



Journal of Molecular Catalysis A: Chemical 140 (1999) 293–305



# JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

*PatentsALERT*

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## Chemicals

### 5733518

#### Process and catalyst for dehydrogenation of organic compounds

Durante Vincent A.; Resasco Daniel E.; Walker Darrell W.; Haller Gary L.; Coggins Eugene L., West Chester, PA, United States assigned to Sun (R&M)

The invention comprises a process for selectively oxidizing hydrogen in a mixture with other gaseous materials by contacting the hydrogen containing gas under oxidation conditions with a catalyst comprising a phosphate of a metal wherein the metal is selected from the group consisting of germanium, tin, lead, arsenic, antimony and bismuth.

### 5734068

#### Silver catalyst for the oxidation of ethylene to ethylene oxide and process for preparing ethylene oxide

Klopries Burkhar; Metz Harald; Dibowski Wilma; Kyewski Dietmar; Pospiech Juml urgen Bottrop, Germany assigned to Huels Aktiengesellschaft

The invention relates to a silver catalyst for the partial oxidation of ethylene with molecular oxygen in the gas phase to form ethylene oxide and a process for preparing ethylene oxide using this catalyst. The catalyst is superior to comparable catalysts of the prior art through an increased selectivity (at high activity) and/or a more favorable ageing behavior. The process for preparing ethylene oxide is distinguished by improved economics.

### 5739070

#### Process for regenerating a fluorination catalyst

Ebmeyer Fran; Finzel Ralf; Siegemund Guml unter; Wanzke Wolfgang, Hattersheim, Germany assigned to Solvay (Societe Anonyme)

Process for regenerating a fluorination catalyst The invention relates to a process for regenerating a fluorination catalyst containing chromium and magnesium after use in a fluorination reaction, in which the used catalyst is treated with a mixture comprising at least 10 mol% of HF, from 30 to 90 mol% of O<sub>2</sub> and from 0 to 60 mol% of inert gas.

### 5739071

#### Method and apparatus for regeneratinig and stabilizing dehydrogenation catalysts

Chen Shiou-Shan; Hwang Shyh-Yuan; Oleksy Slawomir A.; Ram Sanjeev; Peters Joseph, Winchester, MA, United States assigned to Raytheon Engineers and Constructors

A method and apparatus are disclosed for regenerating and/or stabilizing the activity of a dehydrogenation catalyst used in dehydrogenating an alkylaromatic hydrocarbon to obtain an alkenylaromatic hydrocarbon, the method comprising the steps of continuously or intermittently adding to a reactant stream an effective amount of an alkali metal or alkali metal compound without interrupting the dehydrogenation reaction.

### 5739075

#### Process for preparing ethylene oxide catalysts

Matusz Marek Houston, TX, United States assigned to Shell Oil

This invention relates to a process for the preparation of a catalyst suitable for the production of ethylene oxide which process comprises depositing a promoting amount of a salt of a rare earth metal and a promoting amount of a salt of an alkaline earth metal and/or a salt of a Group VIII transition metal on a porous, refractory support, calcining the support, and thereafter depositing a catalytically effective amount of silver, a promoting amount of alkali metal, and optionally, a promoting amount of rhenium and/or a promoting amount of a rhenium co-promoter selected from sulfur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof, on the support, and subsequently drying the support.

### 5739076

#### Catalysts and their use in oxidation of saturated hydrocarbons

Huybrechts Diane Renata Cornelia; Buskens Philip Luc; Mathys Georges Marie Karel; Martens Luc Roger Marc Oud Turnhout, Belgium assigned to Exxon Chemical Patents

PCT No. PCT/EP93/01972 Sec. 371 Date Apr. 19, 1995 Sec. 102(e) Date Apr. 19, 1995 PCT Filed Jul. 23, 1993 PCT Pub. No. WO94/02245 PCT Pub. Date

Feb. 3, 1994. New titanium zeolite Beta catalysts which have been found to be useful as catalysts for the oxidation of organic compounds using organic hydroperoxides as oxidation catalysts. They are particularly useful as ring opening oxidation catalysts and may be used to produce adipic acid from cyclohexane.

