

Description

This invention relates to a process for the in-situ control of catalyst kinetics in a reaction catalyzed by a transition metal catalyst system.

Paradoxically, the high activity at elevated temperatures, which makes many transition metal catalyst systems so attractive, is also responsible for a negative characteristic. This deficiency exhibits itself in the form of a kinetic profile, which can be described as "autoacceleration", and leads to processes, which are, in effect, out of control; processes in which the reactants are "over-reactive"; agglomeration of particulate product; and other various undesirable results such as hot-spotting, chunking, and sheeting.

Autoacceleration can be defined as an abrupt increase in the reaction rate of a process to an undesirable level due to a sudden rise in temperature. In effect, the system is unable to remove the heat as fast as it is generated. Control of this behavior is essential for the smooth operation of the process in the reactor. The usual response to a reactor upset caused by autoacceleration is to have the operator initiate a reactor kill by the rapid injection of a catalyst poison. The initiation of such a drastic measure is made at the discretion of the operator, and depends entirely on his judgment as to the performance of the catalyst in the reactor.

To relieve the operator of the responsibility for making this decision, which, at least in part, tends to be subjective, in-situ control of catalyst kinetics has been suggested, the goal being to let the catalyst monitor its own behavior.

An object of the invention, therefore, is to provide a process for the in-situ control of catalyst kinetics in a reaction catalyzed by a transition metal catalyst system, which process comprises including in said transition metal catalyst system an autoacceleration inhibitor which (i) at about the temperature at which the catalyst system autoaccelerates in said reaction, decomposes into a poison for the catalyst system and (ii) is either essentially inert at the normal operating temperature of the catalyst system in said reaction or will cause substantially less inhibition of the catalyst system at said normal operating temperature than at the autoacceleration temperature; said autoacceleration inhibitor being employed in an amount sufficient to provide the quantity of poison required to inhibit the catalyst system at the autoacceleration temperature of said reaction. Preferred embodiments of this process are given in the dependent claims.

Subject invention is considered to be universal in that the autoacceleration inhibitor can be used advantageously in any transition metal catalyst system employed in a process in which auto-acceleration is a potential problem.

Examples of various catalyst systems and autoacceleration inhibitors therefor are set forth in Table I. It will be understood that autoacceleration and decomposition temperature ranges vary from system to system and inhibitor to inhibitor. Those mentioned in Table I provide some guidance for the particular catalyst systems mentioned.

Table I

Catalyst System	Process In Which The Catalyst System Is Utilized	Autoacceleration Temperature (°C)	Autoacceleration Inhibitor	Decomposition Temperature of Autoacceleration Inhibitor (°C)
1. e.g., $\text{VCl}_3/\text{AlR}_3$ and $\text{TiCl}_3/\text{MgCl}_2/\text{AlR}_3$	Olefin Polymerization, e.g., see U.S. Patents 4,302,566 and 4,508,842	About 110 to 125	Metal Carbonyls, Dicyclopentadiene, Sulfones	About 110 to 130
2. $(\text{R}_3\text{P})_2\text{Rh}(\text{H})(\text{CO})$ (supported liquid phase catalyst)	Olefin Hydroformylation, e.g., see U.S. Patent 3,487,112. Also see J. Mol. Catal. 1985 vol. 31, page 107.	About 100	Dicyclopentadiene, Sulfones	100 to 130
3. Ni Catalysts, i.e., O Ligand Ni P H	Olefin Oligomerization, e.g., see U.S. Patent 4,689,437	About 100	Dicyclopentadiene, Sulfones	100 to 130

Table I (Continued)

Catalyst System	Process In Which The Catalyst System Is Utilized	Autoacceleration Temperature (°C)	Autoacceleration Inhibitor	Decomposition Temperature of Autoacceleration Inhibitor (°C)
4. Pd/Al ₂ O ₃	Hydrogenation of Polyenes	>150	0 Substituted Sulfones metal carbonyls	>150
5. PdCl ₂ /CuCl ₂	Wacker Process (Olefins to aldehydes and ketones)	>130	0 Substituted Sulfones metal carbonyls	>130

The invention will be discussed in terms of a typical catalyst system useful in the polymerization of alpha-olefins, particularly for the production of homopolymers and copolymers of ethylene, i.e., a vanadium catalyst system comprising:

- (i) the reaction product of a vanadium compound and an electron donor, which is a liquid, organic Lewis base in which the vanadium compound is soluble;

- (ii) a silica support into which component (i) is impregnated;
- (iii) a halocarbon promoter;
- (iv) a hydrocarbyl aluminum cocatalyst; and
- (v) as an autoacceleration inhibitor, a Diels-Alder adduct or a transition metal carbonyl,

5 with the proviso that the inhibitor is such that it will decompose when the catalyst system reaches its autoacceleration temperature range.

It will be understood that some inhibitors will be essentially inert in the normal operating temperature range while others will decompose in the normal operating temperature range, but will cause substantially less inhibition of the catalyst system in the normal operating temperature range than in the autoacceleration
10 temperature range.

The vanadium compound can be any one of the well known group of vanadium compounds used to form those complexes, which find use as catalyst precursors in polymerization processes. Examples are vanadium trihalides, vanadium tetrahalides, and vanadium oxyhalides. The halides are generally chlorides, bromides, or iodides, or mixtures thereof. Of these compounds VCl_3 , VCl_4 , and VOCl_3 can be mentioned.
15 The vanadium acetylacetonates such as vanadyl triacetylacetonate are also useful.

The electron donor is a liquid, organic Lewis base in which the vanadium compound is soluble. It can be selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof, each electron donor having 2 to 20 carbon atoms. Among these electron donors, the preferred are alkyl and cycloalkyl
20 ethers having 2 to 20 carbon atoms; dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; and alkyl, alkoxy, and alkylalkoxy esters of alkyl and aryl carboxylic acids having 2 to 20 carbon atoms. The most preferred electron donor is tetrahydrofuran. Other examples of suitable electron donors are methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, and ethyl propionate.

