

Description

Background of the Invention

5 This invention relates to the polymerization of a mono-1-olefin such as ethylene using a modified silica-supported chromium oxide catalyst.

It is well known that mono-1-olefins such as ethylene can be polymerized with catalyst systems employing vanadium, chromium or other metals on a support such as alumina, silica, aluminum phosphate, titania, zirconia, magnesia and other refractory materials. Initially such catalysts were used primarily to form
 10 homopolymers of ethylene. It soon developed, however, that many applications required polymers which were more impact resistant than ethylene homopolymers. Consequently, in order to produce polymer having short chain branching like the more flexible free radical polymerized ethylene polymers, comonomers such as propylene, butene, hexene or other higher olefins were copolymerized with the ethylene to provide resins tailored to specific end uses. The copolymers, however, are more expensive to
 15 produce since inventories of different monomers must be kept and also the comonomers are generally more expensive than ethylene. Linear ethylene polymers with short chain branching can be formed from a pure ethylene feed using the old free radical high pressure process, but the conditions necessary to do this make the product too expensive to be commercially competitive.

Summary of the Invention

Accordingly it is an object of this invention to provide a low cost route to linear ethylene polymers having toughness imparted by short chain branching;

it is a further object of this invention to provide a process by which ethylene polymers having the
 25 properties associated with copolymers can be obtained from a pure ethylene feed; and

it is still yet a further object of this invention to provide an improved polymerization process.

It has now been found that comonomers can be generated in situ to give tough olefin copolymers from a pure ethylene feed by utilizing a catalyst comprising chromium on a predominantly silica support which support is first activated in an oxygen-containing ambient, thereafter reduced with carbon monoxide and
 30 then precontacted with a cocatalyst selected from trialkyl boron compounds and dialkyl aluminum alkoxide compounds prior to contact with the ethylene monomer.

Description of the Preferred Embodiments

35 The support must be a predominantly silica support. By predominantly silica is meant either an essentially pure silica support or a support comprising at least 90 percent silica, the remaining being primarily other oxides such as alumina, zirconia or titania. Preferably the support contains 95 to 98 weight percent silica and 2 to 5 weight percent titania (TiO_2).

Silica titania supports are well known in the art and can be produced as disclosed in Dietz, U.S.
 40 3,887,494.

The catalyst component must be a chromium compound. The chromium component can be combined with the silica component in any manner known in the art such as by forming a coprecipitate with the silica or forming a coprecipitated tergel of the silica, the titanium component and the chromium component. Alternatively an aqueous solution of a water soluble chromium component can be added to the hydrogel of
 45 silica component. Suitable chromium compounds include chromium nitrate, chromium acetate, and chromium trioxide. Alternatively a solution of a hydrocarbon soluble chromium component such as tertiary butyl chromate, a diarene chromium compound, biscyclopentadienyl chromium II or chromium acetyl acetonate can be used to impregnate the silica xerogel which results from removal of water from the hydrogel.

The chromium component is e.g. used in an amount sufficient to give .05 to 5, preferably 0.5 to 2
 50 weight percent chromium based on the total weight of the chromium and support after activation.

The resulting chromium component on the predominantly silica support is then subjected to activation in an oxygen-containing ambient in the manner conventionally used in the art. Because of economy, the preferred oxygen-containing ambient is air, preferably dry air. The activation is carried out at an elevated temperature for e.g. about one half to about 50 hours, preferably 2 to 10 hours at e.g. a temperature within
 55 the range of 400 to 900 °C. Under these conditions at least a substantial portion of any chromium in a lower valent state is converted to the hexavalent form by this calcination procedure.

The resulting calcined supported catalyst component is cooled and then subjected to at least partial reduction of the hexavalent chromium to a lower valent state prior to combining with the cocatalyst. The

reducing agent must be carbon monoxide. The carbon monoxide can be employed at temperatures between 300 and 500°C although it is more often employed at temperatures in the range of about 350 to 450°C. The partial pressure of the reducing gas in the reduction operation can be varied from subatmospheric pressures to relatively high pressures, but the simplest reducing operation is to utilize essentially pure carbon monoxide at about atmospheric pressure.

The reduction time can vary from a few minutes to several hours or more. The extent of reduction can be followed by visual inspection of catalyst color. The color of the initial activated catalyst is generally orange, indicating the presence of hexavalent chromium. The color of the reduced catalyst employed in the invention is blue, indicating that all or substantially all of the initial hexavalent chromium has been reduced to lower oxidation states, generally the divalent state.

The course of the reduction of the air-activated orange catalyst with carbon monoxide can be determined exactly by pulse titration. A known amount of carbon monoxide is added per pulse and the amount of evolved carbon dioxide is measured. When reduction is complete only carbon monoxide will be present and the catalyst is blue in color. The reduced blue catalyst can be titrated with pulses of oxygen to convert the catalyst to the original orange color. When oxidation is complete, oxygen will be evident in the offgas.

