

Description

This invention relates to a novel catalyst for the dimerization of ethylene. This invention also relates to a novel process for the dimerization of ethylene to give 1-butene in high selectivity.

A variety of catalysts, both homogeneous and heterogeneous, have been utilized to dimerize ethylene to butene. For example U.S. 3,564,072 discloses a process for the dimerization of ethylene employing a catalyst formed by combining a nickel (II) phosphate coordination complex, an inorganic Lewis acid, and an excess of phosphine ligand.

U.S. 3,644,564 discloses the dimerization of ethylene in the presence of a catalyst comprising a nickel (0) compound complexed with fluorine containing ligands.

While the catalyst systems disclosed by the above references are operable for the dimerization of ethylene, they are merely typical of other dimerization catalysts known in the art. By using these and other known catalyst systems for the dimerization of ethylene, one has not always achieved high catalyst productivity, good selectivity to desired 1-butene product or a combination of both.

Because of the increasing importance that 1-butene is playing in the chemical industry, as exemplified by the importance of α -olefins, processes which make even slight improvements in the availability of 1-butenes over existing processes are highly desirable.

Therefore, it is an object of this invention to provide an improved catalyst for the dimerization of ethylene. A further object of this invention is to provide an improved process for the dimerization of ethylene. Yet another object of this invention is to provide a highly selective process for the dimerization of ethylene to give 1-butene.

Other aspects, objects and advantages of the present invention will become apparent from a study of this specification and the claims.

In accordance with one embodiment of the present invention, it was discovered a novel catalyst composition for the dimerization of ethylene which is highly productive and affords good selectivity to the desired 1-butene. This improved catalyst composition comprises:

(a) at least one nickel compound selected from the group consisting of: bis(1,5-cyclooctadiene)-nickel(0), bis(tricyclohexylphosphine)nickel(0), (cyclododecatriene)nickel, and bis(ethylene)-dicyclohexylphosphine)nickel;

(b) a phosphine compound of the formula PR_3 wherein each R independently represents H or a C_1 to C_{20} hydrocarbyl radical with the proviso that any alkenyl substitution be at least 3 carbon atoms removed from the phosphorus atom and at least one R is not H; and

(c) at least one acidic compound selected from the groups consisting of:

(i) a sulfonic acid of the formula $R'SO_3H$ wherein R' is H, or a fluorinated or nonfluorinated alkyl, aryl, alkaryl, or aralkyl radical with 1—10 carbon atoms; and

(ii) a carboxylic acid of the formula $R''COOH$ wherein R'' is at least a partially fluorinated alkyl, aryl, alkaryl, or aralkyl radical with 1—9 carbon atoms.

Exemplary of the phosphine compounds of the formula PR_3 are dicyclohexylphosphine, triphenylphosphine, and tris(4-fluorophenyl)phosphine. Preferred is dicyclohexylphosphine.

Examples of non-fluorinated sulfonic acids of the formula $R'SO_3H$ for use in the present invention are para-toluenesulfonic acid, benzenesulfonic acid, naphthalenesulfonic acid, methanesulfonic acid, and mixtures thereof.

Exemplary fluorinated sulfonic acids are trifluoromethanesulfonic acid, 4-fluorobenzenesulfonic acid, pentafluorobenzenesulfonic acid, 4-trifluoromethylbenzenesulfonic acid, and mixtures thereof.

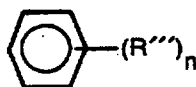
Exemplary carboxylic acids are trifluoroacetic acid, heptafluorobutyric acid, pentafluorobenzoic acid, perfluoropropionic acid, and mixtures thereof.

While the order of addition of catalyst precursors is not thought to be critical in the present invention, preferably the inventive composition is made by contacting the catalyst precursors, i.e., a suitable nickel compound, and phosphine compound, each present in a suitable solvent as described in this specification, at room temperature for about 15 minutes. Subsequently the acidic compound, present in a suitable solvent, is added.

In the catalyst composition, the molar ratio of the phosphine ligand to the nickel compound can be broadly 0.01—4.0 to 1, preferably 0.5—2.5 to 1. The molar ratio of the particular acid compound used to the nickel compound should generally be 0.01—10.0 to 1, preferably 0.05—2.0 to 1.

