ACTIVE CENTER DETERMINATION OF ETHYLENE POLYMERISATION CATALYSTS USING A QUENCHING METHOD WITH TRITIATED METHANOL

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The subject of this work is ethylene polymerisation using Kaminsky type catalysts: Cp2MR2=methylaluminoxane [M=Zr,W,Nb; R=Cl,CH3]. Active center determination and kinetic studies of the (Cp2WC2 + methylaluminoxane) and Cp2ZrCl2 + methylaluminoxane) systems are described, using a quenching method with tritiated methanol. The activity of the polymer was determined by liquid scintillation counting. We have found 0.5% and 87% of active centers, respectively for W and Zr system. The catalytic activity of complexes Cp2WCl2 and Cp2NbCl2 was compared with that of Cp2ZrCl2. The W and Nb complexes are found to be less active than the Zr complex.

Since the discovery of the Kaminsky's catalysts, a lot of papers have been written about the activity of these systems (biscyclopentadienyl complexes + aluminoxanes). The high activity found for these systems justify a very intense research with different metal complexes from those used by Kaminsky and coworkers (Ti, Zr and Hf complexes).1,2,3 On the other hand, the study of polymerisation was not complete without the active center determination and kinetic studies.

There are several methods for active center determination.4,5 In this study we have chosen the quenching method with tritiated methanol, which has been used with good results in active center determination with Ziegler-Natta catalysts.4,6

Experimental

Toluene: this solvent was supplied by BDH Chemicals Ltd Poole England. It was dried with sodium and then refluxed over calcium hydride and distilled. Ethylene: polymerisation grade ethylene was used. This monomer was dried over molecular sieves (zeolites 4A, BDH, nr. 54005). Aluminium Trimethyl: this alkyl was supplied by Aldrich, nr. 25722-2. Methylaluminoxane: the synthesis is described in Ref.2. Cp2ZrCl2, Cp2WCl2 and Cp2NbCl2: the synthesis of these complexes are described respectively in Refs.7,8,9. Tritiated methanol: this was prepared by exchanging 2 cm3 of tritium - labelled water with dried inactive methanol (20 cm3) in the presence of excess sodium methoxide (8 g). The tritiated methanol was purified by fractionation.
**NE 221 scintillation gel:** was supplied by Nuclear Enterprises (G.B.) Ltd, Edinburgh. It was used for assaying the labelled polymer.

**Toluene Scintran:** was supplied by BDM Chemicals Ltd Poole England. It was used for measuring the activity of the methanol.

**Polymerisation Procedure:** All the polymerisations were carried out in jacketed glass reactors in toluene (300 cm³), using an ethylene pressure of 1 bar. The toluene was refluxed inside the reactor (under vacuum) for twenty minutes before the commencement of each run.

The catalyst and cocatalyst were introduced under nitrogen. The supply and consumption of ethylene during a polymerisation run was monitored by an electronic counter system. 10

**Quenching with Tritiated Methanol:** The polymerisation reaction is terminated by the addition of tritiated methanol, which reacts quantitatively with the catalyst-polymer bonds, labelling the polymer molecules. After this, the polymer solution was transferred into a 2M solution of methanol and concentrated hydrochloric acid and this mixture was stirred during 20 minutes. Afterwards the polymer was filtered and dried at 60°C in a vacuum oven during twelve hours. The next step was the soxhlet extraction, during twelve hours, with pure methanol to clean the polymer from traces of tritiated methanol and at last it was dried again at 60°C in a vacuum oven during twelve hours.

**Calibration of the Counting Efficiency:** The efficiency (E) was determined by the Sample Channels Ratio (SCR) method. Using the E% values we can determine the specific activity (A):

$$E\% = \frac{c}{A} = \frac{cpm}{dpm}$$

cpm - counts per minute; dpm - disintegration per minute

The quenching calibration was with CHCl₃ in NE 221 Gel (Fig. 1).

![Fig. 1. Calibration of the Counting Spectrometer. Standard = 1.2 - Tritohexan normal; Extinction agent = chloroform; Solvent = gel NE 211](image)

**Metal Polymer Bonds:** From the radioactivity content of the descontaminated polymer sample, the metal-polymer bond concentration in the catalyst system, [MPB], may be evaluated using the equation:

$$[MPB] = \frac{KAG}{a}$$