POLYMERIZATION OF ETHYLENE BY THE SILANED SiO_2 $-Mg(iBu)_2$ $-TiCl_4-$ $Al(iBu)_3$ CATALYST SYSTEM

BY

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ملخـــص

عند استخدام المحفز المدعوم الممثل بـ Silaned SiO_2 | $Mg(iBu)_2$ | $TiCl_4$ | $Al(iBu)_3$ والمحفز الغير مدعوم الممثل بـ Stauffer AA (type 1.1) لبلمرة الاثيلين عند درجة ٦٠ مئوية وجد أن سرعة التفاعل بالمحفز المدعوم تزيد حوالي ١٠٠ مرة عنه بالمحفز غير المدعوم . كما وجد أن شكل العلاقة بين سرعة التفاعل والزمن للمحفزين من النوع المتسارع . لقد بحثت العلاقة بين سرعة التفاعل اللحظي للمحفز المدعوم مع تركيز الكيل الألمنيوم حيث وصلت السرعة الى القيمة العظمى عندما كانت نسبة Al : Ti تساوي ٥١٢:١ . هذا وقد تحقق زيادة انتاج الاثيلين عند استخدام المحفز المدعوم الى الضعف عند تمرير غاز البروبلين على المحفز لمدة ١٠ دقائق قبل بداية بلمرة غاز الاثيلين .

Abstract

The polymerization of ethylene was conducted over the Silaned SiO_2 / $Mg(iBu)_2$ / $TiCl_4$ / Al $(iBu)_3$ and over the Stauffer AA type (1.1) / Al $(iBu)_3$ catalyst systems at 60 ° C . The activity of the SiO_2 – supported catalyst was about one hundred times higher than that of Stauffer AA . The rate – time profiles for both catalysts were found to be of acceleration type . The dependence of the spontaneous rate of polymerization with [Al $(iBu)_3$] has been established for the SiO_2 – supported catalyst . A maximum rate was achieved at Al: Ti ratio of 512 : 1 . The rate of ethylene production using SiO_2 – supported catalyst was increased by a factor of two when the prepolymerization time with propylene was 10 minutes .

Introduction

In the field of catalytic polymerization of ethylene and propylene the modern trend is to use highly active supported catalysts instead of unsupported Ziegler catalysts in an effort to eliminate one of the more expensive and time consuming stages of the production process , namely the removal of catalytic residues from the polymer [1–8] .

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However , the aim of this work is the preparation of a new type of supported Ziegler – Natta catalyst based on silaned silica and di – isobutyl magnesium . The performance of this catalyst will be investigated , for the polymerization of ethylene , by comparing it with the conventional Stauffer AA ($TiCl_3$ 0.33 $AlCl_3$) catalyst . Moreover , the effects of propylene prepolymerization time and the aluminium alkyl concentration , on the spontaneous rates of ethylene polymerizations , will also be discussed .

Experimental

Materials –

polymerization grade propylene (I.C.I. Plastic Division) was purified by passing over 4A and 13X molecular sieves . Nitrogen and ethylene (B.D.C. Ltd) were purified similarly . Polymerization solvent was EC 180 , pentamethylheptane (I.C.I. Ltd.) . Tri–isobutyl aluminium (Fluoro Chem. Ltd.) , di–isobutyl magnesium (Texas Alkyl Suppliers) and Silaned silica(I.C.I. Plastic Division)were used without further purification . Stauffer AA (tpye 1.1) catalyst was supplied by Stauffer Chemical Company .

Polymerisation Procedure –

The rig used for the polymerization is shown in Figure 1 . The reactor was initially charged with 0.5 dm^3 of dry EC 180 and sealed using a subaseal . The water bath was adjusted at the required temperature before switching on the stirrer and the water pump . Cold water was circulated through the condenser and the EC 180 was refluxed under vacuum for about 1 hour, while purging the system every 15 minutes with dry nitrogen . The system was purged twice with the monomer and brought up to atmospheric pressure using the solenoid valve . After 5 minutes the required amounts of tri–isobutyl aluminium was injected through the subaseal to the reactor . After approximately 3 minutes the catalyst sample was taken and injected into the reactor . The time of injection being noted and the printer – counter being zeroed and the reaction was allowed to proceed for the required time . At the end of reaction time , the monomer supply was turned off and the printer – counter switched off . Vacuum was applied to remove any unreacted monomer and nitrogen was admitted to raise the pressure to one atomosphere . While maintaining a stream of nitrogen , the reactor subaseal was removed and the base of the mushroom was removed in order to discharge the polymer slurry . The polymer slurry was treated with 25 cm^3 . of propan–2–ol and propylene oxide to deactivate the catalyst residue and precipitate any low molecular weight material , and left overnight . The slurry

