

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

J. A. JUSTINO*, A. R. DIAS**, J. P. TAIT***

* *Instituto Politécnico de Santarém - ESAS, Apartado 310, 2004 Santarém Codex, Portugal*

** *C.Q.E. - I.S.T., Av. Rovisco Pais, 1096 Lisboa Codex, Portugal*

*** *Department of Chemistry, UMIST, Manchester M60 1QD, U.K.*

The subject of this work is ethylene polymerisation using Kaminsky type catalysts: Cp_2MR_2 =methylaluminoxane [$M=Zr,W,Nb$; $R=Cl,CH_3$]. Active center determination and kinetic studies of the (Cp_2WCl_2 + methylaluminoxane) and Cp_2ZrCl_2 + 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 Cp_2WCl_2 and Cp_2NbCl_2 was compared with that of Cp_2ZrCl_2 . 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

Cp_2ZrCl_2 , Cp_2WCl_2 and Cp_2NbCl_2 : 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.¹⁰ Using the E% values we can determine the specific activity (A):

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

cpm - counts per minute; dpm - disintegration per minute

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

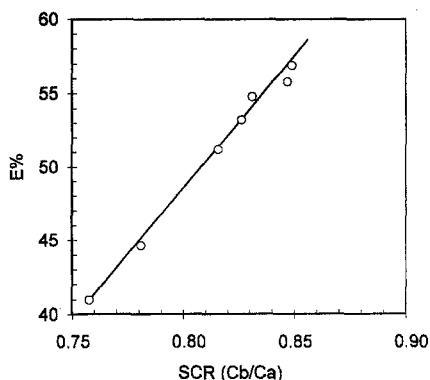


Fig. 1. Calibration of the Counting Spectrometer. Standard = 1.2 - Tritiohexan normal; Extinction agent = chloroform; Solvent = gel NE 211

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 equation⁴:

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

- [MPB] - metal-polymer bond concentration (mol l^{-1})
 G - polymer yield at time of quenching (g l^{-1})
 A - specific activity of the polymer (dpm g^{-1})
 a - specific activity of the methanol (dpm mol^{-1})
 K - correction factor for the isotope effect

Correction Factor for the Isotope Effect: This effect arises due to the difference in reactivity between the oxygen-hydrogen and oxygen-tritium bonds. Tritium, the heavier isotope, has a smaller rate constant for bond rupture. In consequence the amount of tritium incorporated into the polymer is smaller by a factor of KH/KT than the value expected if the reactivities were equal.

In the present study the correction factor has been determined by comparison of the ^3H content of polymer quenched rapidly with an excess of tritiated methanol with the tritium content of polymer quenched by slow tritiation:

$$K = \frac{A_s \times G_s}{A_F \times G_F} \quad \begin{array}{l} \text{S--slow} \\ \text{F--fast} \end{array}$$

Two K factors were determined and the average was calculated.

Active Center Determination: There is a major complication in most Ziegler-Natta polymerisation systems in that chain transfer with alkylaluminium occurs leading to the production of centers of the type $\text{R}_2\text{AlCH}_2\text{CH}_2\text{-P}$ which are non-propagative yet which will react with tritiated alcohols to yield labelled polymer chains. Thus the total concentration of metal-polymer bonds, $[\text{MPB}]_t$, will increase with time and is given by the equation :

$$[\text{MPB}]_t = C_0^* + N_{tr}$$

where: N_{tr} is the concentration of transferred metal-polymer bonds at time t ;

C_0^* is the concentration of active centers at $t=0$.

To evaluate C_0^* it is necessary to use plots of $[\text{MPB}]$ versus time⁵:

$$[\text{MPB}]_t = C_0^* + \int R_{ta} dt$$

where R_{ta} is the rate constant for chain transfer with aluminoxane.

Results and Discussion

Catalytic Activity of Complexes Cp_2ZrCl_2 , Cp_2WCl_2 and Cp_2NbCl_2 at Ethylene Polymerisation: The results are presented in Table 1; the values of rate of polymerisation were obtained for steady state, the rate of polymerisation being almost constant during the experiments.

If we compare the results presented in Table 1 we easily see that the system with Zr is much more active than the others.

Active Center Determination and Kinetic Studies of the (Cp_2ZrCl_2 + Methylaluminoxane) System: Following the method previously described in this paper at Experimental the results and their experimental conditions are as shown in Table 2.

Table 1
Catalytic activity of complexes Cp_2ZrCl_2 , Cp_2WCl_2 and Cp_2NbCl_2

Exp nr.	[Metal] mol	MAO 1 mmol Al	Al metal	t °C	time h	PE g	*R _p gPE mmolM ⁻¹ h ⁻¹	TO s ⁻¹
30	Cp_2ZrCl_2 4.47×10^{-6}	14.25	3188	60	1	24.36	6000	53.9
34	Cp_2WCl_2 4.47×10^{-6}	14.25	3188	60	2	0.94	110	1
153	Cp_2NbCl_2 2.6×10^{-5}	57	2192	70	2	6.8	113	1.29

P_{ethylene} = 1 bar

$$TO \text{ (turnover)} = \frac{\text{mol olef. conv.}}{\text{mol M s}}$$

*R_p - rate of polymerisation in steady state.

