Cr ratio were investigated. The activities of the catalysts system were compared under selected reaction conditions. Kinetic data shows that the rate of the polymerization increased with increase in ethylene pressure. In addition, the polymerization rate was first order with respect to ethylene during the initial stage of the reaction. The activity decreased rapidly, probably due to the deactivation of actives sites, increase in solution viscosity and encapsulation of active centers by the polymer. Complex (B) was found to be more reactive than complex (A) under similar conditions. The maximum activity for the $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ / $AlEt_2Cl$ catalytic system was 13.9 kg-PE/g-Cr/hr/atm, obtained at Al / Cr molar ratio of 45 and initial monomer pressure of 1320 kpa. The maximum activity, with the $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ / $AlEt_2Cl$ catalytic system was 36.71 kg-PE/g-Cr/hr/atm, obtained at Al / Cr ratio of 45 and monomer pressure of 795 kPa.

The produced polymers were characterized using FTIR, TGA, DSC, hardness, density, DMA and NMR techniques. They are high density polyethylene with high melting temperature, molecular weight and crystallinity. Even though the $[Cr_3O(Cl_3CCO_2)_6.2H_2O]Cl_3CCO_2.3H_2O$ / $AlEt_2Cl$ catalytic system shows higher activity than the $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ / $AlEt_2Cl$ catalytic system, polyethylene from this second catalyst was found to have higher melting temperature, degree of crystallinity and density than PE from the first catalytic system.

PUBLICATION

B. B. Mougang D. Soume, Rosiyah Yahya, Seng Neon Gan and Seik Weng Ng, Diaqua-μ_3-oxido-hexakis-(μ_2-trichloroacetato-K^2O:O')(trichloroacetato-KO)-trichromium(III) acetonitrile trisolvate. Acta Cryst., E64, **m1175** (2008).

POSTER (BEST POSTER AWARD)

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ORAL PRESENTATION

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