In accordance with another embodiment of the present invention I have discovered that ethylene is efficiently dimerized by contacting ethylene at a temperature from 0°C to 200°C with the catalyst composition described in an earlier embodiment of the present invention, said catalyst composition being present in at least one solvent selected from the group consisting of:

(i) an aromatic hydrocarbon of the formula

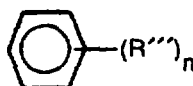


wherein R''' represents a C_1 to C_6 alkyl radical and n is 0, 1, 2, 3, or 4; and

(ii) an alcohol of the formula $(R^{IV})_3COH$ wherein each R^{IV} independently represents H or a C_1 to C_{12} alkyl, cycloalkyl, aryl, alkaryl, or aralkyl radical.

After the inventive catalyst, present in at least one solvent, is prepared as described above, it is contacted with ethylene. The precise method of establishing ethylene/catalyst contact during the reaction is not critical. In one modification, the catalyst system is charged to an autoclave or other similar pressure (vessel) reactor, the ethylene is introduced, and the reaction mixture is maintained with agitation at reaction temperature and pressure for the desired reaction period.

Aromatic hydrocarbon solvents of the formula



contemplated for use in the present invention include benzene, toluene, xylenes, trimethylbenzenes, ethylbenzenes, cumene and mixtures thereof. Toluene is presently preferred.

Exemplary alcohols of the formula $(R^{IV})_3COH$ include ethanol, 2-butanol, isobutanol, tertiary butanol, 2-pentanol, 1-hexanol and mixtures thereof. Presently preferred is 2-pentanol.

Whatever solvent is used, of course, must exist as a liquid at dimerization reaction conditions.

The weight ratio of the solvent employed to the combination of the nickel compound, phosphine compound and acid components can be broadly $1-10^6$ to 1 with the amount of the solvent used limited only by its cost, the ease of product recovery therefrom, the required reaction vessel size, and other practical considerations. The preferred weight ratio is 5-10,000 to 1.

Broadly, reaction temperatures vary from $0^\circ C$ to $200^\circ C$, preferably from $20^\circ C$ to $125^\circ C$.

The reaction pressure is not thought to be critical but typically varies from 5-5000 psig (0.03-34.5 MPa gauge) preferably from 200-2000 psig (1.38-13.8 MPa gauge).

The reaction time is broadly from 1 minute to 18 hours, preferably from 5 minutes to 5 hours.

The dimerization products are separated and recovered from the reaction mixture by conventional methods such as fractional distillation, selective extraction, and adsorption.

It is within the scope of this invention to employ a batchwise or continuous reaction system wherein ethylene is passed in a continuous manner into a reaction zone containing the inventive catalyst system while ethylene dimerization product mixture is concomitantly withdrawn from the reaction mixture.

The following examples further illustrate the present invention.

Example I

All reactions described were carried out in a 300 mL stainless steel (316SS) Autoclave Engineers stirred tank reactor. The reactor was first charged with about 50 mL of solvent, sealed under nitrogen, then pressured with ethylene and vented to aid oxygen removal. Under a sweep of ethylene, bis(1,5-cyclo-octadiene)nickel(0) [Ni(COD)] was added, typically 0.5 g dissolved in a minimum volume of solvent (typically toluene) was employed. Then, the desired amount of a phosphine compound was added, dissolved in a minimum volume of solvent. This mixture was stirred for about 15 minutes, internal standards (pentane and heptane, about 3 g each) added and finally the acid component to be employed was added, dissolved in a minimum volume of solvent. The reactor was then charged with ethylene to a predetermined pressure, and reaction allowed to proceed in the range of room temperature to about $80^\circ C$, heating or cooling provided as necessary. The reaction pressure employed was typically about 700 psig (4.8 MPa gauge). The desired pressure was maintained by periodic incremental additions of ethylene with up to about 15 additions per run. When the reaction was complete, about 10 mL of 2,4-pentanedione was added to the reactor to quench the catalyst, then a liquid sample (about 5-10 mL) was collected in a 75 mL stainless steel pressure bomb and set aside for gas liquid chromatographic (GLC) analysis.

