

TITLE

INSOLUBLE LEWIS ACID PROMOTERS FOR NICKEL-CATALYSED HYDROCYANATION OF MONOOLEFINS

5

BACKGROUND OF THE INVENTION

This invention relates to a process for converting an acyclic monoolefin to its corresponding terminal organonitrile compound by reacting the monoolefin with
10 hydrogen cyanide (HCN) in the presence of zero-valent nickel, a phosphite ligand, and a Lewis acid promoter.

Hydrocyanation catalyst systems, particularly pertaining to the hydrocyanation of olefins, are well known in the art. For example, systems useful for the
15 hydrocyanation of butadiene to form pentenenitrile (PN) and for the subsequent hydrocyanation of pentenenitrile (PN) to form adiponitrile (ADN), are known in the commercially important nylon synthesis field. The hydrocyanation of olefins using transition metal
20 complexes with monodentate phosphite ligands is well documented in the prior art. See for example U.S. Patents 3,496,210, 3,631,191, 3,655,723 and 3,766,237; and Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; and Stevens, W. R.; Advances in
25 Catalysis, 33, 1, 1985. The hydrocyanation of activated olefins, such as conjugated olefins (e.g., butadiene and styrene) and strained olefins (e.g., norbornene), proceeds without the use of a Lewis acid promoter, while hydrocyanation of unactivated olefins,
30 such as 1-octene and 3-pentenenitrile, requires the use of a Lewis acid promoter. Teachings regarding the use of a promoter in the hydrocyanation reaction appear, for example, in U.S. Patent 3,496,217. This patent discloses an improvement in hydrocyanation using a

promoter selected from a large number of soluble metal cation compounds. U.S. Patent 3,496,218 discloses a nickel hydrocyanation catalyst promoted with various boron-containing compounds, including triphenylboron and alkali metal borohydrides. U.S. Patent 4,774,353 discloses a process for the preparation of dinitriles, including ADN, from unsaturated nitriles, including PN, in the presence of a zerovalent nickel catalyst and a triorganotin catalyst promoter. U.S. Patent 4,874,884 discloses a process for producing ADN by the zerovalent nickel-catalyzed hydrocyanation of pentenenitriles in the presence of a synergistic combination of promoters selected on the basis of the reaction kinetics of the ADN synthesis. U.S. Patents 5,233,058 and 5,286,825 disclose the nickel-catalyzed hydrocyanation of perfluoroalkyl ethylene and other partially fluorinated olefins. U. S. Patent 5,087,723 discloses nickel-catalyzed hydrocyanation of penteneoates. In each of these cases, the catalyst and promoter are dissolved in the reaction medium, providing an essentially homogeneous reaction environment (i.e., everything is soluble). The homogeneous nature of this reaction system makes it difficult to recover the catalyst and promoter for reuse. Whereas practical methods for recovery of nickel catalyst are known (see, for example, U.S. Patent 3,773,809), recovery of promoters remains a difficult problem. U.S. Patent 3,846,474 discloses that the addition of aluminosilicate zeolites to a nickel-catalyzed zinc chloride-promoted hydrocyanation reaction of 3-pentenenitrile may improve catalyst utility and product distribution.

SUMMARY OF THE INVENTION

The present invention provides a novel hydrocyanation process wherein the promoter is insoluble in the reaction medium and is, therefore, readily separable from the reagents and reaction products by mechanical means such as filtration. The process of the present invention comprises reacting an acyclic monoolefin with HCN in a temperature range of -25°C to 200°C and in a pressure range of 0.05 to 100 atmospheres in the presence of a nickel catalyst and an insoluble Lewis acid promoter to produce corresponding terminal organonitrile products, and then separating the promoter by mechanical means, such as filtration.

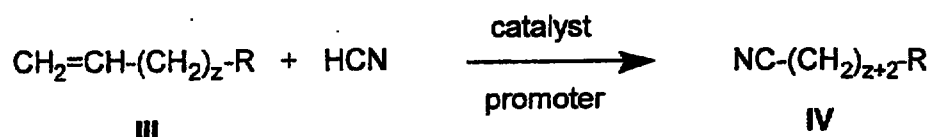
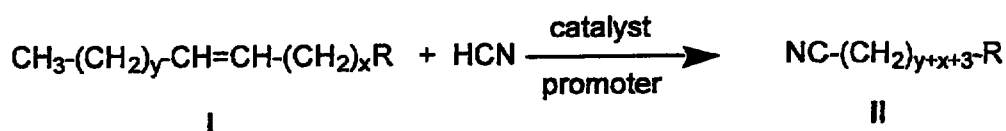
The insoluble promoters of this invention must exhibit Lewis acidity, this acidity being manifested in a theoretical sense by the metal ions' ability to accept donation of an electron pair forming a dative (donor-acceptor) bond (e.g., from a nitrile or pyridine to form a coordination complex). Preferred insoluble promoters may be selected from several classes of materials: (a) polyolefins (such as polystyrene, polyethylene or polypropylene) having metal ions or metal ion complexes covalently bonded to the polyolefin, (b) sulphonate or carboxylate substituted polyolefins having metal ions or metal ion complexes ionically bonded to the polymer, including metal-exchanged perfluorosulphonic acid resins, (c) metal oxides in which the metal ions themselves are the centers of Lewis acidity, and (d) insoluble metal halides, phosphates or sulfates.

DETAILED DESCRIPTION OF THE INVENTION

The present process for hydrocyanating an acyclic monoolefin to form the corresponding nitrile, comprises reacting an acyclic monoolefin with HCN in the presence

of a nickel catalyst and an insoluble Lewis acid promoter. Thereafter, the insoluble promoter may be separated from the reaction mixture by mechanical means, such as filtration.

- 5 The monoolefins of the process are described by Formula I or III, and the corresponding terminal nitrile compounds produced are described by Formula II or IV, respectively,



5 wherein R is H, CN, CO₂R², or perfluoroalkyl; x is 0 to 12; y is 0 to 12; z is 1 to 12 when R is CN or CO₂R² and z is 0 to 12 when R is H or perfluoroalkyl; and R² is C₁ to C₁₂ straight or branched alkyl.

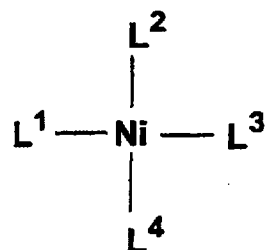
Preferred monoolefins include 2-, 3- and
10 4-pentenitrile, alkyl 2-, 3- and 4-penteneoates, and CH₂=CH-R³, wherein R³ is perfluoroalkyl.