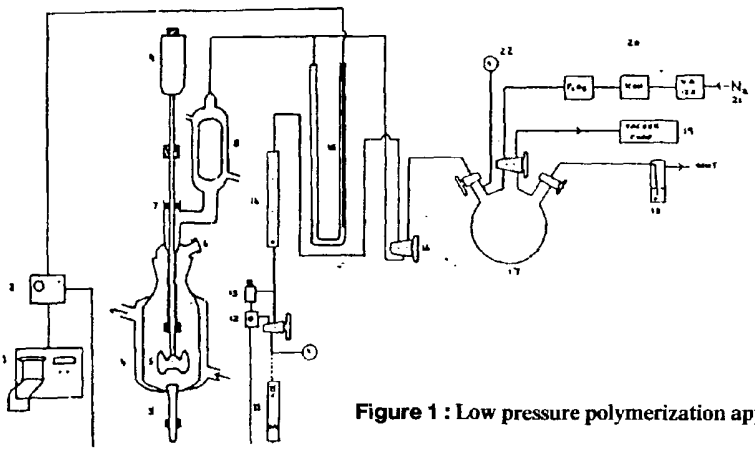

Figure 1 : Low pressure polymerization apparatus .

Fig 1 Low Pressure Polymerization Apparatus , Key to fig. 1 :

1– Sodeco printer counter
2– Pulse flow controller .
3– Reactor outlet .
4– 0.5 dm jacketed glass reactor .
5– Stainless steel, Self balancing, twin bladed paddle stirrer .
6– Reactor injection point .
7– Gaco oil seal .
8– Double wall condenser .
9– Voss S 30 CB electric stirrer motor, 0 + 2000 r.p.m.
10– CP grade ethylene supply .
11– 4A + 13X molecular seive column .
12– Solenoid valve
13– Needle valve .
14– Flow meter .
15– Electrical contact manometer .
16– Two way tap .
17– Buffer flask .
18– Paraffin oil bubbler .
19– Single stage Edwards high vacuum pump .
20– 13X and 14A molecular seive, KOH pellets and P_2O_5.
21– White spot grade nitrogen supply .
22– Vacuum gauge .

was filtered under vacuum and the polymer washed with 60 – 80 pet. ether . The polymer was then dried at 60 °C overnight , allowed to cool and weighed .

Rate Measurement :

The average rate of reaction is measured from the equation

$$R_{av} = \frac{\text{Yield (g Polymer)} \quad X \quad 1}{\text{Amount of titanium (mmol)} \,.\, \text{Time of Polym. (h)}}$$

However , the instantaneous rate is calculated by using the output from the sodeco and the yield of polymer formed , i.e.

$$R_p = \frac{\text{Yield (g Polymer)} \quad X\ 60\ X \text{ number of pulses / minute}}{\text{Total number of pulses} \quad X \quad \text{Amount of titanium (m mol)}}$$

R_p = g Polymer / mmol Ti. hour .

Catalyst preparation –

The method used for the catalyst preparation was as follows [9]:

The silaned silica was dried for 4 hours at 150 ° C in a vacuum oven . 9.6 g of the dried silica were transferred to a 3–necked flask and flushed with N_2 for 30 minutes . After that 36 ml. of the mixture composed of 10 % solution in heptane 1 part $AlEt_3$ and 7.5 parts $Mg(iBu)_2$ and 60 ml of pure heptane were added to the 3–necked flask and stirred for 30 minutes at room temperature . 1.85 ml of $TiCl_4$ were added to the mixture which was stirred for 30 minutes more at room temperature (the mixture color changed from white to black after the addition of $TiCl_4$) . The solvent was then removed by heating in oil bath at 90 ° C for about 3 hours . The catalyst was then dried by heating in vacuum oven at 65 ° C for 3 hours .

The percentage by weight of titanium in the catalyst was determined by measuring the optical density of the yellow solution resulting from the addition of H_2SO_4 / $HClO_4$ and hydrogen peroxide . The % Ti was found to be equal to 4.56 .

Results and Discussion

Comparison of the kinetic behaviour between the supported silaned SiO_2 / Mg $(iBu)_2$ / $TiCl_4$ / Al $(iBu)_3$ and the unsupported $TiCl_3$. 0.33 $AlCl_3$ catalyst systems for the polymerization of ethylene is shown in Table 1 . It can be seen that the activity of SiO_2 – supported catalyst is about 100 times higher than that of the unsupported catalyst .