#### 5739391

##### **Catalytic gas-phase oxidation of acrolein to acrylic acid**

Ruppel Wilhelm; Wegerle Ulrike; Tenten Andreas; Hammon Ulrich, Frankenthal, Germany assigned to BASF Aktiengesellschaft

A process for the catalytic gas-phase oxidation of acrolein to acrylic acid in a multiple contact tube fixed-bed reactor through whose space surrounding the contact tubes only one heat-exchange medium circuit is passed, at elevated temperature on catalytically active multimetal oxides with an acrolein conversion for a single pass of  $\geq 95$  mol% and an acrylic acid formation selectivity of  $\geq 90$  mol%, which comprises firstly passing the heat-exchange medium through the multiple contact tube fixed-bed reactor longitudinally, considered over the reaction container as a whole, to the contact tubes in cocurrent to the reaction-gas mixture and secondly superposing a transverse flow within the reaction container by means of an arrangement of successive baffles along the contact tubes which leaves passage cross sections free, so as to give a meandrous flow of the heat-exchange medium, seen in longitudinal section through the contact tube bundle, and setting the flow rate of the circulated heat-exchange medium so that its temperature rises by from  $2^\circ$  to  $10^\circ\text{C}$  between the point of entry into the reactor and the point of exit out of the reactor.

#### 5741748

##### **Catalyst production for use in a process for fluorination of hydrocarbons**

Allen John Graham; Legg Daniel Howard, Warrington, United Kingdom assigned to Imperial Chemical Industries

PCT No. PCT/GB93/01889 Sec. 371 Date Mar. 17, 1995 Sec. 102(e) Date Mar. 17, 1995 PCT Filed Sep. 7, 1993 PCT Pub. No. WO94/06558 PCT Pub. Date Mar. 31, 1994. A process for the removal of fluoride from a spent chromium-based fluorination cata-

lyst by contacting the catalyst with potassium hydroxide to produce a suspension of solid hydrated chromium oxide in aqueous potassium fluoride. The solid hydrated chromium oxide may be separated from the solution, washed with water and/or aqueous acid, and contacted with nitric acid to produce a chromium (III) nitrate solution from which a chromium-based catalyst may be prepared by precipitation of hydrated chromium oxide therefrom with aqueous alkali, and washing, drying and calcining the hydrated chromium oxide.

#### 5741904

##### **Method of producing epsilon-caprolactam, MFI zeolite catalysts on whose surface symmetrically arranged OH groups are present and to a method of producing them**

Hoelderich Wolfgang; Roeseller Joerg; Arntz Dietrich, Frankenthal, Germany assigned to Degussa Aktiengesellschaft

A method of producing epsilon-caprolactam from cyclohexanone in the gaseous phase using MFI catalysts on whose surface symmetrically arranged OH groups are present.

#### 5741906

##### **Production of triethylenediamine using surface acidity deactivated zeolite catalysts**

Santiesteban Jose Guadalupe; Li Hong-Xi; Armor John Nelson, Allentown, PA, United States assigned to Air Products and Chemicals

A process for preparing triethylenediamine by passing an ethanolamine, ethyleneamine, piperazine or morpholine over a pentasil-type zeolite at elevated temperature characterized by employing a ZSM-5 zeolite in the hydrogen or ammonium form which has been pretreated with an aqueous solution of a chelating agent capable of forming a chelate-aluminum complex.

#### 5744619

##### **Titanovanadosilicalites as epoxidation catalysts for olefins**

Nemeth Laszlo T.; Lewis Gregory J.; Rosin Richard R., Palatine, IL, United States assigned to UOP LLC

Titanovanadosilicalites have been found to be very selective, active catalysts in the epoxidation of olefins

by peroxides. Dilute hydrogen peroxide suffices to afford high yields of the epoxide. Vanadium incorporation at levels of Si:V in the range 100–2500 effectively changes the characteristics of the titanosilicite into which it is incorporated to give near quantitative conversion of propylene at selectivities greater than 90%.

#### 5744620

##### **Catalytic oxidation of cyclic olefins**

Hsiao Yu-Ling; Gray Harry B.; Labinger Jay A., Bridgeville, PA, United States assigned to Bayer

A catalyzed process whereby a cyclic olefin is oxidized to produce an epoxide is disclosed. The inventive process which uses air, or molecular oxygen as the sole oxidizing agent, and which is catalyzed by a specifically structured metallosalen complex is characterized in its high selectivity and high turnover efficiency.

#### 5744636

##### **Process for the production of ethylidene diacetate from dimethyl ether using a heterogeneous catalyst**

Ramprasad Dorai; Waller Francis Joseph, Allentown, PA, United States assigned to Air Products and Chemicals

This invention relates to a process for producing ethylidene diacetate by the reaction of dimethyl ether, acetic acid, hydrogen and carbon monoxide at elevated temperatures and pressures in the presence of an alkyl halide and a heterogeneous, bifunctional catalyst that is stable to hydrogenation and comprises an insoluble polymer having pendant quaternized heteroatoms, some of which heteroatoms are ionically bonded to anionic Group VIII metal complexes, the remainder of the heteroatoms being bonded to iodide. In contrast to prior art processes, no accelerator (promoter) is necessary to achieve the catalytic reaction and the products are easily separated from the catalyst by filtration. The catalyst can be recycled for 3 consecutive runs without loss in activity.