After reduction, the reduced supported catalyst component is e.g. cooled to about room temperature, e.g. 25°C in an inert atmosphere such as argon or nitrogen to flush out the carbon monoxide. After this flushing treatment the catalyst is e.g. kept away from contact with either carbon monoxide or oxygen.

The cocatalyst is either a trialkyl boron component or a dialkyl aluminum alkoxide component wherein the alkyl group has 1 to 10 carbon atoms, preferably 2 to 4 carbon atoms. By far the most preferred component is the single compound triethyl borane.

The cocatalyst is used e.g. in an amount within the range of 0.5 to 10 weight percent based on the weight of the reduced supported chromium component being treated, with about 1 to 8 weight percent being preferred. The blue color of the reduced supported catalyst component can change to greenish-blue after treatment, however it is believed the chromium remains in the divalent state. Stated in parts per million of the cocatalyst based on diluent only, the cocatalyst is used in an amount within the range of 0.5 to 20 preferably 2 to 8 ppm based on diluent in the reactor.

The order of addition of the components is critical to the operation of this invention. It is essential that the cocatalyst and the reduced supported catalyst be precontacted prior to contact with the monomer. In a batch operation this can be carried out by either pretreating the supported catalyst component with the cocatalyst and then adding the resulting composition to the reactor or the supported catalyst and cocatalyst can be added as separate streams to the reactor and thereafter the monomer can be added. It is preferred however to utilize a precontacting vessel. In this manner the supported catalyst and the cocatalyst can be introduced either continuously or batchwise generally utilizing a solution of the cocatalyst in a solvent or diluent, preferably the same material being used as a solvent or diluent in the subsequent polymerization reaction. In this precontacting vessel agitation is provided by means of a stirrer, for instance, to obtain precontacting of the supported catalyst component and the cocatalyst.

Thereafter, the resulting supported catalyst/cocatalyst composition is introduced into the reactor. Preferably the precontacting is carried out immediately prior to the introduction thereof into the reactor although the resulting supported catalyst/cocatalyst composition can be stored under inert conditions if desired prior to being utilized in a polymerization reaction.

The invention is primarily contemplated for in situ generation of comonomer in a polymerization reaction utilizing an essentially pure ethylene feed. By pure ethylene feed is meant polymerization grade ethylene free of any significant amount of other monomers, e.g. not more than 1 mole percent. The affirmative introduction of a comonomer so as to form a copolymer of the ethylene, the introduced comonomer and the comonomers generated in situ could be utilized if desired but this would dilute one important aspect of the invention which is the economy effected by being able to produce copolymers without the use of a separate comonomer feedstream.

While applicants do not wish to be bound by theory, it is believed that comonomer generated in situ is primarily hexene, i.e. the short chain branching in the resulting polymer will be butyl branches. This is particularly true when operating under conditions so as to give higher density, although some octene may also be present. When operating under conditions to give lower density some butene is produced also.

The amount of comonomer generated in situ can be varied so as to adjust the density to the desired level by increasing the amount of cocatalyst which will increase the amount of in-situ generated comonomer. By this means, density from 0.920 to 0.960 can be produced, although generally polymers in the density range of 0.930 to 0.955 are made in accordance with the invention. In addition, a small amount of comonomer can be affirmatively added as noted hereinabove to fine tune the density if desired.

Polymerization can be carried out in any manner known in the art such as gas phase, solution or slurry polymerization conditions. A stirred reactor can be utilized for a batch process, or the reaction can be carried out continuously in a loop reactor or in a continuous stirred reactor.

A preferred polymerization technique is that which is referred to as a particle form or slurry process wherein the temperature is kept below the temperature at which polymer goes into solution. Such polymerization techniques are well known in the art and are disclosed, for instance, in Norwood, U.S. 3,248,179.

The preferred temperature in the particle form process is within the range of 200 to 230°F (193 to 110°C). Two preferred polymerization methods for the slurry process are those employing a loop reactor of the type disclosed in Norwood and those utilizing a plurality of stirred reactors either in series, parallel or combinations thereof wherein the reaction conditions are different in the different reactors. For instance, in a series of reactors a chromium catalyst which has not been subjected to the reduction step can be utilized either before or after the reactor utilizing the catalyst system of this invention. In another specific instance, a conventional chromium oxide on a predominantly silica support can be utilized in a reactor in parallel with a reactor utilizing the catalyst system of this invention and the resulting polymerization effluents combined prior to recovering the polymer.

The molecular weight of the polymer can be controlled by various means known in the art such as adjusting the temperature (higher temperature giving lower molecular weight), introducing hydrogen to lower the molecular weight or varying the catalyst compounds.

Examples

All of the supports utilized in the following examples are commercial silica-titania cogel supports containing a nominal 2.5 weight percent titanium containing a chromium component in an amount sufficient to give a nominal 1 weight percent chromium, these percentages being based on the weight of the calcined silica/titania/chromium compound composite. The cogel support has a nominal pore volume of 2.35 cm³/g and a nominal surface area of 450 m²/g based on nitrogen sorption measurements.