Then the reactor was cooled to below room temperature, the ethylene pressure vented, and the reactor contents purged with nitrogen before opening the vessel. The product mixture was weighed to determine weight gain and then filtered prior to GLC analysis. A $45\text{ m} \times 0.25\text{ mm}$ ($150' \times 0.01''$) glass or stainless steel capillary column coated with OV-101^(TM) (a stationary phase of methylsilicon, trademark of Ohio Valley Specialty Chemical Company) was employed for sample analysis. Analysis conditions were $100^\circ C$ for two minutes after injection, followed by $32^\circ/\text{min}$ temperature program up to $200^\circ C$ final column temperature.

The bomb sample was analyzed in two portions. A first sample was injected under pressure onto a $6\text{ m} \times 7.5\text{ cm}$ ($20' \times \frac{1}{4}'$) stainless steel column packed with 19% bis-2-methoxyethoxyethylene on 60/80 mesh (0.25/0.18 mm) Chromosorb P^(TM) (diatomaceous earth gas chromatography column packing support, trademark of John Mainville). Isothermal analysis conditions at $40^\circ C$ with helium carrier gas gave the amount of light (C_2-C_5) hydrocarbons in the reactor mixture. Another aliquot of the first sample was injected under pressure onto a $3.6\text{ m} \times 3.1\text{ mm}$ ($12' \times \frac{1}{8}''$) stainless steel column packed with 0.19% picric acid on 80/100 mesh (0.18/0.15 mm) Carbowax C^(TM) (graphitized carbon gas column packing support, trademark of Supelco) maintained at $50^\circ C$ isothermal to determine the amount of isobutylene present in the C_4 fraction. Bomb contents were then cooled, vented and poured into an open vessel, then analyzed on a $45\text{ m} \times 0.50\text{ mm}$ od ($150' \times 0.02''$ od) (0.25 mm = 0.01" id) capillary column coated with OV-101^(TM) (see above)

with helium carrier gas and temperature programming at 5°C/min starting at 20°C up to a final temperature of 90°C for heavy (C_6 and greater) hydrocarbons.

Reaction results are reported in terms of catalyst productivity, wt % C_4 , and the % 1-butene in the C_4 fraction. Catalyst productivity is defined as the grams of oligomerized (i.e. C_4 and greater) product produced per gram of Ni per hour. The wt % C_4 is the wt % of C_4 of the total oligomerization product. Percent 1-butene in the C_4 fraction is measured by analyzing the C_4 fraction of the oligomerization product for 1-butene, 2-butenes and branched C_4 olefin.

Example II Effect of Acid

A series of reactions were carried out in 2-pentanol as solvent, with bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)], dicyclohexylphosphine [DCH] or tris(4-fluorophenyl) phosphine [TFP] and a variety of acids, following the general procedure described above in Example I. Thus, 50 mL of 2-pentanol and reagents as listed in Table I were charged to the reactor. Reaction parameters and results are summarized in Table I.

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TABLE I

Reagents, mmol			Reaction Parameters						
Run	Acid	Phosphine*	Ni(COD)	Time, min.	Temp., °C	Press., psig (MPa gauge)	Product-ivity	Wt% C ₄	% 1-Butene in C ₄ -Fraction
1	4-Me(C ₆ H ₄)SO ₃ H,1.6	DCH,1.5	1.5	55	55	700(4.8)	1109	97.7	98.7
2	4-Me(C ₆ H ₄)SO ₃ H,2.2	DCH,2.0	2.0	70	55	700(4.8)	617	97.3	98.7
3	4-Me(C ₆ H ₄)SO ₃ H,1.9	DCH,1.7	1.7	60	57	700(4.8)	800	97.7	98.3
4	F ₃ CSO ₂ H,0.9	DCH,0.9	0.8	50	55	700(4.8)	3994	NA**	81.7
5	F ₃ CCO ₂ H,1.9	DCH,1.8	1.9	40	55	700(4.8)	1243	40.4	NA**
6	F ₃ CCO ₂ H,1.8	DCH,1.8	1.8	90	56	700(4.8)	1139	43.7	NA**
7	F ₃ CCO ₂ H,1.8	DCH,1.9	1.9	50	57	700(4.8)	890	43.5	97.6
8	4-Me(C ₆ H ₄)SO ₃ H,1.9	TFP,1.7	2.0	120	54	700(4.8)	185	98.4	83.7
9	F ₃ CCO ₂ H,1.7	TFP,1.7	1.7	90	55	700(4.8)	85	94.6	88.4