Preferred products are adiponitrile, alkyl
5-cyanovalerate, and R⁴-CH₂CH₂CN, wherein R⁴ is
perfluoroalkyl. Adiponitrile (ADN) is of particular
15 interest because it is an intermediate used in the production of hexamethylenediamine, which, in turn, is used to produce polyhexamethylenedipamide (nylon-6,6), a commercial polyamide useful in forming fibers, films, and molded articles. Adiponitrile may also serve as a
20 precursor for production of caprolactam by a process involving partial hydrogenation of ADN.

The catalysts employed for this process are zerovalent nickel (Ni(0)) compounds, substantially free of carbon monoxide, which may be preformed or prepared
25 in situ. The catalysts include nickel compounds containing ligands such as phosphines, arsines, stibines, phosphites, arsenites, stibites and mixtures thereof. Ligand may be added in excess of what can theoretically be coordinated to the nickel at a given

time. The use of excess ligand often provides improved stability for the nickel catalyst.

A preferred group of these Ni(0) catalysts has the general structure:



5 wherein L^1 , L^2 , L^3 , and L^4 are neutral ligands which may be the same or different and have the formula $P(XYZ)$ wherein X and Y are selected from the group consisting of R and OR' , and Z is OR'' , wherein R, R' , and R'' may be the same or different, and wherein R, R' , and R'' are
10 selected from the group consisting of alkyl and aryl groups containing up to 18 carbon atoms, with aryl being preferred. Alkyl groups may be linear or branched. The term "aryl" is meant to denote an organic radical which is derived from an aromatic
15 hydrocarbon by removal of one atom. Suitable aryl radicals are, for example, phenyl, benzyl, naphthyl, binaphthyl, and anthracenyl.

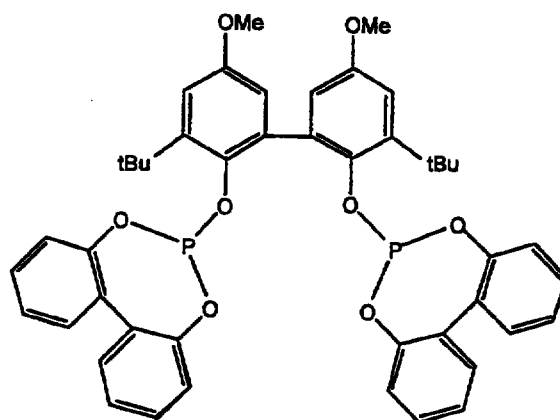
A particularly preferred group within the foregoing zerovalent nickel catalysts is that disclosed
20 in U.S. Patent 3,903,120, which is incorporated herein by reference. This preferred group of catalysts can be described by the general formula NiL_4 , where L is a neutral ligand such as a triarylphosphite of the formula $P(OAr)_3$ wherein Ar is an aryl group of up to 18
25 carbon atoms. Illustrative aryl groups are methoxyphenyl, tolyl, xylyl, and phenyl. Preferred aryl groups are meta-tolyl, para-tolyl, and phenyl, and mixtures thereof.

Another preferred group of zerovalent $\text{Ni}(0)$ catalysts consists of compounds of the general formulae shown below:



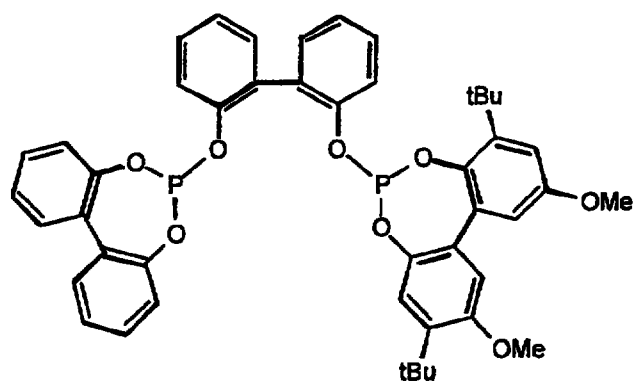
wherein L^5 and L^6 are bidentate ligands which may be the same or different and have the formula $(\text{X})(\text{Y})\text{P-Z}'\text{-P}(\text{X})(\text{Y})$, wherein X and Y are selected from the group
 10 consisting of R and OR' , and Z' has the formula $\text{O-R}''\text{-O}$, wherein R, R' , and R'' may be the same or different, and wherein R, R' , and R'' are selected from the group consisting of alkyl and aryl groups containing up to 18 carbon atoms, with aryl being preferred, and the olefin
 15 contains up to 18 carbon atoms, and is preferably one of the monoolefins being hydrocyanated.

Preferred L^5 and L^6 are described in U. S. Patents 5,512,695, 5,512,696, 5,523,453, 5,543,536, 5,693,843, 5,723,641, 5,821,378, and 5,847,191 and in PCT
 20 applications WO9514659, WO9906146, WO9906355, WO9906356, WO9906357, and WO9906358, the disclosures of which are incorporated herein by reference. Especially preferred L^5 and L^6 are diphosphite ligands illustrated by Ligand formulas A to G below.



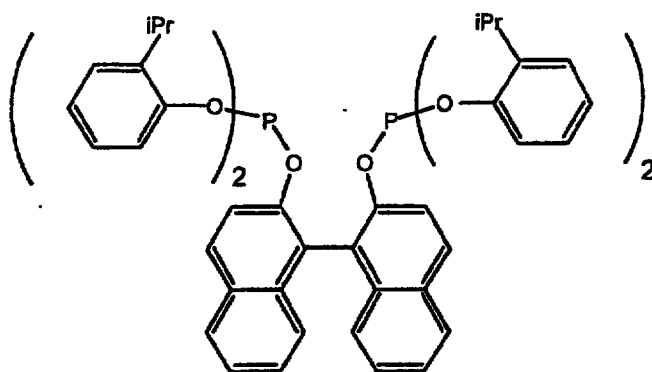
Ligand A

(OMe = methoxy
tBu = tert-butyl)