25 While an excess of electron donor is used initially to provide the reaction product of vanadium compound and electron donor, the reaction product finally contains 1 to 20 moles of electron donor per mole of vanadium compound and preferably 1 to 10 moles of electron donor per mole of vanadium compound. About 3 moles of electron donor per mole of vanadium compound has been found to be most preferable.

30 The silica support is a solid, particulate porous material essentially inert to the polymerization. It is used as a dry powder having an average particle size of 10 to 250 microns and preferably 30 to 100 microns; a surface area of at least 3 square meters per gram and preferably about 50 square meters per gram; and a pore size of at least 8 nm (80 angstroms) and preferably at least 10 nm (100 angstroms). Generally, the amount of support used is that which will provide 0.05 to 0.6 millimole of vanadium compound per gram of support and preferably 0.3 to 0.5 millimole of vanadium compound per gram of support.
35

The halocarbon promoter can have the following formula:



40 wherein

- R = hydrogen or an unsubstituted or halogen substituted alkyl radical having 1 to 6 carbon atoms;
- X = a halogen; and
- a = 0, 1, or 2.

The halogen can be chlorine, bromine, iodine, or fluorine, and each X can be alike or different.
45 Preferred promoters include fluoro-, chloro-, and bromo-substituted methane or ethane having at least 2 halogen atoms attached to a carbon atom, e.g., chloroform, CFCl_3 , CH_3CCl_3 , carbon tetrachloride, and $\text{CF}_2\text{ClCCl}_3$. The first three mentioned promoters are preferred. 0.1 to 10 moles, and preferably 0.2 to 2 moles, of promoter can be used per mole of cocatalyst.

The hydrocarbyl aluminum cocatalyst can be represented by the formula R_3Al wherein each R is an
50 alkyl radical; each R can be alike or different; and each R has 1 to 14 carbon atoms, and preferably 2 to 8 carbon atoms. Further, each alkyl radical can be a straight or branched chain. Examples of suitable radicals are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, 2-methylpentyl, heptyl, octyl, isooctyl, 2-ethylhexyl, 5,5-dimethylhexyl, nonyl, decyl, isodecyl, undecyl, and dodecyl.

55 Examples of suitable hydrocarbyl aluminum compounds are as follows: triisobutylaluminum, trihexylaluminum, di-isobutylhexylaluminum, isobutyl dihexylaluminum, trimethylaluminum, triethylaluminum, tripropylaluminum, triisopropylaluminum, tri-n-butylaluminum, trioctylaluminum, tridecylaluminum, tridodecylaluminum, tribenzylaluminum, triphenylaluminum, trinaphthylaluminum, and tritolylaluminum. The preferred hydrocarbyl aluminums, are triethylaluminum, triisobutylaluminum, and trihexylaluminum.

The cocatalyst and promoter can be added to the supported vanadium complex either before or during the polymerization reaction. They can be added together or separately, simultaneously or sequentially. The cocatalyst and promoter are preferably added separately as solutions in an inert solvent, such as isopentane, to the polymerization reaction at the same time as the flow of the ethylene is initiated. The cocatalyst is necessary to obtain any significant polymerization. The promoter, on the other hand, can be considered a preferred option. 5 to 500 moles, and preferably 10 to 40 moles, of cocatalyst can be used per mole of vanadium catalyst, i.e., the reaction product of the vanadium compound and the electron donor.

The autoacceleration inhibitor can be a Diels-Alder adduct or a transition metal carbonyl with the proviso that the inhibitor is such that it will decompose when the catalyst reaches the autoacceleration temperature range. It is believed that the decomposition product then reacts with the active sites on the catalyst to prevent autoacceleration from occurring. The inhibitor is preferably stable until it reaches the decomposition temperature range. The autoacceleration temperature range, e.g., for a high density polyethylene vanadium catalyst system is in the range of 110 to 125 °C. The decomposition temperature range of the autoacceleration inhibitor, then, preferably begins at the lower end of this range. While the inhibitor can be either dry mixed with the catalyst or added to the reactor as a separate component, it preferably resides in the catalyst particles, e.g., the inhibitor is impregnated into a silica support along with the catalyst precursor.

Diels-Alder adducts are described in Streitwieser et al, Introduction to Organic Chemistry, 3rd edition, Macmillan, New York, 1985, pages 550 to 558. Those which are useful as autoacceleration inhibitors, in accordance with this invention, can have 4 to 20 carbon atoms and preferably have 4 to 10 carbon atoms. They can have one or two carbon to carbon unsaturated bonds and be either monocyclic or polycyclic. Further, they can be substituted or unsubstituted hydrocarbon compounds. Examples of suitable substituents are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, *n*-pentyl, -2-pentyl, -3-pentyl, neopentyl, *n*-hexyl, 2-hexyl and phenyl; examples of dienes, which can be used to make the adducts, are 1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-butadiene (isoprene), 1,3-hexadiene, 2,4-hexadiene, 2,3-dimethyl-1,3-butadiene, 2,4-dimethyl-1,3-hexadiene, 2,5-dimethyl-2,4-hexadiene, cyclopentadiene, methylcyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, and 1,3-cyclooctadiene; and examples of monoenes or dienophiles, which can be used to make the adducts, are sulfur dioxide, carbon monoxide, cyclopentadiene, vinyl acetate, acrylic acid, dimethyl acetylenedicarboxylate, ethylene, methyl vinyl ketone, diethyl acetylenedicarboxylate, acrolein, and methyl acrylate. Examples of useful Diels-Alder adducts are dicyclopentadiene, methylcyclopentadiene dimer, butadiene sulfone, isoprene sulfone, and vinylene carbonate.