* DCH = dicyclohexylphosphine

TFP = tris(4-fluorophenyl)phosphine

** Not analyzed

The results of these experiments demonstrate that 1-butene can be prepared in high yield and selectivity employing the catalysts of this invention. Note especially the outstanding results obtained with a sulfonic acid such as toluene sulfonic acid and a simple phosphine such as dicyclohexylphosphine.

Example III

Effect of phosphine

A series of reactions were carried out in 2-pentanol as solvent with bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)], an acid component, and a variety of phosphine components, following the general procedure set forth above in Example I. Thus, 50 mL of 2-pentanol and reagents as listed in Table II were charged to the reactor. Reaction parameters and results are summarized in Table II.

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TABLE II

Reagents, mmol		Reaction Parameters			Product- ivity	Wt% C ₄	% 1-Butene in C ₄ -Fraction
Run	Phosphine	Acid*	Ni(COD)	Time, Temp., min. °C	Press., psig (MPa gauge)		
1	(cy-C ₆ H ₁₁) ₂ PH, 1.5	TSA, 1.6	1.5	55	700(4.8)	97.7	98.7
2	(cy-C ₆ H ₁₁) ₂ PH, 2.0	TSA, 2.2	2.0	70	700(4.8)	97.3	98.7
3	(cy-C ₆ H ₁₁) ₂ PH, 1.7	TSA, 1.9	1.7	60	700(4.8)	97.7	98.3
4	PPh ₃ , 1.9	TSA, 2.2	2.0	90	700(4.8)	98.5	81.6
5	[4-F(C ₆ H ₄) ₂] ₃ P, 1.7	TSA, 1.9	2.0	120	700(4.8)	98.4	83.7
6	(cy-C ₆ H ₁₁) ₂ PH, 1.8	TFA, 1.9	1.9	40	700(4.8)	40.4	NA**
7	(cy-C ₆ H ₁₁) ₂ PH, 1.8	TFA, 1.8	1.8	90	700(4.8)	43.7	NA**
8	(cy-C ₆ H ₁₁) ₂ PH, 1.9	TFA, 1.8	1.9	50	700(4.8)	43.5	97.6
9	PPh ₃ , 1.6	TFA, 1.7	1.6	65	700(4.8)	91.8	91.3
10	[4-F(C ₆ H ₄) ₂] ₃ P, 1.7	TFA, 1.7	1.7	90	700(4.8)	94.6	88.4

* TSA = 4-toluenesulfonic acid

TFA = trifluoroacetic acid

** Not analyzed

The results of these experiments demonstrate that several phosphines, including dicyclohexylphosphine, triphenylphosphine and tris(4-fluorophenyl)phosphine give excellent ethylene conversion with high selectivity to the desired α -olefin, 1-butene.

Example IV
Effect of Solvent

A series of reactions were carried out with bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)], an acid component, a phosphine component and toluene or 2-pentanol solvent, following the general procedure set forth above. In all cases, 50 mL of solvent were employed, plus quantities of reagents as listed in Table III. Reaction parameters and results are summarized in Table III.

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TABLE III

Run	Solvent	Reagents, mmol		Reaction Parameters			Product- ivity	Wt% C ₄	% 1-Butene in C ₄ -Fraction	
		Acid*	Phosphine**	Ni(COD)	Time, min.	Temp., °C				Press., psig (MPa gauge)
1	2-pentanol	TMS,0.9	DCH,0.9	0.8	50	55	700(4.8)	3994	NA***	81.7
2	toluene	TMS,0.7	DCH,0.7	0.7	20	55	700(4.8)	11810	NA***	88.9
3	2-pentanol	TSA,1.6	DCH,1.5	1.5	55	55	700(4.8)	1109	97.7	98.7
4	2-pentanol	TSA,2.2	DCH,2.0	2.0	70	55	700(4.8)	617	97.3	98.7
5	2-pentanol	TSA,1.9	DCH,1.7	1.7	60	57	700(4.8)	800	97.7	98.3
6	toluene	TSA,2.2	DCH,2.0	2.0	75	56	700(4.8)	475	90.5	99.0
7	2-pentanol	TSA,1.9	TFP,1.7	2.0	120	54	700(4.8)	185	98.4	83.7
8	toluene	TSA,1.9	TFP,1.7	1.7	110	56	700(4.8)	144	98.8	91.1