The supported catalysts were calcined by fluidizing a 55 cm³ portion of the supported catalyst with dry air in a quartz tube heated to the temperature indicated for three hours and then cooling to about 25°C and flushing with argon or nitrogen.

The invention catalysts were prepared by sequential heating of the supported chromium component in air under fluidizing conditions at the temperatures specified in the manner described hereinabove, flushing the air out with nitrogen or argon as the temperature was reduced to the reduction temperature specified and continuing the heating in a CO ambient for the time specified, generally one half or one hour. The resulting blue-colored supported catalysts were then cooled to about 25°C in the inert gas stream and stored in dry vessels under an inert gaseous atmosphere until ready for testing. The thus activated supported catalysts were then impregnated with the specified quantity of a hydrocarbon solution of the cocatalyst in the absence of air and the solvent removed by gentle evaporation to yield greenish-blue colored supported catalyst compositions.

In the control runs demonstrating the necessity for precontacting the supported catalyst was charged to the reactor in the absence of air and the cocatalyst added separately after contact of the ethylene and the supported catalyst.

Example I

The purpose of Example 1 is to demonstrate that only chromium is active under the conditions employed. For this reason triethyl aluminum was used as a cocatalyst since it was believed to be the best cocatalyst for achieving some degree of polymerization in all of the runs.

A variety of transition metals were supported on Davison's 952 silica. After impregnation all the catalysts were vacuum dried and air activated at 800°C, cooled to 400°C in nitrogen and finally reduced with carbon monoxide at 340° or 400°C. Details of the supported catalyst preparation through the calcination stage are as follows.

2 wt.% Mo on 952 Silica: 0.94g of ammonium molybdate were dissolved in 40ml of deionized water and impregnated onto 25g of silica. The catalyst was air activated at 800°C (surface area = 177 m²/g).

4 wt.% W on 952 Silica: 1.55g of ammonium tungstate were dissolved in 40ml of deionized water and impregnated onto 25g of silica. The catalyst was air activated at 800°C (surface area = 177 m²/g).

1 wt.% V on 952 Silica: 0.58g of ammonium vanadate were dissolved in 40 ml of ~2M H₂SO₄ and impregnated onto 25g of silica. The catalyst was air activated at 800°C (surface area = 204 m²/g).

6 wt.% U on 952 Silica: 1.35g of uranyl nitrate were dissolved in 25 ml of deionized water and impregnated onto 10g of silica. The catalyst was air activated at 800 °C (surface area = 230 m²/g).

2 wt.% Nb on 952 Silica: Using a nitrogen filled glove box, 0.5g of NbCl₅ were dissolved in 25ml of absolute ethanol and impregnated onto 10g of silica. The catalyst was air activated at 800 °C (surface area = 248 m²/g).

4 wt.% Ta on 952 Silica: Using a nitrogen filled glove box, 0.85g of TaCl₅ were dissolved in 25ml of absolute ethanol and impregnated onto 10g of silica. The catalyst was air activated at 800 °C (surface area = 243 m²/g).

Table 1 shows that the catalyst must be chromium on silica; other transition metals will not work, even though they are broadly disclosed in the prior art. The CO reduction time was one half hour. Conditions used in Table 1 represent the best known.

TABLE 1

Run	Catalyst	Activation Temp. °C	CO Reduction Temp. °C	Activity g/g cat./min
1	Cr/silica	800	340	1473/30
2	V/silica	800	400	Dead
3	U/silica	800	400	Trace
4	W/silica	800	400	Dead
5	Mo/silica	800	400	Dead
6	Ta/silica	800	400	Dead
7	Nb/silica	800	400	Dead

All runs were made at 95 °C, adding 1 ml of .5% TEA prior to contact with monomer. After 15-20 minutes of inactivity, another ml of 15% TEA was added in runs 2-7, just in case higher concentrations of TEA were needed. However, this did not produce any activity. The Cr/silica catalyst of Run 1 produced polymer having an HLMI of 5.4 and a density of 0.9426.

Example II

The purpose of this example is to compare the effect of various supports for the chromium transition metal component which the previous example showed was the only one capable of giving activity in a catalyst preparation procedure involving calcination followed by carbon monoxide reduction.

This example shows the effect of varying the support in the context of the chromium catalyst Example 1 showed to be critical when using the calcination followed by CO reduction. The supported catalysts were prepared as follows:

1 wt.% Cr on Alumina: 1.17g of chromium nitrate were dissolved in deionized water and impregnated onto 15g of calcined Ketjen G alumina. The catalyst was air activated at 800 °C (surface area = 258 m²/g).

1 wt.% Cr on Magnesia: 1.17g of chromium nitrate were dissolved in deionized water and impregnated onto 15g of calcined magnesia. The catalyst was air activated at 500 °C (surface area = 45.3 m²/g).