Autoacceleration inhibitor compounds also useful in the practice of this invention are transition metal carbonyls. The metal is generally selected from Groups VIB, VIIB, and VIII of the periodic table. Transition metals of particular interest are chromium, molybdenum, iron, tungsten, ruthenium, osmium, rhenium, and manganese. The transition metal carbonyls can be inorganic or organic compounds. The organic compounds can contain either unsubstituted or substituted aliphatic or aromatic organic groups provided that the substituents are inert to the particular process in which the inhibitor is being used. Preferably, the organic groups are limited to 2 to 20 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, isobutyl, pentyl, heptyl, phenyl, or benzyl. Examples of suitable transition metal carbonyl inhibitors are $\text{Cr}(\text{CO})_6$; $\text{Mo}(\text{CO})_6$; $\text{Fe}(\text{CO})_5$; $\text{W}(\text{CO})_6$; $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2$; $\text{C}_7\text{H}_5\text{Mo}(\text{CO})_3$; $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3\text{Cr}(\text{CO})_3$; $\text{C}_6\text{H}_5\text{NHCH}_2\text{Cr}(\text{CO})_3$; $\text{Fe}_3(\text{CO})_{12}$; $\text{Ru}_3(\text{CO})_{12}$; $\text{Os}_3(\text{CO})_{12}$; $\text{Re}_2(\text{CO})_{10}$; and $\text{Mn}_2(\text{CO})_{10}$.

Mixtures of Diels-Alder adducts and mixtures of transition metal carbonyls can be used as well as mixtures of Diels-Alder adducts and metal carbonyls.

The autoacceleration inhibitor is preferably used in a molar ratio of inhibitor to transition metal in the transition metal catalyst in the range of 0.1:1 to 200:1 and preferably a molar ratio in the range of 0.5:1 to 100:1. The inhibitor can be (i) dry mixed with an impregnated silica support; (ii) impregnated from a solution into a silica support, which has been impregnated with a catalyst precursor; (iii) slurried in an electron donor or other inert solvent with silica prior to the addition of the reaction product of vanadium trihalide and the same electron donor; or added to the reactor separately. In all cases, the silica is preactivated by dehydrating with heat. Any of these routes is more effective than dry mixing the inhibitor with the silica supported vanadium catalyst. In any case, the inhibitors used in the preparation of subject catalyst should be essentially free of water. The inhibitors can also be chemically anchored to the support, i.e., a chemical bond is formed between the inhibitor and the support as opposed to a physical adsorption of the inhibitor on the surface of the support. In any of these procedures, the decomposition temperature range of the inhibitor should be avoided.

Optionally, a modifier is included in the vanadium catalyst system and is impregnated into the catalyst support. The formula for the modifier is BX_3 or $\text{AlR}_{(3-a)}\text{X}_a$ wherein each R is an alkyl radical having 1 to 14

carbon atoms; X is chlorine, bromine, or iodine; each R and X are alike or different; and a is 0, 1, or 2. Preferred modifiers include alkylaluminum mono- and di- chlorides wherein each alkyl radical has 1 to 6 carbon atoms, and boron trichloride. A particularly preferred modifier is diethyl aluminum chloride. 0.1 to 10 moles, and preferably 0.2 to 2.5 moles, of modifier are used per mole of electron donor. When the modifier is used it appears to be part of the vanadium trichloride/electron donor complex.

The ethylene polymerization or copolymerization can be conducted in the gas phase or liquid phase using conventional techniques such as fluidized bed, slurry, or solution processes. Solution and slurry polymerizations are described in Stille, Introduction to Polymer Chemistry, Wiley and Sons, New York, 1962, and fluidized bed processes in United States patent 4,482,687. A continuous, fluidized bed process is preferred. Using this fluidized bed process, the vanadium complex, the cocatalyst, the promoter, the ethylene monomer, and any comonomers are continuously fed into the reactor and polyethylene product is continuously removed. The density of ethylene copolymer produced may be varied over a wide range depending upon the amount of alpha-olefin comonomer added and upon the particular comonomer employed. The greater the mole percent of alpha-olefin, the lower the density. The alpha-olefin can have 3 to 12 carbon atoms.

The fluidized bed polymerization is conducted at a temperature below the sintering temperature of the product. The normal operating temperature is generally in the range of 10°C to 115°C. Preferred normal operating temperatures will vary depending upon the density desired. High density polyethylenes of greater than 0.94 grams per cubic centimeter (g/cc) are produced at normal operating temperatures of 85°C to 115°C, and preferably 90°C to 100°C. Low density polyethylenes ranging in density from about 0.91 to about 0.94 g/cc are preferably produced at a normal operating temperature of 75°C to 90°C. Very low density polyethylenes of less than 0.91 g/cc are preferably produced at a normal operating temperature of 10°C to 80°C. In the case of very low density polyethylenes, it is necessary to dilute the reaction mixture with a large quantity of diluent gas in order to prevent the formation of polymer agglomerates and sustain polymerization on a continuous basis.

The fluidized bed reactor is typically operated at pressures of up to 1,000, and preferably 50 to 350, psig (1 psi = 6.89 kPa).

A chain transfer agent, such as hydrogen, can be used to terminate the polymer chain. Usually the ratio of hydrogen employed to ethylene will vary between about 0.001 to about 2.0 moles of hydrogen per mole of ethylene.

The autoacceleration inhibitor acts to essentially curb autoacceleration while not interfering with the high activity of the catalyst at normal operating temperatures to any great extent.

The vanadium based catalyst, except for the autoacceleration inhibitor, and its preparation are closely related to the catalyst described in United States patent 4,508,842.

The patents and publications mentioned in this specification are incorporated by reference herein.

The invention is illustrated by the following examples:

Examples 1 to 21

A supported vanadium based catalyst is typically prepared as follows: silica gel is preactivated at a temperature in the range of about 250°C to about 800°C under a dry, inert gas such as nitrogen for about 8 to about 16 hours to give a support essentially free of adsorbed water and containing less than about 0.7 millimole per gram of silica of surface hydroxy groups. The silica is slurried in freshly distilled tetrahydrofuran (THF), under nitrogen. An amount of $\text{VCl}_3(\text{THF})_3$ is added to give a loading of about 0.2 to about 0.6 millimole of vanadium per gram of support. The mixture is stirred for about 20 to about 40 minutes, then excess THF is removed. If diethylaluminum chloride (DEAC) modification is desired, the DEAC is added after the excess THF is removed. A solution of inhibitor in hexane is then added with additional stirring, after which the solvent is removed to give a free flowing powder.