* TMS = trifluoromethanesulfonic acid

TSA = 4-toluenesulfonic acid

** DCH = dicyclohexylphosphine

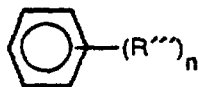
TFP = tris(4-fluorophenyl)phosphine

*** Not analyzed

The results of these experiments demonstrate that both aromatic hydrocarbon solvents such as toluene and alcohol solvents such as 2-pentanol are effective for carrying out the inventive dimerization reaction.

5 Claims

1. A composition comprising
 - (a) at least one nickel compound selected from bis (1,5-cyclooctadiene)nickel (0), bis (tricyclohexylphosphine)nickel(0), (cyclododecatriene)nickel, and bis(ethylene)(dicyclohexylphosphine)nickel;
 - 10 (b) a phosphine compound of the formula PR_3 wherein each R independently represents H or a C_1 to C_{20} hydrocarbyl radical with the proviso that any alkenyl substitution be at least 3 carbon atoms removed from the phosphorus atom and at least one R is not H; and
 - (c) at least one acidic compound selected from
 - (i) a sulfonic acid of the formula $R'SO_3H$ wherein R' is H, or a fluorinated or nonfluorinated alkyl, aryl alkaryl, or aralkyl radical with 1—10 carbon atoms; and
 - 15 (ii) a carboxylic acid of the formula $R''COOH$ wherein R'' is at least a partially fluorinated alkyl, aryl alkaryl, or aralkyl radical with 1—9 carbon atoms; wherein the molar ratio of (b) to (a) is from 0.01:1 to 4:1 and the molar ratio of (c) to (a) is from 0.01:1 to 10:1.
- 20 2. The composition of claim 1 characterized in that (a) is bis(1,5-cyclooctadiene)nickel(0).
3. The composition of claim 1 or 2 characterized in that (b) is selected from triphenylphosphine, tris(4-fluorophenyl)phosphine and dicyclohexylphosphine, preferably wherein (b) is dicyclohexylphosphine.
4. The composition of any of the preceding claims characterized in that (c) is selected from p-toluenesulfonic acid, trifluoromethanesulfonic acid, trifluoroacetic acid and heptafluorobutyric acid.
- 25 5. The composition of any of the preceding claims characterized in that the molar ratio of (b) to (a) is from 0.5:1 to 2.5:1 and the molar ratio of (c) to (a) is from 0.01:1 to 10:1.
6. A process for the oligomerization of ethylene which comprises contacting said ethylene with a catalyst composition in the liquid phase present in at least one solvent, characterized by utilizing a composition as defined in any of claims 1 to 5 and a solvent selected from
 - 30 (i) an aromatic hydrocarbon of the formula



- 35 wherein each R''' independently represents a C_1 to C_6 alkyl radical and n is 0, 1, 2, 3, or 4; and
- (ii) an alcohol of the formula $(R''')_3COH$ wherein each R''' independently represents H or a C_1 to C_{12} alkyl, cycloalkyl, aryl, alkaryl, or aralkyl radical.
7. The process of claim 6 characterized by being carried out at a temperature from 0 to 200°C.
- 40 8. The process of claim 6 or 7 characterized in that said solvent is selected from benzene, toluene, xylenes, trimethylbenzenes, ethylbenzenes, and cumene, preferably wherein said solvent is toluene.
9. The process of claim 6 or 7 characterized in that said solvent is selected from ethanol, 2-pentanol, t-butanol, iso-butanol, 2-butanol, and 2-hexanol, preferably wherein said solvent is 2-pentanol.