Table 1 : Some Typical Values of Catalyst Activities

Catalyst	[Ti] / mmol. dm^{-3}	[Al] : [Ti]	Yield g / 2 h	Average rate g PE. mmol Ti^{-1} $.h^{-1}$
1– S. $TiCl_3$ 0.33 $AlCl_3$ –$Al(iBu)_3$	3	4 : 1	9.3	3.1
2– Silaned SiO_2 / $Mg(iBu)_2$ / $TiCl_4$ / $Al(iBu)_3$	0.3	512 : 1	13.0	380

Solvent EC 180 , Temp. 60 ° C .

The instantaneous rate of polymerization at a given time is represented either by [10]

$$R_p = k_p C^* [M] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

(where [M] is the bulk concentration of monomer , C^* is the concentration of active centres and k_p is the relevent propagation rate constant) , or by [11]:

$$R_p = k_p C^* \theta_M \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

(where θ_M is the fraction of active centres covered by adsorbed monomer , C^* is the total concentration of active centres and k_p is the propagation rate constant for adsorbed monomer) . Therefore equation (1) may be regarded as a special case of equation (2) where the value of θ_M is very low .

According to equation (2) , the influence of the silaned–SiO_2 / $Mg(iBu)_2$ support on the catalyst activity can be attributed to the increase in some or all of C^* , k_p and θ_M . The increase in the concentration of the active centres , when using the silica support , can be attributed to the more efficient use of titanium atoms . This is because the surface area of the support is 295 m^2 / g whereas that of Stauffer is between 10 – 40 m^2 / g . On the other hand , the increase in k_p can be attributed to both steric and electronic effects [2] . Higher values of C^* , k_p and θ_M were also reported [12] for the polymerization of 4-methyl-1-pentene when using the $MgCl_2$ -supported catalyst compared to Stauffer AA catalyst .

The profiles of the rate of polymerization versus time graphs for the Stauffer AA / $Al(iBu)_3$ / ethylene and the silaned – SiO_2 / $Mg(iBu)_2$ / $TiCl_4$ / $Al(iBu)_3$ / ethylene catalyst systems were found to have curves of the acceleration type and not of the decay type often characteristic of $MgCl_2$ – supported catalyst [2] . This indicates that

Fig. (2)

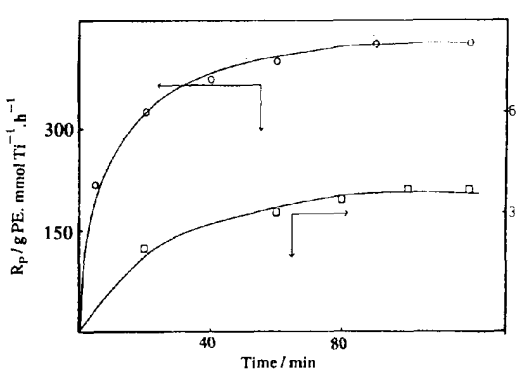

Figure 2 : Plots of rate versus time for the polymerization of ethylene at 60 ° C using :
○ Silaned – SiO_2 / $Mg(iBu)_2$ / $TiCl_4$ / $Al(iBu)_3$ [Ti] = 0.034 m mol. dm^{-3} ; [Ti] : [Al] = 1 : 512 .
□ Stauffer AA (type 1.1) / $Al(iBu)_3$. [Ti] = 3 m mol. dm^{-3} ; [Ti] : [Al] = 1 : 4 .

the titanium active centres located at the SiO_2 matrix in the supported catalyst are stable in just the same way as those located at the $TiCl_3$ matrix in the Stauffer AA catalyst system , whereas those located at the $MgCl_2$ matrix are not stable and decompose with time . Maxima in the instantaneous rates of polymerization are observed in Figure (2) for SiO_2 – supported catalyst and Stauffer AA at about 80 + 100 minutes respectively . After that the rate remains constant with time .

On the other hand , the dependence of the average rate of polymerization on tri-isobutyl aluminium concentration , when using the silica supported catalyst system is shown in Table 2 . The concentration of the catalyst was kept constant while the alkly concentration was varied in the range [Al] / [Ti] = 200 – 700 .

Table 2 : The effect of variation in [Al] / [Ti] ratio using the SiO_2 / $Mg(iBu)_2$ / $TiCl_4$ / $Al(iBu)_3$ catalyst system .