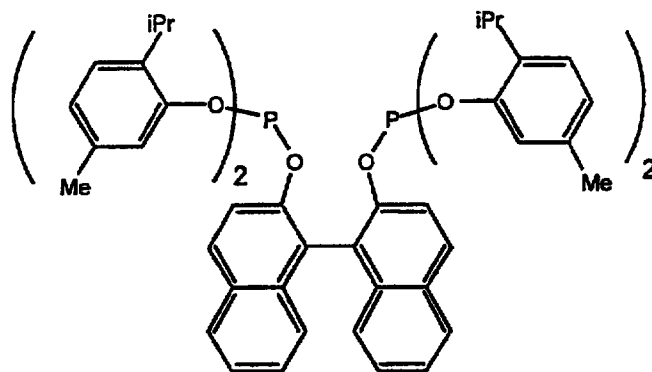


Ligand B

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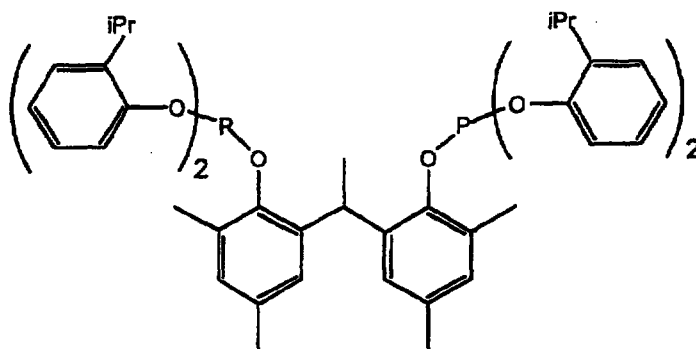
Ligand C



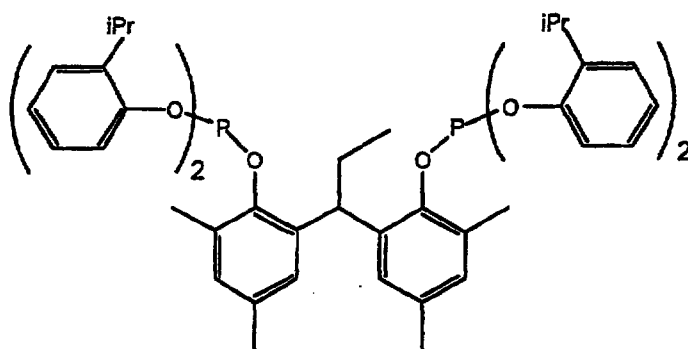
Ligand D

(iPr = isopropyl
Me = Methyl)

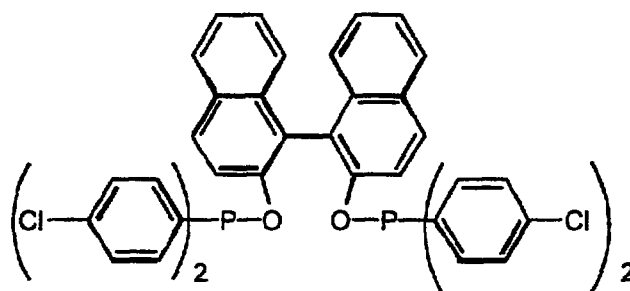
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Ligand E



Ligand F



Ligand G

The promoters of the present invention must be
 10 insoluble in the reaction medium and therefore easily
 recoverable by mechanical means, such as filtration.
 The term "insoluble" means that less than about 0.1% of
 the promoter is dissolved. The insoluble promoters of
 this invention are not believed to be active as a
 15 result of leaching of metal ions from the insoluble
 promoter into the reaction solution. Analysis of

reaction product solutions formed using these promoters indicated metal ion concentrations well below these required for effective promoter activity.

The promoters must have Lewis acidity, as indicated by their ability to coordinate to either a metal-cyanide containing complex or an organonitrile, as measured spectroscopically by a shift in the infrared band assigned to the metal-cyanide or organonitrile stretch upon coordination to the promoter. An example of such a spectroscopically observed shift for a soluble promoter with a nickel-cyanide (Ni-CN) species is described in *Advances in Catalysis*, Vol. 33 (1985), pages 12-13.

Alternatively, Lewis acidity may be measured by spectroscopic measurement of pyridine adsorption onto the insoluble promoters as described by J. A. Lercher, G. Ritter, and H. Vinek, *Journal of Colloid and Interface Science*, Vol. 106 (1985) pages 215-221.

Insoluble promoters may be selected from among several classes of materials consisting of (a) polyolefins (such as polystyrene, polyethylene or polypropylene) having metal ions or complexes covalently bonded to the polyolefin, (b) sulphonate or carboxylate substituted polyolefins (ion exchange resins) having metal ions or metal ion complexes ionically bonded to the polymer, including metal exchanged perfluorosulphonic acid resins, (c) inorganic metal oxides in which the metal ions themselves are the centers of Lewis acidity, and (d) insoluble metal halides, phosphates or sulfates, including those supported on metal oxides.

Preferred members of class (a) include polystyrene, which may contain varying degrees of cross-linking, in which metal or organometal cations

are covalently bonded to an aryl group of the polystyrene. These promoters may be prepared by making a Grignard reagent from p-bromostyrene, reacting the Grignard reagent with a metal or organometal halide to covalently bond the metal or organometal to the styrene group, and then polymerizing the metal-substituted styrene group with or without unsubstituted styrene and cross-linking agents such as divinylbenzene. The metal cation, which may or may not be bonded to other organic groups, is selected from the group consisting of zinc, cadmium, the first transition series (elements 21-29 of the Periodic Table), the second transition series (elements 39-47 of the Periodic Table), the rare earths (elements 57-71 of the Periodic Table), boron, aluminum, gallium, indium, germanium, tin, hafnium, tantalum, tungsten, and rhenium. Preferred metal cations are selected from the group consisting of zinc, aluminum, titanium, manganese, aluminum and tin. Preferred promoters are poly(styrene-Ph-Y)X, wherein Ph is phenyl, Y is $\text{Sn}(\text{R})_2$, wherein R is alkyl, aryl, or Cl, and X is a weakly coordinating counterion such as Cl^- , Br^- , RSO_3^- (wherein R is aryl, alkyl, perfluoralkyl, or perfluoroaryl). Especially preferred promoters are poly(styrene-Sn(Ph) $_2$ X), wherein Ph is phenyl and X is a weakly coordinating counterion such as Cl^- , Br^- , RSO_3^- (wherein R is aryl, alkyl, perfluoralkyl, or perfluoroaryl).

Promoters of class (b) are sulfonated or carboxylated organic polymers known as ion exchange resins, such as polystyrene, in which metal or organometal cations are ionically bonded to the sulfonyl or carboxyl groups. Metal-exchanged perfluorosulphonic acid resins are also members of this class, wherein the metal is Mn, Fe, Co, Zn, La, Ce, Pr,

Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu.