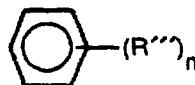
45 Patentansprüche

1. Zusammensetzung, enthaltend
 - (a) mindestens eine Nickelverbindung, ausgewählt aus Bis-(1,5-cyclooctadien)-nickel(0), Bis-(tricyclohexylphosphin)-nickel(0), (Cyclododecatrien)-nickel, und Bis-(ethylen)-(dicyclohexylphosphin)-nickel;
 - 50 (b) eine Phosphinverbindung der Formel PR_3 , wobei jedes R unabhängig H oder einen C_1 -bis C_{20} -Hydrocarbylrest bedeutet, mit der Maßgabe, daß jegliche Alkenylsubstitution mindestens 3 Kohlenstoffatome von dem Phosphoratom entfernt ist und mindestens ein R nicht H ist; und
 - (c) mindestens eine saure Verbindung, ausgewählt aus
 - (i) einer Sulfonsäure der Formel $R'SO_3H$, wobei R' H oder ein fluorierter oder nichtfluorierter Alkyl-, Aryl-, Alkaryl- oder Aralkylrest mit 1—10 Kohlenstoffatomen ist; und
 - 55 (ii) einer Carbonsäure der Formel $R''COOH$, wobei R'' mindestens einen teilweise fluorierten Alkyl-, Aryl-, Alkaryl- oder Aralkylrest mit 1—9 Kohlenstoffatomen bedeutet; wobei das Molverhältnis von (b) zu (a) 0,01:1 bis 4:1, und das Molverhältnis von (c) zu (a) 0,01:1 bis 10:1 beträgt.
- 60 2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß (a) Bis-(1,5-cyclooctadien)-nickel(0) ist.
3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß (b) ausgewählt ist aus Triphenylphosphin, Tris-(4-fluorphenyl)-phosphin und Dicyclohexylphosphin, wobei (b) vorzugsweise Dicyclohexylphosphin ist.
- 65 4. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß (c)

The results of these experiments demonstrate that both aromatic hydrocarbon solvents such as toluene and alcohol solvents such as 2-pentanol are effective for carrying out the inventive dimerization reaction.

5 Claims

1. A composition comprising
 - (a) at least one nickel compound selected from bis (1,5-cyclooctadiene)nickel (0), bis (tricyclohexylphosphine)nickel(0), (cyclododecatriene)nickel, and bis(ethylene)(dicyclohexylphosphine)nickel;
 - (b) a phosphine compound of the formula PR_3 wherein each R independently represents H or a C_1 to C_{20} hydrocarbyl radical with the proviso that any alkenyl substitution be at least 3 carbon atoms removed from the phosphorus atom and at least one R is not H; and
 - (c) at least one acidic compound selected from
 - (i) a sulfonic acid of the formula $R'SO_3H$ wherein R' is H, or a fluorinated or nonfluorinated alkyl, aryl alkaryl, or aralkyl radical with 1—10 carbon atoms; and
 - (ii) a carboxylic acid of the formula $R''COOH$ wherein R'' is at least a partially fluorinated alkyl, aryl alkaryl, or aralkyl radical with 1—9 carbon atoms; wherein the molar ratio of (b) to (a) is from 0.01:1 to 4:1 and the molar ratio of (c) to (a) is from 0.01:1 to 10:1.
2. The composition of claim 1 characterized in that (a) is bis(1,5-cyclooctadiene)nickel(0).
3. The composition of claim 1 or 2 characterized in that (b) is selected from triphenylphosphine, tris(4-fluorophenyl)phosphine and dicyclohexylphosphine, preferably wherein (b) is dicyclohexylphosphine.
4. The composition of any of the preceding claims characterized in that (c) is selected from p-toluenesulfonic acid, trifluoromethanesulfonic acid, trifluoroacetic acid and heptafluorobutyric acid.
5. The composition of any of the preceding claims characterized in that the molar ratio of (b) to (a) is from 0.5:1 to 2.5:1 and the molar ratio of (c) to (a) is from 0.01:1 to 10:1.
6. A process for the oligomerization of ethylene which comprises contacting said ethylene with a catalyst composition in the liquid phase present in at least one solvent, characterized by utilizing a composition as defined in any of claims 1 to 5 and a solvent selected from
 - (i) an aromatic hydrocarbon of the formula