1 wt.% Cr on Titania: Some tetra-n-butoxide titanium was hydrolyzed with water to TiO₂, washed, and then vacuum dried. After drying, 1.17g of chromium nitrate were dissolved in 25ml of deionized water and impregnated onto 15g of the titania. The catalyst was air activated at 500 °C (surface area = 21.6 m²/g).

1 wt.% Cr on Zirconia: Some tetra-n-butoxide zirconium was hydrolyzed with water to ZrO₂, washed, and then vacuum dried. After drying, 1.17g of chromium nitrate were dissolved in 25ml of deionized water and impregnated onto 15g of the zirconia. The catalyst was air activated at 500 °C (surface area = 103.0 m²/g).

Table 2 shows that, although many supports are broadly disclosed in the prior art, only Cr/silica gives this effect of good activity and lowered density.

TABLE 2

Run	Catalyst	Activation Temp. °C	Activity g/g cat./min	HLMl	Density,*	Cocat.
8	Cr/silica	air-800; CO-340	2162/30m	52.3	.9276	TEB
9	Cr/silica	air-800	3522/40m	4.30	.9588	TEB
10	Cr/AlPO ₄ -.4	air-700; CO-300	1072/30m	1.27	.9577	NONE
11	Cr/AlPO ₄ -.4	air-700; CO-300	1130/30m	9.50	.9530	TEB
12	Cr/AlPO ₄ -.4	air-700; CO-300	447/30m	5.0	.9598	H ₂
13	Cr/MgO	air-500; CO-400	DEAD	--	--	TEB
14	Cr/ZrO ₂	air-500; CO-400	DEAD	--	--	TEB
15	Cr/TiO ₂	air-500; CO-400	DEAD	--	--	TEB
16	Cr/Alumina	air-800; CO-400	519/30m	0	.9492	TEB
17	Cr/Alumina	air-800;	619/30m	0	.9487	TEB
18	Cr/AlPO ₄ -.9	air-700;	1890/45m	0.4	.9609	None
19	Cr/AlPO ₄ -.9	air-700; CO-300	1545/30m	66.6	.9650	TEB

*Density in g/cm³ was determined on a compression molded sample cooled at 15 °C/hour and conditioned for 40 hours at room temperature in accordance with ASTM D1505 and ASTM D1928 condition C.

Runs 8 and 9 used a Cr/silica Tergel having 2 wt.% Ti.

All runs were made at 95 °C with 1ml of .5 wt.% TEB precontacted with 0.05 to 0.1g of supported catalyst, except the AlPO₄ runs were made at 100 °C.

These runs also show that with the chromium/silica composition the carbon monoxide treatment is essential to effect a lowering of the density.

Table 2 shows that only silica in combination with the CO treatment works to give high productivity and to lower the density, thus indicating in-situ production of comonomer.

Example III

This example shows the effect of various cocatalysts used with the chromium on silica support which is calcined and subsequently reduced in CO. The cocatalyst which is precontacted with the support prior to contact with the monomer.

TABLE 3

Run	Cocatalyst	Activity g/g cat/min	MI ⁽⁵⁾	HLMl ⁽⁶⁾	Ratio	Density
20	1ml TEB (OX)*	3522/40	0	4.3	-	.9580
21	1ml TEB (OX)*	4675/45	.04	2.7	68	.9588
22	1ml TEB	2162/30	1.41	51.3	36	.9276
23	1ml TEA ⁽¹⁾	1473/30	.075	5.37	72	.9426
24	1ml TMA ⁽²⁾	1221/30	0	3.10	-	.9435
25	1ml DEZ ⁽³⁾	2600/30	.05	2.80	55	.9527
26	1ml DEALE	597/30	.43	26.3	61	.9348
27	1ml MgBu ₂	1741/30	.10	6.00	60	.9431
28	1ml DEAC ⁽⁴⁾	629/30	0	1.90	-	.9529

* not reduced

⁽¹⁾ triethyl aluminum

⁽²⁾ trimethyl aluminum

⁽³⁾ diethyl zinc

⁽⁴⁾ diethylaluminum chloride

⁽⁵⁾ Melt index, g/10 min, ASTM-D-1238 cond. F

⁽⁶⁾ High load melt index, g/10 min, ASTM-D-1238 cond. E

All runs were made with Tergel catalyst 2% Ti, Air 800 °C, CO 340 °C, adding catalyst and cocatalyst to the

reactor first with isobutane, i.e. before the ethylene monomer.

Clearly TEB stands alone as the best cocatalyst. DEALE (diethylaluminum ethoxide) is a second best choice. A comparison of runs 20 and 21 with 22 further shows that the reduction treatment is essential.

5 Example IV

This example shows another comparison of the different metal alkyls, but at half the concentration in Table 3. The results are shown in Table 4.