#### 5747408

##### **Supported catalysts containing rhenium and aluminium, preparation thereof and use thereof for the metathesis of olefins**

Commereuc Dominique Meudon, France assigned to Institut Francais du Petrole

The present invention concerns new catalysts based on compounds containing both rhenium and aluminum, which are deposited on an organic or inorganic support. The compounds of rhenium and aluminum correspond to the general formula: (\*See Patent for Tabular Presentation \*) PS in which R is a hydrocarbyl residue, for example alkyl, cycloalkyl, alkenyl, aryl, and aryl or cycloalkyl which are substituted, containing from 1 to 40 carbon atoms, which residue can be substituted by alkoxy groups or by halogens, L is the synthesis solvent,  $x$  is equal to 0 or 1 and  $n$  is an integer of from 1 to 10. The invention also concerns the preparation of such catalysts and the use thereof for the metathesis of olefins.

#### 5747409

##### **Catalytic compositions based on compounds of rhenium and aluminium, preparation thereof and use thereof for the metathesis of olefins**

Commereuc Dominique Meudon, France assigned to Institut Francais Du Petrole

The present invention concerns new catalytic compositions containing at least one compound of rhenium and aluminium corresponding to the general formula:  $O_3Re-O-(Al(OR)(L)_x-O)_n-ReO_3$  in which R is a hydrocarbyl residue, for example alkyl, cycloalkyl, alkenyl, aryl and aryl or cycloalkyl which are substituted, containing from 1 to 40 carbon atoms, which residue can be substituted by alkoxy groups or by halogens, L is the synthesis solvent,  $x$  is equal to 0 or 1 and  $n$  is an integer of from 1 to 10. The invention also concerns the preparation of such compositions and the use thereof for the metathesis of olefins in a homogeneous phase.

#### 5747411

##### **Supported catalysts which are suitable for ammonoxidation**

Karrer Lothar; Pape Frank-Friedrich; Kuml ohler Ulrich; Becker Rainer; Weidlich Peter; Huml ullmann Michael; Kneuper Heinz-Josef, Pfungstadt, Germany assigned to BASF Aktiengesellschaft

Supported catalysts which are suitable for ammonoxidation, comprising (a) a spherical or approximately spherical support material which essentially comprises aluminum oxide, silicon dioxide, titanium dioxide and/or zirconium dioxide and whose bulk density is

from 0.6 to 1.2 kg/l, and (b) an active material which comprises, as essential components, vanadium and antimony in oxidic form.

## Environmental Catalysis

**5736114**

### Spinel-based catalysts for reducing exhaust emissions of NO<sub>x</sub>

Barthe Philippe; Macaudiere Pierre; Seguelong Thierry, Saint Martin du Tertre, France assigned to Rhone-Poulenc Chimie

Oxygen-rich exhaust gases, for example those emanating from internal combustion engines, e.g., diesel engines, are catalytically treated/converted to reduce emissions of NO<sub>x</sub>, in the presence of a catalytically effective amount of either (a) a spinel mass oxide essentially having the formula ZnAl<sub>2</sub>O<sub>4</sub>, or (b) a normal or inverse spinel oxide other than ZnAl<sub>2</sub>O<sub>4</sub>, for example ZnGa<sub>2</sub>O<sub>4</sub>, SnZnGa<sub>2</sub>O<sub>4</sub> or MgAl<sub>2</sub>O<sub>4</sub>.

**5736482**

### Catalysts for reducing nitrogen oxides to molecular nitrogen in a superstoichiometric medium of oxidizing compounds, process for preparation, and uses

Durand Danie; Mabilon Gil; Mouchot Paul Rueil Malmaison, France assigned to Institut Francais du Petrole

Described is catalyst that is active and selective for reducing to molecular nitrous oxides contained in a superstoichiometric medium of oxidizing agents, said reduction being conducted with agents such as carbon monoxide, hydrogen, hydrocarbons, alcohols, ethers, and other oxidized organic compounds and also with ordinary fuels such as gasolines, gas oils, liquefied gases, and compressed natural gases, whereby said catalyst comprises: at least one refractory inorganic oxide, including alumina; at least one element (A) that belongs to the group of rare earths; at least one element (B) that belongs to groups VIB, VIIB, VIII and IB of transition metals; at least one metal (C) that belongs to the group of precious metals of the platinum family, and optionally at least one element (D) that belongs to group IIA of alkaline-earths; at least a portion of elements (A) is combined with alumina to form at the

surface of the latter a microlayer of rare-earth aluminate.