- wherein each R''' independently represents a C_1 to C_6 alkyl radical and n is 0, 1, 2, 3, or 4; and
- (ii) an alcohol of the formula $(R''')_3COH$ wherein each R''' independently represents H or a C_1 to C_{12} alkyl, cycloalkyl, aryl, alkaryl, or aralkyl radical.
7. The process of claim 6 characterized by being carried out at a temperature from 0 to 200°C.
8. The process of claim 6 or 7 characterized in that said solvent is selected from benzene, toluene, xylenes, trimethylbenzenes, ethylbenzenes, and cumene, preferably wherein said solvent is toluene.
9. The process of claim 6 or 7 characterized in that said solvent is selected from ethanol, 2-pentanol, t-butanol, iso-butanol, 2-butanol, and 2-hexanol, preferably wherein said solvent is 2-pentanol.

45 Patentansprüche

1. Zusammensetzung, enthaltend
 - (a) mindestens eine Nickelverbindung, ausgewählt aus Bis-(1,5-cyclooctadien)-nickel(0), Bis-(tricyclohexylphosphin)-nickel(0), (Cyclododecatrien)-nickel, und Bis-(ethylen)-(dicyclohexylphosphin)-nickel;
 - (b) eine Phosphinverbindung der Formel PR_3 , wobei jedes R unabhängig H oder einen C_1 -bis C_{20} -Hydrocarbylrest bedeutet, mit der Maßgabe, daß jegliche Alkenylsubstitution mindestens 3 Kohlenstoffatome von dem Phosphoratom entfernt ist und mindestens ein R nicht H ist; und
 - (c) mindestens eine saure Verbindung, ausgewählt aus
 - (i) einer Sulfonsäure der Formel $R'SO_3H$, wobei $R'H$ oder ein fluorierter oder nichtfluorierter Alkyl-, Aryl-, Alkaryl- oder Aralkylrest mit 1—10 Kohlenstoffatomen ist; und
 - (ii) einer Carbonsäure der Formel $R''COOH$, wobei R'' mindestens einen teilweise fluorierten Alkyl-, Aryl-, Alkaryl- oder Aralkylrest mit 1—9 Kohlenstoffatomen bedeutet; wobei das Molverhältnis von (b) zu (a) 0,01:1 bis 4:1, und das Molverhältnis von (c) zu (a) 0,01:1 bis 10:1 beträgt.
2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß (a) Bis-(1,5-cyclooctadien)-nickel(0) ist.
3. Zusammensetzung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß (b) ausgewählt ist aus Triphenylphosphin, Tris-(4-fluorphenyl)-phosphin und Dicyclohexylphosphin, wobei (b) vorzugsweise Dicyclohexylphosphin ist.
4. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß (c)



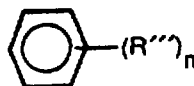
ausgewählt ist aus p-Toluolsulfonsäure, Trifluormethansulfonsäure, Trifluoressigsäure und Heptafluorbuttersäure.

5. Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Molverhältnis von (b) zu (a) 0,5:1 bis 2,5:1 und das Molverhältnis von (c) zu (a) 0,01:1 bis 10:1 beträgt.

6. Verfahren zur Oligomerisierung von Ethylen, wobei das Ethylen kontaktiert wird mit einer Katalysatorzusammensetzung in flüssiger Phase, die in mindestens einem Lösungsmittel vorliegt, dadurch gekennzeichnet, daß man eine Zusammensetzung wie in einem der Ansprüche 1 bis 5 definiert und ein Lösungsmittel verwendet, das ausgewählt ist aus

(i) einem aromatischen Kohlenwasserstoff der Formel

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15 wobei jedes R''' unabhängig ein C₁- bis C₆-Alkylrest ist und n den Wert 0, 1, 2, 3 oder 4 bedeutet; und
(ii) einem Alkohol der Formel (R^{iv})₃COH, wobei jedes R^{iv} unabhängig H oder einen C₁- bis C₁₂-Alkyl-, Cycloalkyl-, Aryl-, Alkaryl- oder Aralkylrest bedeutet.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß es bei Temperaturen von 0 bis 200°C durchgeführt wird.