In these examples, a $\text{VCl}_3(\text{THF})_3$ solution was added to a slurry of preactivated silica in THF and then dried at 45°C to a free-flowing powder. This is the catalyst precursor. It was then treated with DEAC as described above. The result was a silica-supported $\text{VCl}_3(\text{THF})_3(\text{DEAC})_{1.5}$ catalyst. Except for examples 1 and 8, an autoacceleration inhibitor was added by one of three different methods as follows:

- A. added as a separated component to the reactor;
- B. dry-mixed with the catalyst; or
- C. co-impregnated with the catalyst precursor and DEAC into the silica support. This is accomplished by dissolving the inhibitor in hexane or methylene chloride and mixing the catalyst with this solution for 30 minutes. The solvent is then removed to give a free-flowing powder.

The catalyst, the inhibitor (according to methods A, B or C), a triethylaluminum (TEAL) cocatalyst, and a fluorotrichloromethane promoter (except in example 7 where the promoter is 1,1,1-trichloroethane) were added to a reactor containing 600 milliliters of hexane. An amount of catalyst sufficient to give a charge of 0.05 millimole of vanadium was used. Forty equivalents each of cocatalyst and promoter were used per equivalent of vanadium.

Two runs of 30 minutes each were carried out for each example. One run was effected at 85°C, which is within the normal operating range for the catalyst system. In this case, the reactor was initially pressurized with ethylene and one psi of hydrogen for a total pressure of 160 psig. The other run was effected at 125°C, which is within the autoacceleration temperature range for the catalyst system. In this run, the cocatalyst and the ethylene were added when the reactor reaches a temperature of 120°C. The hydrogen was added at 60°C.

Variables and results are set forth in Tables II and III.

Notes with respect to the Examples and Tables:

1. THF = tetrahydrofuran

2. DEAC = diethylaluminum chloride

3. Inhibitor = autoacceleration inhibitor

4. Inhibitor/V = mole ratio of inhibitor to vanadium.

5. Method of Incorporation = A, B, or C, as above.

6. The activity of the catalyst was measured in grams of polyethylene per millimole of vanadium per hour per 100 psig of ethylene.

7. % Change = the difference in activity between control examples without inhibitors and examples with inhibitors. Examples 2 to 7 are compared to example 1 and examples 9 to 21 are compared to example 8.

8. Examples 1 to 7 were performed by adding the catalyst, the cocatalyst, the promoter, and the inhibitor (examples 2 to 7) as separate components directly to the reactor. In contrast, examples 8 to 21 were carried out by first mixing together the catalyst, the cocatalyst, the promoter, and the inhibitor (examples 9 to 21) in a small bottle, and then adding the mixture to the reactor.

9. The controls (no inhibitor) differ in that example 1 shows no major activity change in going from 85°C to 125°C whereas example 8 shows a nearly two-fold increase in activity from 85°C to 125°C. This difference in behavior is believed to result from the two different addition methods that were used (see Note 8).

Activity_____

Example	Inhibitor	Inhibitor/V	Method of Incorporation	Activity		
				125°C	% Change 85°C	% Change 125°C
1	-	-	-	1077	-	-
2	dicyclopentadiene	20	A	751	+5	-30
3	dicyclopentadiene	40	A	453	+31	-58
4	dicyclopentadiene	160	A	270	+7	-75
5	butadiene sulfone	5	B	177	-45	-84
6	isoprene sulfone	4	B	65	-46	-94
7	vinylene carbonate	5	B	668	+41	-38

Table III

Example	Inhibitor	Inhibitor/V	Method of Incorporation	Activity	
				% Change 85°C	% Change 125°C
8	-	-	-	1473	-
9	Cr(CO) ₆	1	A	495	-66
10	Mo(CO) ₆	0.5	A	511	-65
11	Mo(CO) ₆	1	A	422	-71
12	Mo(CO) ₆	2	A	328	-78
13	Mo(CO) ₆	1	B	966	-34
14	Mo(CO) ₆	1	C	934	-37
15	W(CO) ₆	1	A	837	-43
16	Fe(CO) ₅	1	A	405	-73
17	C ₅ H ₅ Fe(CO) ₂	1	A	417	-72
18	C ₇ H ₈ Mo(CO) ₃	1	A	372	-75
19	C ₇ H ₈ Mo(CO) ₃	1	C	439	-70
20	C ₆ H ₅ CO ₂ CH ₃ Cr(CO) ₃	1	C	905	-39
21	C ₆ H ₅ NHCH ₃ Cr(CO) ₃	1	C	812	-45

Examples 22 to 27

The solid catalyst described above was employed together with a cocatalyst (triethylaluminum), a promoter (CHCl₃), and an inhibitor (dicyclopentadiene) to copolymerize ethylene and 1-hexene in a fluid bed reactor system similar to that described in United States patent 4,482,687.

In each polymerization, the solid catalyst component was continually fed to the polymerization reactor along with the cocatalyst, the promoter, and the inhibitor.

Hydrogen was added to the reactor as a chain transfer agent to control the molecular weight of the polymer produced. Nitrogen was also used to maintain the total pressure at a set point.

Table IV below sets forth the catalyst composition and the reaction conditions that were employed. Table V presents two control experiments (examples 22 and 23), run without the inhibitor, which show the normal variation of catalyst activity (vanadium in resin, parts per million). Examples 24 to 27 are experiments to ascertain the effect of temperature on catalyst activity in the presence of the inhibitor.

The examples show that the inhibitor has a stabilizing effect within the normal operating range of the catalyst system.