(Perfluorosulphonic acid resin is sold under the trademark "Nafion" by E. I. du Pont de Nemours and Company, Wilmington, Delaware, U.S.A.) Sulfonated or
5 carboxylated polystyrene resins are commercially available under a variety of trade names, for example, "Amberlyst" 21 (sold by Rhom and Haas, Philadelphia, Pennsylvania, U.S.A.). These resins may be obtained in acid or ion exchanged forms and the promoters of this
10 invention may be readily prepared by ion exchange. The metal cation, which may or may not be bonded to other organic groups, is selected from the group consisting of zinc, cadmium, the first transition series (elements 21-29), the second transition series (elements 39-47),
15 the rare earths (elements 57-71), boron, aluminum, gallium, indium, germanium, tin, hafnium, tantalum, tungsten, and rhenium. Preferred metal cations are selected from the group consisting of zinc, aluminum, titanium, manganese, aluminum and tin. Particularly
20 preferred promoters are metal or organometal exchanged poly(styrene-SO₃⁻) resins. Especially preferred is poly(styrene-SO₃-Sn(Ph)₃), wherein Ph is phenyl.

Promoters of class (c) are metal oxides in which the metal ions themselves are the centers of Lewis
25 acidity, this acidity being manifested by the metal ions' ability to accept an electron pair forming a dative (donor-acceptor) bond (e.g., from a nitrile or pyridine to form a coordination complex). Such promoters may be selected from the class consisting of
30 crystalline silicoaluminate clays in their acid forms. Clays such as the natural mineral compositions pyrophyllite, micas, vermiculites or smectites and synthetic clays such as laponite may be used. Essentially amorphous silicoaluminates, with a Si/Al

ratio ranging from 10 to 0.05, either native or treated with chloride, sulphate or phosphate to enhance the surface acidity, may be used. The following may also be used: large pore silicoaluminate zeolites (greater
5 than about 8 Angstrom pore size), alumina, hydrous zirconia, zirconia, and zirconia whose surface has been treated with sulfate ion rendering it superacidic; niobic acid and hydrous niobia, acidic gamma alumina, tungstic acid, chromia, molybdic acid, hydrous titania,
10 zinc oxide, iron(III) oxide, lanthanum oxide, heteropolyacids, magnesia/alumina, aluminophosphates, non-Si/Al zeolite-type materials such as ALPOs (crystalline, microporous aluminum phosphate structures), SAPOs (silica-aluminophosphates where
15 silicon ions occupy some of the aluminum sites in a crystalline alumino-phosphate structure), MeAPOs (metal ions such as Co, Mn etc., substituted onto the Al sites of crystalline aluminosilicates), conventional zeolites in which Al is substituted by Ga, B, or Fe, plain or
20 sulfated forms of SnO_2 and HfO_2 , boric acid and boron-containing solid compositions that present surface coordination sites at boron atoms. Any of these suitable promoters may be dispersed onto a high surface area ($>20\text{m}^2/\text{gm}$) support such as silica, alumina or
25 carbon. Members of this class are most effective when calcined to remove water and Bronsted (protonic) acid sites. Such calcination requires heating in flowing air to temperatures in excess of 400°C .

Class (d) promoters of this invention consist of a
30 metal cation with an anion which renders it insoluble in the reaction medium, the anion being selected from the class consisting of halide, sulfate and phosphate. Preferred members of this class are metal fluorides and metal fluorides supported on silicoaluminates, iron

phosphates, zinc sulfates and iron sulfates and zirconium hydrogen phosphate. Especially preferred members of this class are AlF_3 , ZnF_2 , and SbF_5 on aluminosilicate. Any of these suitable promoters may be
5 dispersed onto a high surface area ($>20\text{m}^2/\text{gm}$) support such as silica, alumina or carbon.

The present hydrocyanation process may be carried out by charging a reactor with all of the reactants, or, preferably, by charging the reactor with the
10 catalyst precursor or catalyst components, the aliphatic monoolefin, the promoter and the solvent to be used and adding the hydrogen cyanide slowly. HCN may be added to the reaction as vapor or liquid, or released to the system utilizing cyanohydrin. See, for
15 example, U.S. Patents 3,655,723 and 5,107,012 which are incorporated herein by reference. The reactor may also be charged with the catalyst, promoter, and the solvent to be used, and both monoolefin and HCN added slowly to the reaction mixture. The molar ratio of monoolefin to
20 catalyst may be from about 10:1 to 2000:1. The insoluble promoter is generally present in the range of about 0.1 wt% to 50 wt% of the reaction mass. Preferably the insoluble promoter is present in the range of about 1 wt% to 25 wt% of the reaction mass.

25 The hydrocyanation reaction can be carried out with or without a solvent. The solvent should be liquid at the reaction temperature and pressure and inert towards the acyclic monoolefin and the catalyst. Generally, such solvents are hydrocarbons such as
30 benzene or xylene, or nitriles such as acetonitrile or benzonitrile. In some cases, the acyclic monoolefin to be hydrocyanated may serve as the solvent.

The reaction temperature is dependent to a certain extent on the particular catalyst being used, the

particular monoolefin being used and the desired reaction rate. Generally, temperatures of from -25 to 200°C can be used, with from 0 to 150°C being preferred.

5 Atmospheric pressure is satisfactory for carrying out the present process, and hence pressures of from about 0.05 to 100 atmospheres are preferred for economic reasons.

Preferably, the reaction medium is agitated, such
10 as by stirring or shaking. The reaction may be run either batchwise or in a continuous manner. The promoter may be recovered for further use by mechanical means such as filtration, decantation or centrifugation. The cyanated product can be recovered
15 by conventional techniques, such as distillation.

EXAMPLES

The following nonlimiting examples illustrate the invention. As used herein, "m,p-TTP" refers to
20 tritolylphosphite which contains a mixture of meta- and para-tolyl groups. PNs refers to a mixture of 3-pentenitrile and 4-pentenitrile. ADN refers to adiponitrile, MGN to methylglutaronitrile, and ESN to ethylsuccinonitrile.

25

Example 1

Illustrates that Fe₂O₃ (class C) Promotes Hydrocyanation of PNs to ADN

30 Under nitrogen, a portion (21.58 g) of a mixture of Ni(m,p-TTP)₄ (23.72 g) (the catalyst), m,p-TTP (4.665 g) (excess ligand) and PNs (95.5 g) (acyclic monoolefin) was added to a flask containing Fe₂O₃ (0.180 g) (insoluble promoter). The Fe₂O₃ formed a slurry in

this mixture. The flask and its contents were heated to 60°C. HCN vapor was introduced to the flask by sparging N₂ through a chilled trap (0°C) and into the flask. Liquid samples were withdrawn at 45 minutes, 2, 5 and 3 hours. Infrared analyses showed HCN concentrations to be 385, 640, and 973 ppm at each of these times respectively. The reaction was stopped at the end of 4 hours, and the product, analyzed by gas chromatography (GC), contained 24.53 wt% ADN, 5.77 wt% 10 MGN, and 0.84 wt% ESN. Distribution: 78.7% ADN (the Distribution was obtained by dividing the wt% ADN by the sum of the wt% of ADN, MGN, and ESN).