10 TABLE 4

Run	Cocatalyst	Activity g/g cat/min	MI	HLMI	Ratio	Density
29	.5ml TEB	1344/30	.83	32.7	39	.9353
30	.5ml TMA	1183/30	.06	3.21	53	.9453
31	.5ml DEZ	2256/30	.08	4.50	56	.9529
32	.5ml DEALE	1230/30	.18	9.60	53	.9424
33	.5ml MgBu ₂	1303/30	.07	3.12	44	.9484
34	.5ml DEAC	809/30	0	2.70	-	.9529
35	.5ml TEA	1565/30	.06	4.00	67	.9452

All runs were made with Cr/silica-titania, air 800°C, CO 340°C, polymerization at 95°C, with cocatalyst added with the initial isobutane charge of supported catalyst so that the supported catalyst contacted the cocatalyst before monomer addition. Again TEB is clearly superior, and DEALE is the second choice. DEAC and DEZ had no effect at all on the density. Table 5 shows the effect of metal alkyl concentration.

TABLE 5

Run	Cocatalyst	Activity g/g cat/min	MI	HLMI	Ratio	Density
36	None	745/45	.42	30.6	73	.9639
37	.25ml TEB	2153/30	.22	10.8	49	.9440
38	.50ml TEB	1344/30	.83	32.9	39	.9353
39	1.0ml TEB	2162/30	1.4	51.3	36	.9276

Thus it is seen that the more metal alkyl added to the reactor, the lower the density.

Example V

This example shows the results of using different reducing treatments. In each example, Cr/silica-titania catalyst (2%Ti) was calcined in air at 800°C for three hours, then reduced for 30 minutes at the temperature shown with the treatment listed. Polymerization runs were then made at 95°C using TEB as cocatalyst. TEB was added with the initial isobutane charge of supported catalyst, so that the catalyst contacted the TEB before the ethylene. The results are shown in Table 6.

TABLE 6

Run	Reducing Treatment	Catalyst Color	Flashed w Air	Activity g/g cat/30min	MI	HLMI	Ratio	Density
40	None	Orange	NO	4675/45	.04	2.70	68	.9588
41	None	Orange	NO	3522	0	4.30	--	.9580
42	CO-340 °C	Blue	YES	2162	1.41	51.2	36	.9276
43	CO-500 °C	Blue	YES	2610	0.32	16.8	53	.9346
44	Hexane-200 °C	Green	YES	3117/45	0	0.80	--	.9569
45	Hexane-150 °C	Green	NO	2110	0	2.30	--	.9578
46	Hexane-300 °C	Green	YES	2030/47	0	0.96	--	.9467
47	Hexane-500 °C	Brown	NO	DEAD				
48	3-Hexene-200 °C	Green	YES	222/45	0	1.50	--	.9592
49	3-Hexene-200 °C	Green	YES	DEAD				
50	Methane-400 °C	Blue-Gr	YES	4000	0	0.61	--	.9472
51	Methane-500 °C	Blue-Gr	YES	643	0	2.00	--	.9490
52	Acetylene-200 °C	Brown	NO	DEAD				
53	CS ₂ -350 °C	Brown	NO	DEAD				
54	MeOH-350 °C	Blue-Gr	NO	DEAD				
55	Ti(OEt) ₄ -300 °C	Blue-Gr	NO	DEAD				
The Following Runs made at 102 °C instead of 95 °C:								
56	None	Orange	NO	754/45	.42	30.6	73	.9639
57	Hexane-200 °C	Green	YES	2000/45	.09	5.47	62	.9556
58	Hexane-300 °C	Green	YES	536/46	.17	7.40	44	.9500
59	3-Hexene-200 °C	Green	YES	DEAD				
The Following Runs made at 95 °C with .5ml instead of 1ml of cocatalyst solution:								
60	Hexane-200 °C	Green	YES	1860/45	0	1.80	--	.9639
61	3-Hexene-150 °C	Green	NO	154	--	--	--	--
62	CO-340 °C	Blue	YES	1344	.83	32.7	39	.9353

Clearly CO stands alone as the preferred reducing treatment, and the preferred temperature of reduction is 300-600 °C. No other treatment lowered the density enough to be useful. CO is only treatment that gave a high enough melt index to allow the production of polymers having a spectrum of melt processing characteristics through known process variables to lower and raise the MI.

Example VI

Example VI shows some runs made with diethyl aluminum ethoxide (DEALE) as the cocatalyst. This time a solution of 1 g DEALE in 100 ml of isobutane was used. Again the cocatalyst was charged to the reactor with the initial charge of isobutane and supported catalyst so that the catalyst contacted the DEALE before it contacted the ethylene. Again the catalyst was silica titania (2% Ti).