Table IV

Catalyst	Reaction Conditions	
Support: Silica gel	Temp. (°C)	90 to 110
Precursor: VCl_3/THF	Total pressure	315 psia
Modifier: DEAC	C_2H_4 pressure	230 psia
Modifier/V Molar Ratio: 1.78	N_2 pressure	80 psia
Cocatalyst: TEAL	H_2 pressure	3.7 to 5.8 psia
Promoter: CHCl_3	Comonomer	1-hexene
Al/V Molar Ratio: 24	Comonomer/ C_2H_4 (molar ratio)	0.004 to 0.017
Promoter/V Molar Ratio: 24	$\text{H}_2/\text{C}_2\text{H}_4$ (molar ratio)	0.016 to 0.025
	Residence Time	4 hr
	Inhibitor	Dicyclopentadiene
	Inhibitor/V (molar ratio)	5.0 to 11.0

Table V

Example	Dicyclopentadiene/V (molar ratio)	Temp. (°C)	Vanadium in Resin (ppm)	Comments
22	0	90	7.4	--
23	0	105	2.5	--
24	8.0	90	6.5	More stable operation
25	7.8	100	6.0	More stable operation
26	11.2	110	6.0	More stable operation
27	5.0	110	6.9	More stable operation

Claims

1. Process for the in-situ control of catalyst kinetics in a reaction catalyzed by a transition metal catalyst system, which process comprises including in said transition metal catalyst system an autoacceleration inhibitor which (i) at about the temperature at which the catalyst system autoaccelerates in said reaction, decomposes into a poison for the catalyst system and (ii) is either essentially inert at the normal operating temperature of the catalyst system in said reaction or will cause substantially less inhibition of the catalyst system at said normal operating temperature than at the autoacceleration temperature; said autoacceleration inhibitor being employed in an amount sufficient to provide the quantity of poison required to inhibit the catalyst system at the autoacceleration temperature of said reaction.
2. The process defined in claim 1 wherein the inhibitor is a Diels-Alder adduct.
3. The process defined in claim 2 wherein the Diels-Alder adduct has 4 to 20 carbon atoms.
4. The process defined in claim 2 or 3 wherein the Diels-Alder adduct is monocyclic or polycyclic.
5. The process defined in claim 4 wherein the Diels-Alder adduct is dicyclopentadiene.
6. The process defined in any one of claims 2-4 wherein the Diels-Alder adduct is a sulfone or a carbonate.
7. The process defined in claim 1 wherein the inhibitor is a transition metal carbonyl.
8. The process defined in claim 7 wherein the transition metal of the transition metal carbonyl is molybdenum, chromium, tungsten, or iron.



Table IV

Catalyst	Reaction Conditions	
Support: Silica gel Precursor: VCl_3/THF Modifier: DEAC Modifier/V Molar Ratio: 1.78 Cocatalyst: TEAL Promoter: CHCl_3 Al/V Molar Ratio: 24	Temp. ($^{\circ}\text{C}$) Total pressure C_2H_4 pressure N_2 pressure H_2 pressure Comonomer Comonomer/ C_2H_4 (molar ratio)	90 to 110 315 psia 230 psia 80 psia 3.7 to 5.8 psia 1-hexene 0.004 to 0.017
Promoter/V Molar Ratio: 24	$\text{H}_2/\text{C}_2\text{H}_4$ (molar ratio) Residence Time Inhibitor Inhibitor/V (molar ratio)	0.016 to 0.025 4 hr Dicyclopentadiene 5.0 to 11.0

Table V

Example	Dicyclopentadiene/V (molar ratio)	Temp. ($^{\circ}\text{C}$)	Vanadium in Resin (ppm)	Comments
22	0	90	7.4	--
23	0	105	2.5	--
24	8.0	90	6.5	More stable operation
25	7.8	100	6.0	More stable operation
26	11.2	110	6.0	More stable operation
27	5.0	110	6.9	More stable operation

Claims

- Process for the in-situ control of catalyst kinetics in a reaction catalyzed by a transition metal catalyst system, which process comprises including in said transition metal catalyst system an autoacceleration inhibitor which (i) at about the temperature at which the catalyst system autoaccelerates in said reaction, decomposes into a poison for the catalyst system and (ii) is either essentially inert at the normal operating temperature of the catalyst system in said reaction or will cause substantially less inhibition of the catalyst system at said normal operating temperature than at the autoacceleration temperature; said autoacceleration inhibitor being employed in an amount sufficient to provide the quantity of poison required to inhibit the catalyst system at the autoacceleration temperature of said reaction.
- The process defined in claim 1 wherein the inhibitor is a Diels-Alder adduct.
- The process defined in claim 2 wherein the Diels-Alder adduct has 4 to 20 carbon atoms.
- The process defined in claim 2 or 3 wherein the Diels-Alder adduct is monocyclic or polycyclic.
- The process defined in claim 4 wherein the Diels-Alder adduct is dicyclopentadiene.
- The process defined in any one of claims 2-4 wherein the Diels-Alder adduct is a sulfone or a carbonate.
- The process defined in claim 1 wherein the inhibitor is a transition metal carbonyl.
- The process defined in claim 7 wherein the transition metal of the transition metal carbonyl is molybdenum, chromium, tungsten, or iron.