Example 2

15 Illustrates that Fe₂O₃ is Acting as a Insoluble Promoter.

Fe₂O₃ (0.216 g) was incubated with 30 mL of a catalyst mixture of the same composition used in 20 Example 1 above. The mixture was stirred under nitrogen for 40 hours at 40°C, and 1 hour at 60°C. The mixture was filtered (syringe filter), and the filtrate was transferred to the same hydrocyanation apparatus used in Example 1. Hydrogen cyanide was introduced, as 25 in Example 1, but for a period of only one hour. ADN (0.54 wt%) was formed. A control experiment, using only the same catalyst mixture, but without prior incubation with Fe₂O₃, and without other added promoters, was reacted, in the same apparatus, with 30 hydrogen cyanide for 1 hour. In the control experiment, only 0.32 wt% ADN was formed. In Example 1, in which Fe₂O₃ is present during the HCN reaction, 2.18 wt% ADN was formed after only 45 minutes, showing

that Fe_2O_3 acts as an insoluble promoter of the PN to ADN reaction.

Example 3

5 Illustrates that Fe_2O_3 is not a Catalyst for
 Hydrocyanation.

Fe_2O_3 (0.036 g) was mixed with PNs (4.0 mL).
Liquid HCN (0.40 mL) was added to the mixture, which
10 was then heated to 60°C for a period of 2 hours. No
 ADN was detected by GC.

Example 4

Illustrates that a Soluble Promoter Does Not Form
15 When Fe_2O_3 Reacts With HCN During Hydrocyanation.

Two reactors were set up. Reactor 1 contained the same
charge as in Example 1 and 0.180 g Fe_2O_3 . Reactor 2
was empty. Both reactors were heated to 60°C and HCN
20 flow was started to reactor 1. After 1 hour, HCN flow
 was stopped to reactor 1 and nitrogen flow was started.
Approximately one half of the contents of reactor 1
were filtered (using a syringe filter) and transferred
to reactor 2. HCN flow was started on reactor 2, while
25 N_2 flow was maintained on reactor 1. Samples were
 taken from both reactors at 1 hour (the time of
 filtration and transfer) and at two hours, the time at
 which HCN was stopped to reactor 2. The results (Table
 1) show no more accumulation of ADN during the second
30 hour in reactor 2 (filtered material, under HCN) than
 occurred during the second hour of reactor 1
 (unfiltered material, under N_2).

Table 1

Reactor	Time (h)	ADN, wt%	MGN, wt%	ESN, wt%
1	1	10.47	2.53	0.403
1	2	12.18	3.02	0.478
2	1	11.51	2.87	0.479
5 2	2	12.44	3.18	0.540

Examples 5 - 9

Illustrate the Use of Other Insoluble Promoters.

10 In a manner similar to that described in Example 1, other insoluble promoters were demonstrated to be active insoluble promoters as illustrated in Table 2:

Table 2

15 Ex.	Compound	Weight, g	Wt% ADN	Distribution
5	FeO(OH)	0.182	3.12	76.8%
6	Fe ₃ (PO ₄) ₂ ·8H ₂ O	1.03	2.092	79.5%
7	TiO ₂	0.167	1.14	78.6
8	ZnO	0.170	18.24	78.6
20 9	ZrO ₂ (2 hour run)	0.259	1.56	-

Examples 10 - 41

Additional Examples of Insoluble Promoters

25 The examples in Table 3 utilized bidentate ligands (diphosphites) and were carried out using the following common procedure, unless otherwise noted. Ligands A to G are identified in Table 3 and are described above. In some cases, identified as "recycle", the promoter was isolated
30 after the run and reused in a subsequent run with no further treatment.

A glass reactor fitted with a nitrogen bubbler was charged with 3-pentenitrile (5 mL; 52 mmol), ligand (see Table 3) (0.28 mmol), (ligand)Ni(C₂H₄) (0.14 mmol) and

promoter (see Table 3 for amount) under inert nitrogen atmosphere. The mixture was heated to temperature (see Table 3) and agitated with a magnetic stirrer. HCN was delivered to the reactor by sparging a source of liquid HCN (cooled to 0°C) with dry nitrogen (see Table 3 for flow rate) and directing the resulting saturated HCN/N₂ mixture into the reactor below the liquid level. Progress of the reaction was monitored by removing aliquots and analyzing by gas chromatography. After 1 hr the reaction was terminated. Results are given in Table 3.

(% PN conv = 100 x total dinitriles product / initial PN's)

(% ADN distribution = 100 x ADN / total dinitriles product)

Table 3

Ex. Promoter	Amount grams	Ligand	Temp °C	N ₂ flow	%PN Conv.	%ADN Distribution
10 Polystyrene-SnPh ₂ (CH ₃ SO ₃)	1.0	A	70	30	66	92
11 recycle 2nd time of same sample		A	70	30	61	93
13 recycle 3rd time of same sample		A	70	30	51	94
14 Polystyrene-SnPh ₂ (CF ₃ SO ₃)	1.0	A	70	30	73	90
15 recycle 2nd time of same sample		A	70	30	62	90
16 recycle 3rd time of same sample		A	70	30	58	90
17 Polystyrene-SnPh(HSO ₄) ₂	1.0	A	70	30	6	90
18 Polystyrene-CH ₂ -SnPhCl ₂	0.3	A	70	30	12	77
19 Polystyrene-SnPh ₂ (CH ₃ SO ₃)	1.0	D	50	30	12	90
20 Polystyrene-SnPh ₂ (CH ₃ SO ₃)	1.0	C	50	30	10	89
21 Poly (4-styrene-sulfonate) [Ph ₃ Sn]	0.06	A	80	30	31	94
22 Ph ₃ Sn Nafionate	0.06	A	70	30	22	81
23 Yb Nafionate	0.06	A	70	30	21	77
24 Sulfated zirconia dried 500°C	0.5	A	70	30	8	77
25 Cl-promoted silico-aluminate,	0.5	A	70	30	46	88
26 Recycle 2nd time same sample	0.5	A	70	30	17	84
27 PO-promoted silico-aluminate,	0.5	A	70	30	27	83
28 theta-AlF ₃ on silico-aluminate,	0.5	A	80	12	14	83
29 theta-AlF ₃ , pure	0.5	A	80	12	21	77
30 Acidic alumina, dried 500°C,	0.5	A	70	30	10	76
31 Sulfated zirconia calcined 600°C,	0.5	A	80	30	11	75