20 8. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß das Lösungsmittel ausgewählt ist aus Benzol, Toluol, Xylole, Trimethylbenzolen, Ethylbenzolen und Cumol, wobei das Lösungsmittel vorzugsweise Toluol ist.

9. Verfahren nach Anspruch 6 oder 7, dadurch gekennzeichnet, daß das Lösungsmittel ausgewählt ist aus Ethanol, 2-Pentanol, t-Butanol, Isobutanol, 2-Butanol und 2-Hexanol, wobei das Lösungsmittel vorzugsweise 2-Pentanol ist.

Revendications

1. Composition comprenant:

30 (a) au moins un composé du nickel choisi parmi le bis (1,5-cyclooctadiène)nickel (0), le bis (tricyclohexylphosphine)nickel(0), le (cyclododécatriène)nickel et le bis (éthylène)(dicyclohexylphosphine)nickel;

(b) une phosphine répondant à la formule PR₃ dans laquelle chacun des R représente indépendamment H ou un radical hydrocarbyle en C₁ à C₂₀, sous réserve que toute substitution d'alcényle soit éloignée d'au moins 3 atomes de carbone de l'atome de phosphore et qu'au moins un des R ne soit pas H; et

35 (c) au moins un composé acide choisi parmi

(1) un acide sulfonique répondant à la formule R'SO₃H, dans laquelle R' est H, ou un radical alkyle, aryle, alkaryl ou aralkyle en C₁ à C₁₀ fluoré ou non fluoré; et

(2) un acide carboxylique répondant à la formule R''COOH, dans laquelle R'' est un radical alkyle, aryle, alkaryl ou aralkyle en C₁ à C₉ au moins partiellement fluoré;

40 dans laquelle le rapport molaire de (b) à (a) est de 0,01:1 à 4:1 et le rapport molaire de (c) à (a) est de 0,01:1 à 10:1.

2. Composition selon la revendication 1, caractérisée en ce que (a) est le bis(1,5-cyclooctadiène)nickel(0).

3. Composition selon les revendications 1 ou 2, caractérisée en ce que (b) est choisi parmi la triphénylphosphine, la tris(4-fluorophényl)phosphine et la dicyclohexylphosphine, de préférence dans laquelle (b) est la dicyclohexylphosphine.

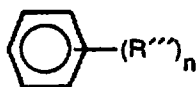
4. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que (c) est choisi parmi l'acide p-toluènesulfonique, l'acide trifluorométhanesulfonique, l'acide trifluoroacétique et l'acide heptafluorobutyrique.

50 5. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce que le rapport molaire de (b) à (a) est de 0,5:1 à 2,5:1 et en ce que le rapport molaire de (c) à (a) est de 0,01:1 à 10:1.

6. Procédé pour l'oligomérisation de l'éthylène qui consiste à mettre en contact cet éthylène avec une composition de catalyseur en phase liquide présente dans au moins un solvant, caractérisé en ce qu'on utilise une composition telle que définie dans l'une quelconque des revendications 1 à 5, et un solvant choisi parmi:

(1) un hydrocarbure aromatique répondant à la formule

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65 dans laquelle chacun des R''' représente indépendamment un radical alkyle en C₁ à C₆ et n est 0, 1, 2, 3; ou 4; et



(2) un alcool répondant à la formule $(R^{IV})_3COH$, dans laquelle chacun des R^{IV} représente indépendamment H ou un radical alkyle, cycloalkyle, aryle, alkaryle ou aralkyle en C_1 à C_{12} .

7. Procédé selon la revendication 6, caractérisé en ce qu'il est effectué à une température de 0 à 200°C.

8. Procédé selon les revendications 6 ou 7, caractérisé en ce que ce solvant est choisi parmi le benzène, le toluène, les xylènes, les triméthylbenzènes, les éthylbenzènes et le cumène, de préférence dans lequel ce solvant est le toluène.

9. Procédé selon les revendications 6 ou 7, caractérisé en ce que ce solvant est choisi parmi l'éthanol, le 2-pentanol, le t-butanol, l'isobutanol, le 2-butanol, et le 2-hexanol, et est de préférence le 2-pentanol.

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