9. The process defined in claim 7 or 8 wherein the transition metal carbonyl contains, in addition to the carbonyl groups, unsubstituted or substituted organic groups having 2 to 20 carbon atoms with the proviso that the substituent is inert insofar as the process in which the inhibitor is used is concerned.
- 5 10. The process defined in any one of claims 1-9 wherein the inhibitor is employed in a molar ratio of inhibitor to transition metal in the range of 0.1:1 to 200:1, preferably 0.5:1 to 100:1.
11. The process defined in any one of claims 1-10 wherein the transition metal catalyst is particulate and the inhibitor resides in substantially or essentially all of the transition metal catalyst particles.
- 10 12. The process defined in claim 1 wherein said transition metal catalyst system comprises a vanadium catalyst composition comprising:
 - (i) the reaction product of a vanadium compound and an electron donor, which is a liquid, organic Lewis base in which the vanadium compound is soluble;
 - 15 (ii) a silica support into which component (i) is impregnated;
 - (iii) a halocarbon promoter;
 - (iv) a hydrocarbyl aluminum cocatalyst;
 and said autoacceleration inhibitor is a Diels-Alder adduct or a transition metal carbonyl, with the proviso that the inhibitor is such that it will decompose when the catalyst reaches its autoac-
 20 celeration temperature.
13. The process defined in claim 12 wherein the Lewis base is an alkyl ester of an aliphatic or an aromatic carboxylic acid, an aliphatic ketone, an aliphatic amine, an aliphatic alcohol, an alkyl or cycloalkyl ether, or a mixture thereof.
- 25 14. The process defined in claim 12 or 13 wherein the vanadium catalyst composition additionally comprises a modifier having the formula BX_3 or $AlR_{3-a}X_a$ wherein each R is an alkyl radical having 1 to 14 carbon atoms; X is chlorine, bromine, or iodine; each R and X are alike or different; and a is 0, 1, or 2.
- 30 15. The process defined in claim 14 wherein the modifier is diethylaluminium chloride.
16. The process defined in claim 14 or 15 wherein the modifier is employed in an amount of 0.1 to 10 moles, preferably 0.2 to 2.5 moles per mole of electron donor.
- 35 17. The process defined in any one of claims 12-16 wherein the Diels-Alder adduct has 4 to 20 carbon atoms.
18. The process defined in any one of claims 12-17 wherein the Diels-Alder adduct is monocyclic or polycyclic.
- 40 19. The process defined in any one of claims 12-16 wherein the transition metal of the transition metal carbonyl is selected from Groups VIB, VIIB, and VIII of the periodic table.
- 45 20. The process defined in claim 19 wherein the transition metal of the transition metal carbonyl is chromium, molybdenum, tungsten, or iron.
21. The process defined in claim 19 wherein the transition metal carbonyl is $Cr(CO)_6$; $Mo(CO)_6$; $Fe(CO)_5$; $W(CO)_6$; $C_5H_5Fe(COP)_2I$; $C_7H_5Mo(CO)_3$; $C_6H_5CO_2CH_3Cr(CO)_3$; $C_6H_5NHCH_3Cr(CO)_3$; $Fe_3(CO)_{12}$; Ru_3-
 50 $(CO)_{12}$; $Os_3(CO)_{12}$; $Re_2(CO)_{10}$; or $Mn_2(CO)_{10}$.
22. The process defined in any one of claims 12-21 wherein the inhibitor is present in a molar ratio of inhibitor to vanadium in the range of 0.1:1 to 200:1, preferably 0.5:1 to 100:1.
- 55 23. The process defined in any one of claims 12-22 wherein the inhibitor resides in the impregnated support.



24. The process defined in any one of claims 12-23 wherein the cocatalyst is triisobutyl aluminum, triethylaluminum or trihexylaluminum.

25. The process defined in any one of claims 12-24 wherein the promoter is CHCl_3 , CH_3CCl_3 , or CFCI_3 .

26. The process defined in any one of claims 12-25 wherein the reaction catalyzed by the vanadium catalyst composition is the polymerization of ethylene and comprises passing ethylene and, optionally, one or more alpha-olefin comonomers into contact with said vanadium catalyst composition under polymerization conditions.

Patentansprüche

1. Verfahren zur in situ-Steuerung der Katalysatorkinetik in einer von einem Übergangsmetall-Katalysatorsystem katalysierten Reaktion, umfassend den Einschluß in das Übergangsmetall-Katalysatorsystem eines Autobeschleunigungs-Inhibitors, der (i) sich bei etwa der Temperatur, bei der sich das Katalysatorsystem in der Reaktion autobeschleunigt, in ein Gift für das Katalysatorsystem zersetzt, und (ii) entweder bei der normalen Arbeitstemperatur des Katalysatorsystems in der Reaktion praktisch inert ist oder bei dieser normalen Arbeitstemperatur merklich weniger Inhibierung des Katalysatorsystems verursacht als bei der Autobeschleunigungs-Temperatur; wobei der Autobeschleunigungs-Inhibitor in einer Menge eingesetzt wird, die ausreicht, die Menge an Gift zu liefern, die erforderlich ist, um das Katalysatorsystem bei der Autobeschleunigungs-Temperatur der Reaktion zu inhibieren.

2. Verfahren nach Anspruch 1, in welchem der Inhibitor ein Diels-Alder-Addukt ist.

3. Verfahren nach Anspruch 2, in welchem das Diels-Alder-Addukt 4 bis 20 Kohlenstoffatome aufweist.

4. Verfahren nach Anspruch 2 oder 3, in welchem das Diels-Alder-Addukt monocyclisch oder polycyclisch ist.

5. Verfahren nach Anspruch 4, in welchem das Diels-Alder-Addukt Dicyclopentadien ist.

6. Verfahren nach irgendeinem der Ansprüche 2 - 4, in welchem das Diels-Alder-Addukt ein Sulfon oder ein Carbonat ist.

7. Verfahren nach Anspruch 1, in welchem der Inhibitor ein Übergangsmetallcarbonyl ist.

8. Verfahren nach Anspruch 7, in welchem das Übergangsmetall des Übergangsmetallcarbonyls Molybdän, Chrom, Wolfram oder Eisen ist.

9. Verfahren nach Anspruch 7 oder 8, in welchem das Übergangsmetallcarbonyl zusätzlich zu den Carbonylgruppen unsubstituierte oder substituierte organische Gruppen mit 2 bis 20 Kohlenstoffatomen aufweist, mit der Maßgabe, daß der Substituent bezüglich des Verfahrens, in welchem der Inhibitor eingesetzt wird, inert ist.

10. Verfahren nach irgendeinem der Ansprüche 1 - 9, in welchem der Inhibitor in einem Molverhältnis von Inhibitor zu Übergangsmetall im Bereich von 0,1:1 bis 200:1, vorzugsweise 0,5:1 bis 100:1, eingesetzt wird.

11. Verfahren nach irgendeinem der Ansprüche 1 - 10, in welchem der Übergangsmetall-Katalysator teilchenförmig ist und der Inhibitor sich in praktisch allen oder im wesentlichen allen Übergangsmetall-Katalysatorteilchen befindet.