32	Cl-promoted Si/Al calcined 200°C,	0.5	A	80	30	29	78
33	Cl-promoted Si/Al calcined 700°C	0.5	A	80	30	37	84
34	AlPO ₄ calcined 600°C,	0.5	A	80	30	12	74
35	Montmorillonite clay, calcined 600°C	0.5	A	80	30	27	78
36	-4% Ti(OH) ₄ on silica, dried 300°C	0.5	A	80	30	13	74
37	-5% HNbO ₃ on silica, dried 300°C	0.5	A	80	30	19	76
38	-5% Zr(OH) ₄ on silica, dried 300°C	0.5	A	80	30	18	76
39	Fe ₂ O ₃	0.05	A	70	15	11	76
40	FeO	0.5	A	70	10	19	73
41	Cl-promoted silico-aluminate	0.5	C	80	12	12	86

Examples 42-143

A 4 mL reactor equipped with a magnetic stir bar, was charged with 0.025 g of promoter and 0.2 mL of catalyst solution comprised of Ni(COD)₂ ("COD" is 1,5-cyclooctadiene) (0.038 g; 0.14 mmol), diphosphite ligand (0.42 mmol, see Table 4), 3-pentenitrile (5 mL; 4.2 g; 51.9 mmol), and Ligand A only, toluene (5 mL) to aid in solubilizing ligand. The reaction mixture was heated to 50°C and agitated while being exposed to an atmosphere of N₂ containing 35% v/v HCN, generated by passing a stream of dry N₂ through liquid HCN at 0°C. After 1.5 hours the reactor was purged with N₂ and the reaction solution diluted with 3 mL acetone. The liquid phase was analyzed by GC chromatography. Results are presented in Table 4 below.

Table 4

20

Ex	Promoter	Ligand	% PN Conv	% ADN Distribution
42	-4% Ti(OH) ₄ on SiO ₂ (300°C)	A	6.9	79.5
43	-5% HNbO ₃ on SiO ₂ (300°C)	A	21.2	81.2
44	-5% Zr(OH) ₄ on SiO ₂ (300°C)	A	24.6	86.1
45	theta-AlF ₃	A	18.3	74.7
46	theta-AlF ₃ on silicoaluminate	A	40.0	88.0

47	Silicoaluminate (600°C/4h)	A	72.1	87.8
48	Acidified silicoaluminate (600°C/4h)	A	58.2	87.6
49	Chloride promoted silicoaluminate (200	A	29.7	83.1
50	Chloride promoted silicoaluminate (700	A	58.9	87.3
51	Phosphate promoted silicoaluminate (700	A	61.9	87.1
52	AlPO ₄ (600°C/4h)	A	19.2	74.5
53	Commercial silicoaluminate cracking	A	66.3	88.1
54	Acidic g-alumina (500°C)	A	0.6	80.9
55	Boric acid promoted g-alumina	A	27.5	80.9
56	ZnO on g-alumina	A	3.5	77.2
57	ZnO on SiO ₂ granules	A	3.4	75.8
58	Sulfated zirconia (600°C/4h)	A	23.4	75.3
59	Sulfated zirconia (500°C/4h)	A	23.1	76.4
60	Acid form of Zeolite Y	A	20.6	76.3
61	Acid form of Zeolite mordenite	A	18.2	74.6
62	MoO ₃	A	6.3	74.1
63	WO ₃	A	17.2	74.0
64	La ₂ O ₃	A	16.2	74.2
65	Ba(OTf) ₂	A	18.3	75.0
66	K10 Montmorillonite (200°C)	A	0	
67	K10 Montmorillonite (400°C)	A	0.1	
68	K10 Montmorillonite (600°C/6h)	A	49.0	84.1
69	K10 Montmorillonite (800°C)	A	40.1	85.4
70	Al Montmorillonite	A	36.1	86.5
71	Al Laponite	A	23.0	78.0
72	Na-Montmorillonite (500°C)	A	26.6	76.4
73	Al-Montmorillonite (500°C)	A	11.2	87.6
74	Zn-Montmorillonite (500°C)	A	15.7	84.8
75	Zn-Montmorillonite (200°C)	A	16.9	84.4
76	100-Al-Montmorillonite (500°C)	A	16.0	87.8
77	100-Al-Montmorillonite (700°C)	A	35.8	86.5
78	100-Zn-Montmorillonite (500°C)	A	1.5	
79	100-Zn-Montmorillonite (700°C)	A	4.8	87.0
80	-4% Ti(OH) ₄ on SiO ₂ (300°C)	C	5.4	85.2
81	-4% Ti(OH) ₄ on SiO ₂ (500°C)	C	8.1	84.0
82	-5% HNbO ₃ on SiO ₂ (300°C)	C	4.0	83.8
83	-5% HNbO ₃ on SiO ₂ (500°C)	C	6.6	81.8
84	-5% Zr(OH) ₄ on SiO ₂ (300°C)	C	5.9	85.0
85	-5% Zr(OH) ₄ on SiO ₂ (500°C)	C	7.9	82.3
86	theta-AlF ₃	C	3.8	78.6
87	theta-AlF ₃ on silicoaluminate	C	5.3	82.8
88	Silicoaluminate (600°C/4h)	C	13.0	85.8
89	Acidified silicoaluminate (600°C/4h)	C	11.9	85.0
90	Chloride promoted silicoaluminate (200	C	6.5	82.0
91	Chloride promoted silicoaluminate (700	C	9.6	84.9
92	Phosphate promoted silicoaluminate (700	C	6.3	82.2