TABLE 7

Run	Activation		Reac tor Temp. °C	DEALE CONC.	ACTIVITY g/g cat/min	MI	HLMI	RATIO	DEN.	FLEX. ⁽²⁾ MPa	ESCR ⁽¹⁾
	Air	CO									
60	850 °C	None	102	1ml	3870/30	.12	8.0	67	.9577	1347	82
61	700 °C	350 °C	"	"	970/30	.95	48	50	.9261	--	--
62	"	"	"	"	2260/85	.97	55	56	.9325	--	--
63	850 °C	NONE	"	"	3790/30	.10	8.9	89	.9584	1290	128
64	850 °C	NONE	95	1ml	9801/51	0	.80	--	.9585	1282	320
65	"	"	96-H ₂	"	6520/55	.28	17.3	62	.9574	1531	41
66	"	"	96-H ₂	"	2228/84	.22	17.0	77	.9601	1523	58
67	"	350 °C	"	"	2861/50	.28	15.8	56	.9442	877	200
68	"	"	"	"	1480/60	.87	49.1	56	.9303	501	--
69	850 °C	NONE	96	2ml	10904/60	.02	2.70	136	.9587	1290	267
70	850 °C	350 °C	90-H ₂	1ml	1320/47	1.4	80.6	59	.9283	521	--
71	"	"	90	"	1430/40	.33	19.6	59	.9317	551	>1000
72	"	"	90	2ml	1390/40	.27	17.6	65	.9330	572	288

The following catalysts were made by impregnating DEALE on Cat.

73	850 °C	NONE	96	4ml/g	4142/60	.03	2.70	90	.9626	1560	113
74	"	"	" -H ₂	"	600/52	.19	13.5	71	.9636	1585	--
75	"	"	" -H ₂	"	1154/40	.68	37	54	.9640	1710	14
76	"	350 °C	90-H ₂	"	1400/50	.37	15.8	43	.9418	789	>1000
77	"	"	90	"	875/30	.26	16.7	65	.9381	695	108

Run 60 yielded the following SEC* data: Mw = 144,000, Mn = 17,200, HI = 8.3.

Run 61 shows a little broader MWD. Mw = 137,000, Mn = 11,900, HI = 11.4.

*SEC = size exclusion chromatography

(1) Environmental stress crack resistance, ASTM D 1693, cond. A, F⁵⁰ (hrs).

(2) Flexural modulus, ASTM D-790

Clearly the lowering of density can be achieved by DEALE in combination with CO reduction. Productivity is somewhat lower for each invention run since copolymers were made at fairly high temperatures.

Example VII

The following experiment demonstrates that the reduced catalyst must contact the metal alkyl before it contacts ethylene. A sample of Cr/silica-titania catalyst was calcined at 800 °C in air as before, then reduced with CO at 340 °C for 30 minutes. The CO was flushed out with nitrogen as the sample was cooled. Then it was charged to the reactor in the normal way, except that no cocatalyst was added. Instead isobutane and ethylene were added and the mixture was stirred for about 10 minutes. At first no activity was noticed, but after ten minutes some polymerization did begin to show. Then 1ml of .5% TEB was added to the reactor and a strong polymerization began. After 30 more minutes, the run was stopped and the polymer recovered. Total productivity was 1575 g/g. The polymer had a 4.2 HLMI and a density of .9470. This compares to .9276 when the TEB was added immediately and thereafter the ethylene. Thus the density lowering effect seems to be suppressed when the ethylene is added before contact of the supported catalyst with the cocatalyst.

Claims

1. A method for producing a catalyst system characterized by
 - (a) forming a chromium catalyst component on a predominantly silica support;
 - (b) subjecting the composition of (a) to activation in an oxygen-containing ambient at an elevated temperature to convert at least a portion of any chromium in a lower valent state to the hexavalent

TABLE 7

Run	Activation		Reac tor Temp. °C	DEALE CONC.	ACTIVITY g/g cat/min	MI	HLMI	RATIO	DEN.	FLEX. ⁽²⁾ MPa	ESCR ⁽¹⁾
	Air	CO									
60	850 °C	None	102	1ml	3870/30	.12	8.0	67	.9577	1347	82
61	700 °C	350 °C	"	"	970/30	.95	48	50	.9261	--	--
62	"	"	"	"	2260/85	.97	55	56	.9325	--	--
63	850 °C	NONE	"	"	3790/30	.10	8.9	89	.9584	1290	128
64	850 °C	NONE	95	1ml	9801/51	0	.80	--	.9585	1282	320
65	"	"	96-H ₂	"	6520/55	.28	17.3	62	.9574	1531	41
66	"	"	96-H ₂	"	2228/84	.22	17.0	77	.9601	1523	58
67	"	350 °C	"	"	2861/50	.28	15.8	56	.9442	877	200
68	"	"	"	"	1480/60	.87	49.1	56	.9303	501	--
69	850 °C	NONE	96	2ml	10904/60	.02	2.70	136	.9587	1290	267
70	850 °C	350 °C	90-H ₂	1ml	1320/47	1.4	80.6	59	.9283	521	--
71	"	"	90	"	1430/40	.33	19.6	59	.9317	551	>1000
72	"	"	90	2ml	1390/40	.27	17.6	65	.9330	572	288
The following catalysts were made by impregnating DEALE on Cat.											
73	850 °C	NONE	96	4ml/g	4142/60	.03	2.70	90	.9626	1560	113
74	"	"	"-H ₂	"	600/52	.19	13.5	71	.9636	1585	--
75	"	"	"-H ₂	"	1154/40	.68	37	54	.9640	1710	14
76	"	350 °C	90-H ₂	"	1400/50	.37	15.8	43	.9418	789	>1000
77	"	"	90	"	875/30	.26	16.7	65	.9381	695	108
Run 60 yielded the following SEC* data: Mw = 144,000, Mn = 17,200, HI = 8.3.											
Run 61 shows a little broader MWD. Mw = 137,000, Mn = 11,900, HI = 11.4.											