Run no.	[Al] / [Ti]	Yield g/h	Average rate $g\,PE.mmd\,Ti^{-1}.h^{-1}$	Average rate $g\,PE.g\,cat^{-1}.h^{-1}$
1	234	4.8	271	356
2	351	4.9	287	363
3	512	5.9	345	437
4	702	5.2	304	385

[Ti] = 0.0342 mmol. dm^{-3} , $[Al(iBu)_3]$ = 8,12,17.5 and 24 mmol. dm^{-3} , Temp. = 60 ° C , diluent volume = 500 cm^{-3} , % Ti = 4.56

It can be seen that a maximum in the average rate was achieved at a molar ratio of Al : Ti of 512 : 1 , whereas further increase in Al:Ti ratio caused a decrease in the average rate of polymerization as previously observed by other workers [13–14] . Tait attributed the increase in the maximum rate with increase in the alkly concentration to the increase in the number of active centres whereas he explained the decrease in the rate after the maximum to the competitive adsorption of aluminium alkyl with monomer . However , Figure 3 illustrates the form of rate–time plots with variation of alkyl concentration . The form of the plot did not change appreciably with increasing concentration of aluminium alkyl . The large difference in the Al : Ti molar ratio for the two catalyst systems , shown in Table 1 , can be attributed to the higher values in the number of active centres and the rate of transfer with respect to the aluminium alkyl for the SiO_2_ supported catalyst system [12] .

Fig. (3)

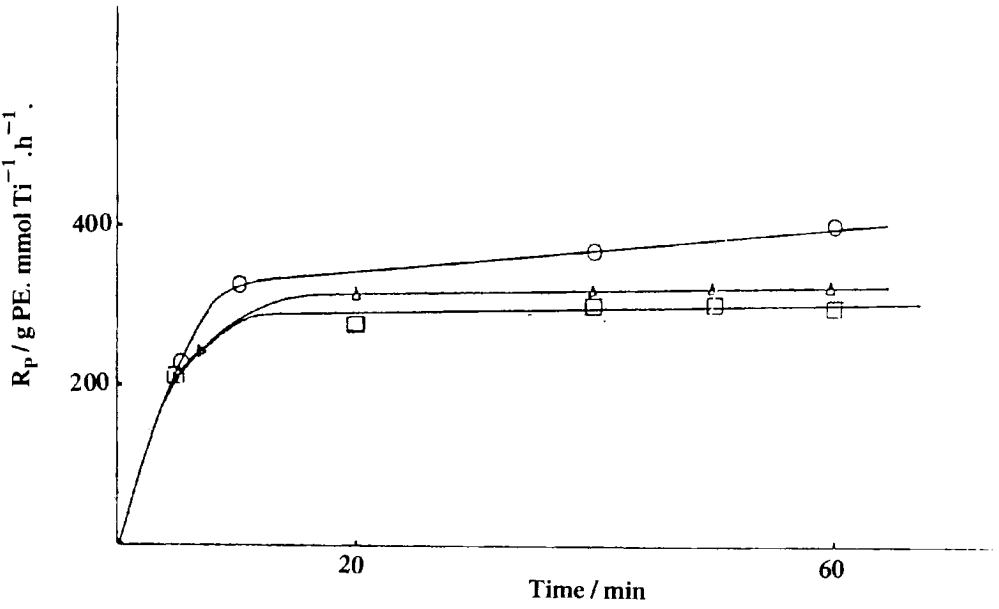

Figure 3 : Plots of rate versus time for the polymerization of ethylene at 60 ° C using the Silaned $-SiO_2$ / Mg $(iBu)_2$ / $TiCl_4$ catalyst for varying concentrations of triisobutyl aluminium . [Ti] = 0.034 m mol. dm^{-3} .
○ [$Al(iBu)_3$] = 17.4 m mol. dm^{-3} .
△ [$Al(iBu)_3$] = 24 m mol. dm^{-3} .
□ [$Al(iBu)_3$] = 8 m mol. dm^{-3} .

The effect of variation in the prepolymerization time of propylene on the average rate of ethylene polymerization using the SiO_2_ supported catalyst is shown in Table 3 . The polymerization rate rises to a maximum value at prepolymerization time of 10 minutes followed by a gradual fall in rate with increase in the prepolymerization time . No consumption of propylene was observed during the prepolymerization periods of this study , since polymerization of propylene requires higher concentration of catalyst than the one used in case of ethylene polymerization . The results in Table 3 can be attributed to the change in the crystallite size or the catalyst during the prepolymerization times . To get more information about this dependence we intend to study , the effect of prepolymerization time on the propagation rate constant and the number of active centres .

Table 3 : The effect of variation in the prepolymerization time of propylene using the SiO_2 / $Mg(iBu)_2$ / $TiCl_4$/ $Al(iBu)_3$ / ethylene catalyst system .

Run no.	Prepoly. time / min	Yield g / 2h	Average rate $gPE.mmol\,Ti^{-1}.h^{-1}$	Average rate $g\,PE.g\,cat^{-1}.h^{-1}$
1	0	13.0	380	481
2	5	18.0	526	667
3	10	27.0	790	1000
4	20	21.8	637	807
5	30	16.3	497	604

[Ti] = 0.0342 mmol. dm^{-3} ., [Al] = 17.4 mmol. dm^{-3} , Temp. = 60 ° C , % Ti = 4.56

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