93	AlPO ₄ (600°C/4h)	C	3.0	82.5
94	Commercial silicoaluminate cracking	C	44.8	85.0
95	Acidic g-alumina (500°C)	C	0.7	61.1
96	Boric acid promoted g-alumina	C	4.6	79.1
97	ZnO on g-alumina	C	3.9	74.3
98	ZnO on SiO ₂ granules	C	16.0	84.8
99	Sulfated zirconia (600°C/4h)	C	3.1	76.5
100	Sulfated zirconia (500°C/4h)	C	4.8	80.0
101	Acid form of Zeolite Y	C	5.8	80.2
102	Acid form of Zeolite mordenite	C	3.5	76.8
103	MoO ₃	C	1.1	64.7
104	WO ₃	C	2.8	75.4
105	La ₂ O ₃	C	2.7	75.2
106	Ba(OTf) ₂	C	4.24	79.3
107	K10 Montmorillonite (200°C)	C	6.7	82.6
108	K10 Montmorillonite (400°C)	C	19.3	84.5
109	K10 Montmorillonite (600°C/6h)	C	49.4	85.1
110	K10 Montmorillonite (800°C)	C	51.8	84.8
111	Al Montmorillonite	C	34.8	84.7
112	Al Laponite	C	4.7	84.0
113	Na-Montmorillonite (500°C)	C	5.2	84.6
114	Al-Montmorillonite (500°C)	C	58.0	85.1
115	Al-Montmorillonite (200°C)	C	10.5	85.2
116	Zn-Montmorillonite (500°C)	C	55.4	85.7
117	Zn-Montmorillonite (200°C)	C	20.7	85.6
118	Fe-Montmorillonite (500°C)	C	21.6	85.2
119	Fe-Montmorillonite (200°C)	C	36.4	85.3
120	100-Al-Montmorillonite (500°C)	C	14.0	84.1
121	100-Al-Montmorillonite (700°C)	C	48.5	84.6
122	100-Zn-Montmorillonite (500°C)	C	4.9	78.2
123	100-Zn-Montmorillonite (700°C)	C	18.3	83.4
124	~4% Ti(OH) ₄ on SiO ₂ (300°C)	D	3.1	73.7
125	~5% HNbO ₃ on SiO ₂ (300°C)	D	2.0	74.5
126	~5% Zr(OH) ₄ on SiO ₂ (300°C)	D	2.3	75.6
127	theta-AlF ₃	D	3.0	73.4
128	theta-AlF ₃ on silicoaluminate	D	2.4	75.4
129	Silicoaluminate (600°C/4h)	D	3.3	76.3
130	Acidified silicoaluminate (600°C/4h)	D	2.8	75.1
131	Chloride promoted silicoaluminate (200	D	2.6	72.4
132	Chloride promoted silicoaluminate (700	D	5.3	80.6
133	Phosphate promoted silicoaluminate (700	D	3.2	76.8
134	AlPO ₄ (600°C/4h)	D	2.7	69.9
135	Commercial silicoaluminate cracking	D	3.7	83.6*
136	Acidic g-alumina (500°C)	D	0.3	49.8
137	Sulfated zirconia (600°C/4h)	D	3.5	74.0
138	Sulfated zirconia (500°C/4h)	D	3.3	73.9

139	K10 Montmorillonite (200°C)	D	1.46	35.9*
140	K10 Montmorillonite (400°C)	D	1.64	40.8*
141	K10 Montmorillonite (600°C/6h)	D	4.7	83.5*
142	K10 Montmorillonite (800°C)	D	4.4	65.9*
143	Al Montmorillonite	D	1.5	72.4*

Ligand D: 250 uL, 50 mg promoter. Not corrected for 2M3 contribution to MGN

* Ligand D: 200 uL, 25 mg promoter. Corrected for MGN

5 contribution

100-E-Montmorillonite series - totally exchanged Montmorillonites

Example 144

10 A 25 mL reactor was charged with 0.058 g Ni(COD)₂, 0.559 g Ligand C, 0.75 g K10 Montmorillonite calcined at 500°C for 4 hours and 7.5 mL 3-pentenitrile. The reaction mixture was heated to 50°C and agitated vigorously while a continuous stream of N₂ containing
15 35% v/v HCN was passed through the reactor at a rate of 25 mL/min. After 1.5 hours, the solution phase was diluted with acetone and analyzed by GC chromatography. 60.7% conversion of pentenenitriles, 85.0% selectivity to adiponitrile.

20

Examples of the Preparation of class (c) Heterogeneous Promoters for Hydrocyanation:

Example 145 - H-Montmorillonite Clay.

25 5g commercial montmorillonite clay (K-10, Aldrich) was slurried into a solution of 5g ammonium nitrate in 100 mL water. After stirring overnight the solid was collected by filtration, washed with water and suction dried. The wet filter cake was then calcined in flowing
30 air by ramping to 600°C over 1 hour and held there for

4 hours. The sample was flushed with nitrogen and taken into a nitrogen filled dry-box for collection and storage.

5 Example 146 - Silicoaluminate.

5g commercial silicoaluminate cracking catalyst grade 979 (W.R. Grace) was calcined in flowing air by ramping to 600°C over 1 hour and holding for 4 hours. The sample was flushed with nitrogen and taken into a
10 nitrogen filled dry-box for collection and storage.

Example 147 - Chloride promoted silicoaluminate.

5g commercial silicoaluminate powder was slurried into 50mL water. The pH was adjusted to 1 with HCl and
15 the slurry stirred for 30 mins. The slurry was then evaporated to dryness under reduced pressure. The recovered powder was calcined in flowing air by ramping to 700°C over 1 hour and holding for 2 hours. The sample was flushed with nitrogen and taken into a
20 nitrogen filled dry-box for collection and storage.

Example 148 - Phosphate promoted silicoaluminate.

5g commercial silicoaluminate powder was slurried into 50mL water. The pH was adjusted to 1 with 85%
25 phosphoric acid and the slurry stirred for 30 mins. The slurry was then evaporated to dryness under reduced pressure. The recovered powder was calcined in flowing air by ramping to 700°C over 1 hour and holding for 2 hours. The sample was flushed with nitrogen and taken
30 into a nitrogen filled dry-box for collection and storage.

Example 149 - Sulfate-treated zirconia.

5g zirconium hydroxide was placed on a frit and

75mL 0.5M sulfuric acid was poured through the bed and allowed to drain slowly. The solid was suction dried and then calcined in flowing air by ramping to 500°C over 1 hour and holding for 2 hours. The sample was
5 flushed with nitrogen and taken into a nitrogen filled dry-box for collection and storage.

Example 150 - theta-AlF₃.

5g Collidinium tetrafluoroaluminate (Herron et al.
10 J.Amer.Chem.Soc, 1993, 115, 3028) was calcined in flowing air by ramping to 350°C over 1 hour and holding for 1 hour. The sample was flushed with nitrogen and taken into a nitrogen filled dry-box for collection and storage.

15

Example 151 - Zinc oxide on silica.

5g gamma alumina was stirred into a solution of 2g zinc nitrate in 25mL water. After 30 mins the solution was evaporated to dryness under reduced pressure and
20 the recovered solid was calcined in flowing air by ramping to 350°C over 1 hour and holding for 4 hours. The sample was flushed with nitrogen and taken into a nitrogen filled dry-box for collection and storage.