**5738024**

### Catalytic reduction apparatus for nox reduction

Winegar Phillip, New York, NY, United States

An apparatus and method for reducing NO<sub>x</sub> pollution in flue gas produced by a power plant uses heat exchanger elements having extended surfaces which contain a SCR catalyst, with the heat exchanger elements located in the flue gas stream. Coolant is passed through the heat exchanger elements to cool the catalyst, with a temperature control system used to maintain the catalyst at its optimum temperature such that the maximum conversion of NO<sub>x</sub> is achieved. Utilizing the present invention, temperature cycling of the catalyst is avoided, prolonging the life of the catalyst, while at the same time optimizing the efficiency of conversion regardless of variations in the flue gas flow or temperature.

**5738835**

### Process for the purification of process gases by catalytic oxidation

Brueck Matthias; Reitz Hans, Rodenbach, Germany assigned to Zimmer Aktiengesellschaft

Process for purification of essentially oxygen-free process gases by catalytic oxidation of the oxidizable, mainly organic impurities with the addition of a oxygen-containing gas, where oxygen-containing gas is added to the process gas in an amount responsive to the carbon monoxide content of the process gas measured after oxidation. The carbon monoxide set point is in the range of 10 to 1000 vpm.

**5741467**

### Palladium catalyst washcoat supports for improved methane oxidation in natural gas automotive emission catalysts

Williamson W. Burton; Silver Ronald G., Broken Arrow, OK, United States assigned to ASEC

The invention provides a catalyst which can convert methane, carbon monoxide, and nitrogen oxides in lean, stoichiometric, and rich air/fuel environments. Support (A) of the catalyst comprises an alumina support impregnated with Pd providing lean methane conversions and support (B) of the catalyst comprises ceria/lanthana/alumina impregnated with Pd providing stoichiometric methane conversion. Rhodium may be substituted for all or part of the Pd on an alumina support.

#### **5744103**

#### **Hydrocarbon adsorbent for exhaust gas cleaning, exhaust gas cleaning catalyst and exhaust gas cleaning device**

Yamada Hiroshi; Ueoka Toshitsugu; Takami Akihide; Sakatani Naoko; Hatsukaichi, Japan assigned to Mazda Motor

In order to adsorb effectively various kind of hydrocarbons each having a different size, a zeolite having a larger pore 8, a zeolite having a smaller pore 6 and a zeolite having an in-between pores 7 are present together very closely located very closely to one another by means of, for example, physically mixing them.

#### **5744113**

#### **Process and catalyst for decomposing oxides of nitrogen**

Hums Erich, Hessdorf, Germany assigned to Siemens Aktiengesellschaft

In order to achieve a high degree of conversion, oxides of nitrogen are contacted with a catalyst containing an aluminum silicate having a three-sheet structure as a catalytically active component at a temperature between 100°C and 700°C. With this type of catalyst, the decomposition of the oxides of nitrogen proceeds without the presence of a reducing agent. Additionally, the degree of decomposition for the oxides of nitrogen is not adversely affected by the oxygen present in the flue gas. Degrees of decomposition greater than 60% were achieved with this catalyst in the temperature range between 200°C and 600°C. The catalysts of the invention can replace the previous catalysts, which use a reducing agent, for decreasing the amount of oxides of nitrogen in waste gases, for example in flue gas and

exhaust gas purification in power stations and combustion engines, respectively.

### **Fine Chemicals and Pharmaceuticals**

#### **5731472**

#### **Metal–ligand complex catalyzed processes**

Leung Tak Wai; Bryant David Robert; Shaw Bernard Leslie, Houston, TX, United States assigned to Union Carbide Chemicals and Plastics Technology

This invention relates to a method of stabilizing a metal-organopolysphosphite ligand complex catalyst against deactivation in a process which comprises reacting one or more reactants in the presence of a metal-organopolysphosphite ligand complex catalyst and optionally free organopolysphosphite ligand to produce a reaction product fluid comprising one or more products, which method comprises conducting said process in the presence of one or more free heterocyclic nitrogen compounds sufficient to prevent and/or lessen deactivation of the metal-organopolysphosphite ligand complex catalyst.