Cocatalyst = MAO 1 (methylaluminoxane prepared according to the relation Al/H₂O = 2)

PE - polyethylene

M - transition metal

Table 2
Relation between metal polymer bonds and time. (Cp_2ZrCl_2 + methylaluminoxane) system

catalyst - $Cp_2ZrCl_2 = 7.1 \times 10^{-6}$ mol

$$\frac{Al}{Zr} = 1338$$

methylaluminoxane = 9.5 mmolAl

T = 60 °C

K = 1.35

stirrer = 500 rot. min⁻¹

Solvent = 300 cm³ toluene

a = 6×10^{11} dpm mol⁻¹

P_{ethylene} = 1 bar

t min	G g l ⁻¹	A dpm g ⁻¹	[MPB] mol l ⁻¹
15	9.60	3.02×10^6	0.65×10^{-4}
30	23.37	3.01×10^6	1.58×10^{-4}
45	36.40	2.41×10^6	1.97×10^{-4}
60	52.67	2.18×10^6	2.58×10^{-4}
75	63.73	2.16×10^6	3.1×10^{-4}

The representation of the metal polymer bonds versus time is a linear correlation (see Fig. 2).

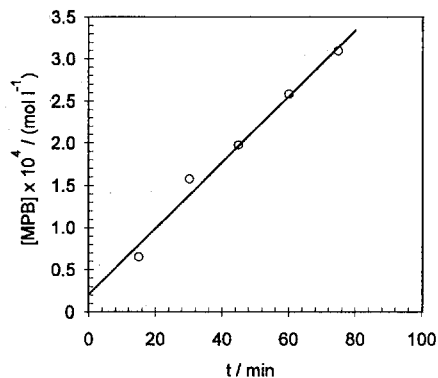


Fig. 2. Metal polymer bonds versus time. Catalytic system = Cp_2ZrCl_2 + MAO 1
 $[MPB] = 0.206 + 0.0393t$.

If we compare the equation $[MPB] = 0.206 + 0.0393t$ with:

$$[MPB]_t = C_o^* + \int_0^t R_{ta} dt$$

we have then:

$$C_o^* = 0.206 \times 10^{-4} \text{ mol l}^{-1} \quad \text{or} \quad C_o^* = 0.873 \text{ mol}(\text{molZr})^{-1} \approx 87\% \text{ active centers}$$

$$R_{ta} = 0.0393 \times 10^{-4} \text{ mol l}^{-1} \text{ min}^{-1} = 3.9 \times 10^{-6} \text{ mol l}^{-1} \text{ min}^{-1} = 6.5 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$$

Starting from the general equation $*R_p = k_p C_o^* [M]$, where:

k_p - rate constant for chain propagation

$[M]$ - the monomer concentration at the propagation centers (0.99 g l⁻¹ in toluene at 60 °C),

the experimental value for $*R_p$ is: $*R_p = 2375 \text{ g}(\text{mmolZr})^{-1} \text{ h}^{-1} = 659.72 \text{ g}(\text{mmolZr})^{-1} \text{ s}^{-1}$

$$k_p = \frac{*R_p}{C_o^* [M]} = \frac{659.72}{0.873 \times 0.99} = 763.3 \text{ l mol}^{-1} \text{ s}^{-1}$$

Starting from the general equation $R_{ta} = k_{ta} C_o^* [Al]$,

$$k_{ta} = \frac{R_{ta}}{C_o^* [Al]}$$

$$\text{where: } R_{ta} = 6.5 \times 10^{-8} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$C_o^* = 0.873 \text{ mol}(\text{molZr})^{-1}$$

$$k_{ta} = \frac{6.5 \times 10^{-8}}{0.873 \times 3.2 \times 10^{-2}}$$

$$[Al] = 3.2 \times 10^{-2} \text{ mol l}^{-1}$$

$$k_{ta} = 2.3 \times 10^{-6} \text{ s}^{-1}$$

Active Center Determination and Kinetic Studies of (Cp_2WCl_2 + Methylaluminoxane) System: An identical study for active center determination with the W system was done and the results are as shown in Table 3.

Table 3
Relation between metal polymer bonds and time. (Cp_2WCl_2 + methylaluminoxane) system

catalyst - $Cp_2WCl_2 = 1.27 \times 10^{-5}$ mol $\frac{Al}{W} = 1122$
 methylaluminoxane = 14.25 mmolAl
 T = 60 °C Solvent = 300 cm³ toluene
 K = 1.46 a = 7.99×10^{11} dpm mol⁻¹
 stirrer = 600 rot. min⁻¹ P_{ethylene} = 1 bar

Exp. nr.	t min	G g l ⁻¹	A dpm g ⁻¹	[MPB] mol l ⁻¹
23	60	0.845	1.94×10^5	2.99×10^{-7}
24	120	1.023	2.04×10^5	3.81×10^{-7}
25	180	1.360	2.15×10^5	5.34×10^{-7}
26	240	1.470	2.35×10^5	6.31×10^{-7}
27	300	1.635	2.34×10^5	6.99×10^{-7}

The representation of the metal polymer bonds versus time is a linear correlation (see Fig. 3).