*SEC = size exclusion chromatography

(1) Environmental stress crack resistance, ASTM D 1693, cond. A, F⁵⁰ (hrs).

(2) Flexural modulus, ASTM D-790

Clearly the lowering of density can be achieved by DEALE in combination with CO reduction. Productivity is somewhat lower for each invention run since copolymers were made at fairly high temperatures.

Example VII

The following experiment demonstrates that the reduced catalyst must contact the metal alkyl before it contacts ethylene. A sample of Cr/silica-titania catalyst was calcined at 800 °C in air as before, then reduced with CO at 340 °C for 30 minutes. The CO was flushed out with nitrogen as the sample was cooled. Then it was charged to the reactor in the normal way, except that no cocatalyst was added. Instead isobutane and ethylene were added and the mixture was stirred for about 10 minutes. At first no activity was noticed, but after ten minutes some polymerization did begin to show. Then 1ml of .5% TEB was added to the reactor and a strong polymerization began. After 30 more minutes, the run was stopped and the polymer recovered. Total productivity was 1575 g/g. The polymer had a 4.2 HLMI and a density of .9470. This compares to .9276 when the TEB was added immediately and thereafter the ethylene. Thus the density lowering effect seems to be suppressed when the ethylene is added before contact of the supported catalyst with the cocatalyst.

Claims

1. A method for producing a catalyst system characterized by
 - (a) forming a chromium catalyst component on a predominantly silica support;
 - (b) subjecting the composition of (a) to activation in an oxygen-containing ambient at an elevated temperature to convert at least a portion of any chromium in a lower valent state to the hexavalent



state;

(c) thereafter subjecting the activated catalyst composition of (b) to carbon monoxide under reducing conditions; and

(d) thereafter contacting the thus reduced supported catalyst composition of (c) with a cocatalyst selected from trialkyl boron compounds and dialkyl aluminum alkoxide compounds in the absence of monomer.

2. The method of claim 1 characterized in that said silica support is selected from pure silica, a support comprising at least 90 weight percent silica the remainder being primarily metal oxides, and a cogel of 95 to 98 weight percent silica, the remainder being coprecipitated titania.

3. The method of claim 1 or 2 characterized in that said activation is carried out in air at a temperature within the range of 400 to 900 ° C.

4. The method of any of the preceding claims characterized in that said carbon monoxide reduction is carried out at a temperature within the range of 300 to 500 ° C.

5. The method of any of the preceding claims characterized in that the reduced supported catalyst component of (c) is contacted in a mixing vessel with a hydrocarbon solution of said cocatalyst.

6. The method of any of the preceding claims characterized in that said cocatalyst is triethyl borane.

7. The use of the catalyst system as defined in any of claims 1 to 6 for preparing polymers of an ethylene feed stream.

8. The use of claim 7 characterized in that said feedstream consists of polymerization grade ethylene; in particular wherein the polymerization is carried out under slurry conditions.

9. The use of claim 7 or 8 characterized in that the polymerization is carried out in a reactor connected in series with a second reactor utilizing a different catalyst.

10. The use of any of claims 7 to 9 characterized in that said polymer product has a density within the range of 0.920 to 0.960 g/cm³; in particular wherein said polymer has a density within the range of 0.930 to 0.955 g/cm³.

Revendications

1. Procédé de production d'un système de catalyseur, caractérisé en ce que :

(a) on forme un composant de catalyseur contenant du chrome sur un support constitué de manière prédominante par de la silice;

(b) on fait subir à la composition de (a) une activation dans une atmosphère contenant de l'oxygène à une température élevée pour amener au moins une partie du chrome présent à un état de valence inférieur à l'état hexavalent;

(c) on soumet ensuite la composition de catalyseur activé de (b) à une exposition à du monoxyde de carbone dans des conditions de réduction; et

(d) on met ensuite en contact la composition de catalyseur fixée sur un support ainsi réduite de (c) avec un co-catalyseur choisi parmi les composés de trialkyl bore et des composés d'alkylate de dialkyl aluminium en l'absence de monomère.