25

Comparative Examples 1 - 4

The following comparative examples illustrate that small pore aluminosilicate Zeolites 3A and 4A utilized in U.S. Patent 3,846,474, examples 5 and 6, do not perform as promoters for the nickel-catalyzed hydrocyanation of 3-
30 pentenenitrile.

Comparative Example 1

A reactor was charged with Ni(tritolylphosphite)₄ (0.49 g; 0.34 mmol), ZnCl₂ (0.095 g; 0.67 mmol) and 3-

pentenenitrile (10 mL; 8.4 g; 104 mmol). The reaction mixture was maintained at 25°C while introducing HCN at a rate of 20 mmol/hr over a period of 16 hrs. Analysis of the resulting product solution by GC showed 3-pentenenitrile conversion of 14% and ADN distribution of 78%. When the reaction was repeated without ZnCl₂, less than 0.4% 3-pentenenitrile conversion resulted.

Comparative Example 2

Hydrocyanation of 3-pentenenitrile was carried out in a manner similar to Comparative Example 1 except that 0.90 g of 3A Molecular Sieves (an aluminosilicate Zeolite) were added to the mixture. Analysis of the resulting product solution by GC showed 3-pentenenitrile conversion of 24% and ADN distribution of 80%. When the reaction was repeated without the ZnCl₂, less than 0.2% 3-pentenenitrile conversion resulted.

Comparative Example 3

A reactor was charged with Ni(tritolylphosphite)₄ (0.49 g; 0.34 mmol), tritolylphosphite (0.59 g; 1.7 mmol), ZnCl₂ (0.095 g; 0.67 mmol) and 3-pentenenitrile (10 mL; 8.4 g; 104 mmol). The reaction mixture was maintained at 25°C while introducing HCN at a rate of 120 mmol/hr over a period of 4.5 hrs. Analysis of the resulting product solution by GC showed 3-pentenenitrile conversion of 5% and ADN distribution of 78%. When the reaction was repeated without ZnCl₂, less than 0.4% 3-pentenenitrile conversion resulted.

Comparative Example 4

Hydrocyanation of 3-pentenenitrile was carried out in a manner similar to Comparative Example 3 except that 0.95 g of 4A Molecular Sieves (an aluminosilicate Zeolite) were added to the mixture. Analysis of the resulting product

solution by GC showed 3-pentenitrile conversion of 19% and ADN distribution of 81%. When the reaction was repeated without the ZnCl_2 , less than 0.2% 3-pentenitrile conversion resulted.

What is claimed:

1. A process for converting an acyclic monoolefin to its corresponding terminal organonitrile by reacting
5 the monoolefin with HCN, at a temperature of -25°C to 200°C and a pressure of 0.05 to 100 atmospheres, in the presence of a zerovalent nickel compound, a phosphorous-containing ligand and an insoluble Lewis acid promoter.
- 10 2. The process of claim 1 further comprising mechanically separating the insoluble Lewis acid promoter from the monoolefin, HCN, zero-valent nickel compound, ligand and organonitrile.
- 15 3. The process of claim 2 wherein the acyclic olefin is selected from the group consisting of $\text{CH}_2=\text{CH}(\text{CH}_2)_x\text{R}$ and $\text{CH}_3-(\text{CH}_2)_y-\text{CH}=\text{CH}-(\text{CH}_2)_z\text{R}$, wherein:
R is H, CN, CO_2R^2 , or perfluoroalkyl;
20 x is 0 to 12,;
y is 0 to 12;
z is 1 to 12 when R is CN or CO_2R^2 and z is 0 to 12 when R is H or perfluoroalkyl; and
 R^2 is an alkyl group containing 1 to 12 carbon atoms.
- 25 4. The process of claim 3 wherein the phosphorous-containing ligand is selected from the group consisting of PXYZ and $(\text{X})(\text{Y})\text{P}-\text{Z}'-\text{P}(\text{X})(\text{Y})$, wherein:
X and Y are independently R^3 or OR^4 ;
30 Z is OR^5 ;
Z' is $\text{O}-\text{R}^6-\text{O}$; and
 R^3 , R^4 , R^5 and R^6 are independently alkyl or aryl groups containing 1 to 18 carbon atoms.



5. The process of claim 4 in which the insoluble promoter is the only promoter.

6. The process of claim 4 in which the promoter is an aryl-group containing polystyrene having metal cations covalently bound to the aryl groups, the metal cations being selected from the group consisting of zinc, cadmium, the first transition series (elements 21-29 of the Periodic Table), the second transition series (elements 39-47 of the Periodic Table), the rare earths (elements 57-71 of the Periodic Table), boron, aluminum, gallium, indium, germanium, tin, hafnium, tantalum, tungsten, and rhenium.

7. The process of claim 4 in which the promoter is a sulphonated or carboxylated polystyrene having metal cations ionically bound to the sulphonate or carboxylate groups, the metal cations being selected from the group consisting of zinc, cadmium, the first transition series (elements 21-29 of the Periodic Table), the second transition series (elements 39-47 of the Periodic Table), the rare earth metals (elements 57-71 of the Periodic Table), boron, aluminum, gallium, indium, germanium, tin, hafnium, tantalum, tungsten, and rhenium.

8. The process of claim 4 in which the promoter is a metal oxide selected from the group consisting of crystalline silicoaluminate clays or large pore zeolites having a pore size greater than about 8 Angstroms in their acid forms; substantially noncrystalline silicoaluminates, optionally promoted with chloride, sulfate or phosphate; zirconia and sulfate; niobic acid; acidic gamma-alumina; tungstic



acid; molybdic acid; hydrous titania; zinc oxide;
iron(III) oxide; and lanthanum oxide.

9. The process of claim 8 in which the promoter is on
5 a support selected from the group consisting of silica,
alumina and carbon.

10. The process of claim 4 in which the promoter is a
metal-exchanged perfluorosulphonic acid resin, wherein
10 the metal is Mn, Fe, Co, Zn, La, Ce, Pr, Nd, Sm, Eu,
Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu.

11. The process of claim 4 in which the promoter is a
metal cation with an anion which renders it insoluble
15 in the reaction, the anion being selected from the
group consisting of halide, sulfate and phosphate.

12. The process of claim 11 in which the promoter is
on a support selected from the group consisting of
20 silica, alumina and carbon.

13. The process of claim 4 in which the promoter is
selected from the group consisting of metal fluorides,
metal fluorides supported on a silicoaluminate support,
25 iron phosphates, zinc sulfates, iron sulfates and
zirconium hydrogen phosphate.

14. The process of claim 4 in which the promoter is
selected from a group consisting of AlF_3 , ZnF_2 , and SbF_5
30 supported on an aluminosilicate support.