12. Verfahren nach Anspruch 1, in welchem das Übergangsmetall-Katalysatorsystem eine Vanadium-Katalysatorzusammensetzung umfaßt, welche umfaßt:

- (i) das Reaktionsprodukt einer Vanadium-Verbindung und eines Elektronendonors, der eine flüssige, organische Lewis-Base, in der die Vanadium-Verbindung löslich ist, ist;
- (ii) einen Siliciumdioxid-Träger, in den die Komponente (i) einimpfprägniert ist;
- (iii) einen Halogenkohlenstoff-Promotor;



(iv) einen Hydrocarbylaluminium-Cokatalysator;
und der Autobeschleunigungs-Inhibitor ein Diels-Alder-Addukt oder ein Übergangsmetallcarbonyl ist,
mit der Maßgabe, daß der Inhibitor derart ist, daß er sich zersetzt, wenn der Katalysator seine
Autobeschleunigungs-Temperatur erreicht.

- 5 13. Verfahren nach Anspruch 12, in welchem die Lewis-Base ein Alkylester einer aliphatischen oder einer aromatischen Carbonsäure, ein aliphatisches Keton, ein aliphatisches Amin, ein aliphatischer Alkohol, ein Alkyl- oder Cycloalkylether oder eine Mischung davon ist.
- 10 14. Verfahren nach Anspruch 12 oder 13, in welchem die Vanadium-Katalysatorzusammensetzung zusätzlich ein Modifizierungsmittel mit der Formel BX_3 oder $AlR_{(3-a)}X_a$, in welcher R ein Alkylrest mit 1 bis 14 Kohlenstoffatomen ist; X für Chlor, Brom oder Iod steht; jedes R und X gleich oder verschieden ist; und a 0, 1 oder 2 ist; umfaßt.
- 15 15. Verfahren nach Anspruch 14, in welchem das Modifizierungsmittel Diethylaluminiumchlorid ist.
16. Verfahren nach Anspruch 14 oder 15, in welchem das Modifizierungsmittel in einer Menge von 0,1 bis 10 Mol, vorzugsweise 0,2 bis 2,5 Mol, pro Mol Elektronendonator eingesetzt wird.
- 20 17. Verfahren nach irgendeinem der Ansprüche 12 - 16, in welchem das Diels-Alder-Addukt 4 bis 20 Kohlenstoffatome aufweist.
18. Verfahren nach irgendeinem der Ansprüche 12 - 17, in welchem das Diels-Alder-Addukt monocyclisch oder polycyclisch ist.
- 25 19. Verfahren nach irgendeinem der Ansprüche 12 - 16, in welchem das Übergangsmetall des Übergangsmetallcarbonyls aus den Gruppen VIB, VIIB und VIII des Periodensystems ausgewählt wird.
- 30 20. Verfahren nach Anspruch 19, in welchem das Übergangsmetall des Übergangsmetallcarbonyls Chrom, Molybdän, Wolfram oder Eisen ist.
- 35 21. Verfahren nach Anspruch 19, in welchem das Übergangsmetallcarbonyl $Cr(CO)_6$; $Mo(CO)_6$; $Fe(CO)_5$; $W(CO)_6$; $C_5H_5Fe(COP)_2I$; $C_7H_5Mo(CO)_3$; $C_6H_5CO_2CH_3Cr(CO)_3$; $C_6H_5NHCH_3Cr(CO)_3$; $Fe_3(CO)_{12}$; $Ru_3(CO)_{12}$; $Os_3(CO)_{12}$; $Re_2(CO)_{10}$ oder $Mn_2(CO)_{10}$ ist.
- 40 22. Verfahren nach irgendeinem der Ansprüche 12 - 21, in welchem der Inhibitor in einem Molverhältnis von Inhibitor zu Vanadium im Bereich von 0,1:1 bis 200:1, vorzugsweise 0,5:1 bis 100:1, anwesend ist.
23. Verfahren nach irgendeinem der Ansprüche 12 - 22, in welchem der Inhibitor im imprägnierten Träger vorliegt.
- 45 24. Verfahren nach irgendeinem der Ansprüche 12 - 23, in welchem der Cokatalysator Triisobutylaluminium, Triethylaluminium oder Trihexylaluminium ist.
- 50 25. Verfahren nach irgendeinem der Ansprüche 12 - 24, in welchem der Promotor $CHCl_3$, CH_3CCl_3 oder $CFCI_3$ ist.
26. Verfahren nach irgendeinem der Ansprüche 12 - 25, in welchem die durch die Vanadium-Katalysatorzusammensetzung katalysierte Reaktion die Polymerisation von Ethylen ist und das In-Kontakt-Bringen von Ethylen und gegebenenfalls einem oder mehreren alpha-Olefin-Comonomeren mit der Vanadium-Katalysatorzusammensetzung unter Polymerisationsbedingungen umfaßt.

Revendications

- 55 1. Procédé pour la régulation in situ de la cinétique d'un catalyseur dans une réaction catalysée par un catalyseur à base d'un métal de transition, procédé qui comprend l'incorporation audit catalyseur à base d'un métal de transition d'un inhibiteur d'auto-accélération qui (i) à une température approximativement identique à la température à laquelle le catalyseur subit une auto-accélération dans ladite