2. Procédé selon la revendication 1, caractérisé en ce que le support de silice est choisi parmi de la silice pure, un support comprenant au moins 90 % en poids de silice, le complément étant principalement constitué par des oxydes de métaux, et un cogel de 95 à 98 % en poids de silice, le complément étant constitué par de l'oxyde de titane co-précipité.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'on met en oeuvre l'activation dans l'air à une température comprise entre 400 et 900 ° C.

4. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on met en



oeuvre la réduction par le monoxyde de carbone à une température comprise entre 300 et 500 ° C.

- 5 5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'on met en contact le composant de catalyseur fixé sur un support réduit de (c) dans un récipient de mélange avec une solution du co-catalyseur dans un hydrocarbure.
6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que le co-catalyseur est le triéthyl borane.
- 10 7. Utilisation du système de catalyseur selon l'une quelconque des revendications 1 à 6 pour la préparation de polymères d'un courant d'alimentation d'éthylène.
8. Utilisation selon la revendication 7, caractérisée en ce que le courant d'alimentation est constitué par de l'éthylène de qualité de polymérisation et, plus particulièrement, en ce que l'on met en oeuvre la polymérisation dans des conditions sous forme de bouillie.
- 15 9. Utilisation selon la revendication 7 ou 8, caractérisée en ce qu'on met en oeuvre la polymérisation dans un réacteur relié en série avec un second réacteur utilisant un catalyseur différent.
- 20 10. Utilisation selon l'une quelconque des revendications 7 à 9, caractérisée en ce que le polymère produit présente une masse volumique comprise entre 0,920 et 0,960 g/cm³, et, plus particulièrement, en ce que le polymère présente une masse volumique comprise entre 0,930 et 0,955 g/cm³.

Patentansprüche

- 25 1. Verfahren zur Herstellung eines Katalysatorsystems, dadurch gekennzeichnet, daß man
 - (a) eine Chrom-Katalysatorkomponente auf einem vorwiegend aus Siliciumdioxid bestehenden Träger bildet;
 - 30 (b) die Zusammensetzung gemäß (a) einer Aktivierung in einer sauerstoffhaltigen Umgebung bei einer erhöhten Temperatur unterwirft, um zumindest einen Teil von etwaigem Chrom, das in einem Zustand geringerer Wertigkeit vorliegt, in den sechswertigen Zustand überzuführen;
 - (c) anschließend die aktivierte Katalysatorzusammensetzung gemäß (b) der Behandlung mit Kohlenmonoxid unter reduzierenden Bedingungen aussetzt; und
 - 35 (d) die auf diese Weise reduzierte Katalysatorzusammensetzung gemäß (c) mit einem Cokatalysator, der unter Trialkylborverbindungen und Dialkylaluminiumoxidverbindungen ausgewählt ist, in Abwesenheit von Monomerem in Kontakt bringt.
- 40 2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Siliciumdioxidträger unter reinem Siliciumdioxid, einem Träger mit einem Gehalt an mindestens 90 Gew.-% Siliciumdioxid, wobei der Rest vorwiegend aus Metalloxiden besteht, und einem mit Cogel mit 95 bis 98 Gew.-% Siliciumdioxid, wobei es sich beim Rest um copräzipitiertes Titanoxid handelt, ausgewählt ist.
- 45 3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Aktivierung in Luft bei einer Temperatur im Bereich von 400 bis 900 ° C durchgeführt wird.
- 50 4. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Kohlenmonoxid-Reduktion bei einer Temperatur im Bereich von 300 bis 500 ° C durchgeführt wird.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die reduzierte Katalysatorkomponente gemäß (c) in einem Mischgefäß mit einer Kohlenwasserstofflösung des Cokatalysators in Kontakt gebracht wird.
- 55 6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß es sich beim Cokatalysator um Triethylboran handelt.
7. Verwendung des Cokatalysatorsystems gemäß einem der Ansprüche 1 bis 6 zur Herstellung von Polymeren aus einem Ethylen-Einsatzmaterialstrom.



8. Verwendung nach Anspruch 7, dadurch gekennzeichnet, daß der Einsatzmaterialstrom aus Ethylen von Polymerisationsqualität besteht; wobei insbesondere die Polymerisation unter Aufschlämmungsbedingungen durchgeführt wird.
9. Verwendung nach Anspruch 7 oder 8, dadurch gekennzeichnet, dass die Polymerisation in einem Reaktor durchgeführt wird, der in Serie mit einem zweiten, sich eines unterschiedlichen Katalysators bedienenden Reaktor verbunden ist.
10. Verwendung nach einem der Ansprüche 7 bis 9, dadurch gekennzeichnet, daß das Polymerprodukt eine Dichte im Bereich von 0,920 bis 0,960 g/cm³ aufweist; wobei insbesondere das Polymer eine Dichte im Bereich von 0,930 bis 0,955 g/cm³ aufweist.