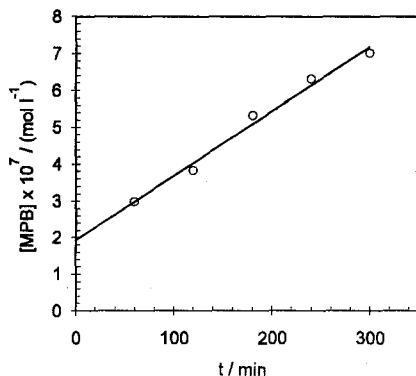


Fig. 3. Metal polymer bonds versus time. Catalytic system = Cp_2WCl_2 + MAO 1
 $[MPB] = 1.93 + 0.0175t$.

If we compare the equation $[MPB] = 1.93 + 0.0175t$ with: $[MPB]_t = C_o^* + \int_0^t R_{ta} dt$
 we have then: $C_o^* = 1.93 \times 10^{-7} mol l^{-1}$ or $C_o^* = 4.56 \times 10^{-3} mol(molW)^{-1} \approx 0.5\%$ active centers

$$R_{ta} = 0.0175 \times 10^{-7} mol l^{-1} min^{-1} =$$

$$= 1.75 \times 10^{-9} mol l^{-1} min^{-1} = 2.92 \times 10^{-11} mol l^{-1} s^{-1}$$

Starting from the general equation $R_p = k_p C_o^* [M]$

where the experimental value for ${}^*R_p = 20 \text{ g (mmolW)}^{-1} \text{ h}^{-1}$
 $= 5.55 \text{ g (molW)}^{-1} \text{ s}^{-1}$

and $[M] = 0.99 \text{ g l}^{-1}$

$$k_p = \frac{{}^*R_p}{C_o^*[M]} = \frac{5.55}{4.56 \times 10^{-3} \times 0.99} = 1.23 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$$

Starting from the general equation $R_{ta} = k_{ta} C_o^* [Al]$

$$k_{ta} = \frac{R_{ta}}{C_o^*[Al]} \quad \text{where: } R_{ta} = 2.92 \times 10^{-11} \text{ mol l}^{-1} \text{ s}^{-1}$$

$$C_o^* = 4.56 \times 10^{-3} \text{ mol (molW)}^{-1}$$

$$[Al] = 4.7 \times 10^{-2} \text{ mol l}^{-1}$$

$$k_{ta} = \frac{2.92 \times 10^{-11}}{4.56 \times 10^{-3} \times 4.7 \times 10^{-2}}$$

$$k_{ta} = 1.4 \times 10^{-7} \text{ s}^{-1}$$

Differences in Active Center and Kinetic Constants of Cp₂ZrCl₂ + MAO 1 and Cp₂WCl₂ + MAO 1: The differences are presented in Table 4.

Table 4
 Active centers and kinetic constants of Cp₂ZrCl₂ + MAO 1 and Cp₂WCl₂ + MAO 1, by quenching with tritiated methanol

System	$\frac{Al}{M}$	$\frac{{}^*R_p}{\text{g mol}^{-1} \text{ s}^{-1}}$	$\frac{C_o^*}{\%}$	$\frac{k_p}{\text{l mol}^{-1} \text{ s}^{-1}}$	$\frac{R_{ta}}{\text{mol l}^{-1} \text{ s}^{-1}}$	$\frac{k_{ta}}{\text{s}^{-1}}$
Cp ₂ ZrCl ₂ + MAO 1	1388	659.72	87	763.3	6.5 × 10 ⁻⁸	2.3 × 10 ⁻⁶
Cp ₂ WCl ₂ + MAO 1	1122	5.55	0.5	1229.4	2.9 × 10 ⁻¹¹	1.4 × 10 ⁻⁷

C_o^* - concentration of active centers at t=0

k_p - rate constant for chain propagation

R_{ta} - rate for chain transfer with aluminoxane

k_{ta} - rate constant for chain transfer with aluminoxane

The experiments were performed following identical conditions and some important conclusions could be taken.

Conclusions: As expected there is a greater activity for the Cp₂ZrCl₂ compared with Cp₂WCl₂ and Cp₂NbCl₂ (see Table 1).

For these systems, the active center determination with tritiated methanol, proved to be a quite satisfactory method and the values obtained, 80% and 0.5% for the Zr and W systems respectively, are in good agreement with the experimental results, showing a smaller activity for the (Cp₂WCl₂ + methylaluminoxane) system. Although the value $C_o^* = 4.56 \times 10^{-3} \text{ mol}$

$(\text{molW})^{-1}$ for this system seems a lower value than it was expected and this implies the high value of $k_p = 1.23 \times 10^{-3} \text{ l mol}^{-1} \text{ s}^{-1}$. Looking to the Table 4, the R_{ta} and k_{ta} values indicate that there is more chain transfer to the aluminoxane with the Zr system than with the W system.

Relatively to the $(\text{Cp}_2\text{ZrCl}_2 + \text{methylaluminoxane})$ system, the experimental results are in perfect agreement with the literature.¹¹

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