- réaction, se décompose en un poison pour le catalyseur, et (ii) est pratiquement inerte à la température normale de fonctionnement du catalyseur dans ladite réaction, ou bien provoque une inhibition du catalyseur à ladite température normale de fonctionnement notablement inférieure à celle existant à la température d'auto-accélération ; ledit inhibiteur d'auto-accélération étant utilisé en une quantité suffisante pour fournir la quantité de poison requise pour inhiber le catalyseur à la température d'auto-accélération de ladite réaction.
2. Procédé suivant la revendication 1, dans lequel l'inhibiteur est un produit d'addition de Diels-Alder.
 3. Procédé suivant la revendication 2, dans lequel le produit d'addition de Diels-Alder possède 4 à 20 atomes de carbone.
 4. Procédé suivant la revendication 2 ou 3, dans lequel le produit d'addition de Diels-Alder est monocyclique ou polycyclique.
 5. Procédé suivant la revendication 4, dans lequel le produit d'addition de Diels-Alder est le dicyclopentadiène.
 6. Procédé suivant l'une quelconque des revendications 2 à 4, dans lequel le produit d'addition de Diels-Alder est une sulfone ou un carbonate.
 7. Procédé suivant la revendication 1, dans lequel l'inhibiteur est un composé carbonylé de métal de transition.
 8. Procédé suivant la revendication 7, dans lequel le métal de transition du composé carbonylé de métal de transition est le molybdène, le chrome, le tungstène ou le fer.
 9. Procédé suivant la revendication 7 ou 8, dans lequel le composé carbonylé de métal de transition contient, en plus des groupes carbonyle, des groupes organiques non substitués ou substitués ayant 2 à 20 atomes de carbone, sous réserve que le substituant soit inerte dans la mesure où le procédé dans lequel l'inhibiteur est utilisé est concerné.
 10. Procédé suivant l'une quelconque des revendications 1 à 9, dans lequel l'inhibiteur est utilisé en un rapport molaire de l'inhibiteur au métal de transition compris dans l'intervalle de 0,1:1 à 200:1, de préférence de 0,5:1 à 100:1.
 11. Procédé suivant l'une quelconque des revendications 1 à 10, dans lequel le catalyseur à base d'un métal de transition est un catalyseur en particules et l'inhibiteur se trouve dans pratiquement ou essentiellement toutes les particules du catalyseur à base d'un métal de transition.
 12. Procédé suivant la revendication 1, dans lequel le catalyseur à base d'un métal de transition comprend une composition de catalyseur au vanadium comprenant :
 - (i) le produit de réaction d'un composé de vanadium et d'un donneur d'électrons, qui est une base de Lewis organique liquide dans laquelle le composé de vanadium est soluble ;
 - (ii) un support consistant en silice imprégné avec le constituant (i) ;
 - (iii) un promoteur consistant en un hydrocarbure halogéné ;
 - (iv) un cocatalyseur consistant en un hydrocarburealuminium ;
 et l'inhibiteur d'auto-accélération est un produit d'addition de Diels-Alder ou un composé carbonylé de métal de transition, sous réserve que l'inhibiteur soit tel qu'il se décompose lorsque le catalyseur atteint sa température d'auto-accélération.
 13. Procédé suivant la revendication 12, dans lequel la base de Lewis est un ester alkyle d'un acide carboxylique aliphatique ou aromatique, une cétone aliphatique, une amine aliphatique, un alcool aliphatique, un éther alkyle ou cycloalkyle ou un de leurs mélanges.
 14. Procédé suivant la revendication 12 ou 13, dans lequel la composition de catalyseur au vanadium comprend en outre un modificateur répondant à la formule BX_n ou $AlR_{(3-n)}X_n$ dans laquelle chaque radical R est un radical alkyle ayant 1 à 14 atomes de carbone ; X représente le chlore, le brome ou



l'iode ; les groupes R et X sont identiques ou différents ; et a est égal à 0, 1 ou 2.

15. Procédé suivant la revendication 14, dans lequel le modificateur consiste en chlorure de diéthylaluminium.
16. Procédé suivant la revendication 14 ou 15, dans lequel le modificateur est utilisé en une quantité de 0,1 à 10 moles, de préférence de 0,2 à 2,5 moles, par mole de donneur d'électrons.
17. Procédé suivant l'une quelconque des revendications 12 à 16, dans lequel le produit d'addition de Diels-Alder possède 4 à 20 atomes de carbone.
18. Procédé suivant l'une quelconque des revendications 12 à 17, dans lequel le produit d'addition de Diels-Alder est monocyclique ou polycyclique.
19. Procédé suivant l'une quelconque des revendications 12 à 16, dans lequel de métal de transition du composé carbonylé de métal de transition est choisi dans des Groupes VIB, VIIB et VIII du Tableau Périodique.
20. Procédé suivant la revendication 19, dans lequel de métal de transition du composé carbonylé de métal de transition est le chrome, le molybdène, le tungstène ou le fer.
21. Procédé suivant la revendication 19, dans lequel le composé carbonylé de métal de transition est $\text{Cr}(\text{CO})_6$; $\text{Mo}(\text{CO})_6$; $\text{Fe}(\text{CO})_5$; $\text{W}(\text{CO})_6$; $\text{C}_5\text{H}_5\text{Fe}(\text{COP})_2\text{I}$; $\text{C}_7\text{H}_8\text{Mo}(\text{CO})_3$; $\text{C}_6\text{H}_5\text{CO}_2\text{CH}_3\text{Cr}(\text{CO})_3$; $\text{C}_6\text{H}_5\text{NHCH}_3\text{Cr}(\text{CO})_3$; $\text{Fe}_3(\text{CO})_{12}$; $\text{Ru}_3(\text{CO})_{12}$; $\text{Os}_3(\text{CO})_{12}$; $\text{Re}_2(\text{CO})_{10}$; ou $\text{Mn}_2(\text{CO})_{10}$.
22. Procédé suivant l'une quelconque des revendications 12 à 21, dans lequel l'inhibiteur est présent en un rapport molaire de l'inhibiteur au vanadium compris dans l'intervalle de 0,1:1 à 200:1, de préférence de 0,5:1 à 100:1.
23. Procédé suivant l'une quelconque des revendications 12 à 22, dans lequel l'inhibiteur est présent dans le support imprégné.
24. Procédé suivant l'une quelconque des revendications 12 à 23, dans lequel le cocatalyseur consiste en triisobutylaluminium, triéthylaluminium ou trihexylaluminium.
25. Procédé suivant l'une quelconque des revendications 12 à 24, dans lequel le promoteur consiste en CHCl_3 , CH_3CCl_3 ou CFCl_3 .
26. Procédé suivant l'une quelconque des revendications 12 à 25, dans lequel la réaction catalysée par la composition de catalyseur au vanadium est la polymérisation de l'éthylène et comprend le passage d'éthylène et, facultativement, d'un ou plusieurs comonomères alpha-oléfiniques en contact avec ladite composition de catalyseur au vanadium dans des conditions de polymérisation.