#### **5736479**

#### **Oxidation catalysts**

Schodel Rainer; Birke Peter; Geyer Reinhard; Kraak Peter; Muller Willibal; Neubauer Hans-Dieter; Pester Rolf; Vogt Fritz; Wendlandt Klaus-Peter, Halle, Germany assigned to Leuna-Katalysatoren

PCT No. PCT/DE93/01117 Sec. 371 Date May 24, 1995 Sec. 102(e) Date May 24, 1995 PCT Filed Nov. 24, 1993 PCT Pub. No. WO94/12277 PCT Pub. Date Jun. 9, 1994. The invention concerns new oxidation catalysts, methods of producing them and their use. These catalysts consist of titanium silicalites crystallized in situ onto activated charcoal or metal oxides. The titanium silicalite content lies preferably in the range of 30 to 60% by wt. The atomic ratio of Si to Ti in the carrier-borne phase is 10 to 100. Such catalysts are particularly suitable for oxidation reactions with H<sub>2</sub>O<sub>2</sub> under mild conditions, such as temperatures of 20° to 120°C and pressures equal to or higher than atmospheric.

**5731473****Metal–ligand complex catalyzed processes**

Bryant David Robert; Nicholson James Clair; Bunning Donald Leroy; Eisenschmid Thomas Carl; Morrison Donald Lee, South Charleston, WV, United States assigned to Union Carbide Chemicals and Plastics Technology

This invention relates to a process which comprises reacting one or more reactants in the presence of a metal–organophosphite ligand complex catalyst and dissolved water and optionally free organophosphite ligand to produce a reaction product fluid comprising one or more products, wherein said process is conducted in the presence of carbon dioxide in an amount sufficient not to effect substantial degradation of any said organophosphite ligand and/or substantial deactivation of said metal–organophosphite ligand complex catalyst.

**5736480****Supported phase chiral sulfonated binap catalyst solubilized in alcohol and method of asymmetric hydrogenation**

Davis Mark E; Wan Kam To, Pasadena, CA, United States assigned to California Institute of Technology

Supported phase catalysts in which the support phase, is non-aqueous and highly polar, such as a primary alcohol, and most preferably ethylene glycol, are disclosed. An organometallic compound, preferably a metal complex of chiral sulfonated 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl is dissolved in the ethylene glycol. Such supported phase catalysts are useful for asymmetric synthesis of optically active compounds, such as the preparation of dehydronaproxen.

**5739396****Asymmetric ligands useful for transition metal catalyzed bond forming reactions**

Trost Barry M.; Van Vranken David; Bunt Richard C., Los Altos Hills, CA, United States assigned to Stanford University

Ligands useful for transition metal catalyzed bond forming reactions are provided with a metal binding

portion having at least one metal binding moiety (\* See Patent for Chemical Structure\*) wherein Ar and Ar' each is an aryl or a heteroaryl. These ligands may be prepared by providing an aromatic carboxylic acid having a diarylphosphino or diheteroarylphosphino substituent on the aromatic ring, and forming an ester or an amide derivative of the carboxylic acid by coupling with a chiral diol or a chiral diamine. The ligands facilitate, for example, flexible strategies for enantiocontrolled construction of five membered carbocyclic rings with varying substitution patterns and high enantioselectivity.

**Polymers****5739073****Addition of lithium compounds to Ziegler–Natta catalysts for increased molecular weight in polyolefins**

Shamshoum Edwar S.; Bauch Christopher G., Houston, TX, United States assigned to Fina Technology

This invention relates to a conventional supported heterogeneous Ziegler–Natta catalyst for the polymerization of olefins. It has been found that adding a lithium compound to a transition metal catalyst component and then adding an organoaluminum co-catalyst and an organosilicon electron donor produces a catalyst which yields polymer with increased molecular weight. The lithium compound is of the general formula LiCp wherein Cp is a cyclopentadienyl or substituted cyclopentadienyl and is preferably lithium cyclopentadienide or lithium indene. Preferably, the molar ratio of lithium compound/transition metal is at least 0.2.

**5739224****Supported catalyst for olefin polymerization**

Luciani Luciano; Neissl Wolfgang; Wenidoppler Birgit, Ferrara, Italy assigned to PCD Polymere Gesellschaft

Procedure for the preparation of a solid catalyst component which is active in the polymerization of olefins, comprising the steps: (a) contacting a silylated silica support with a solution of Mg-halide or Mg-alkyl-halide or a mixture of both, (b) contacting the catalyst-precursor obtained in (a) with Mg-alkyl or Mg-alkyl-halide or a mixture of both, optionally in presence of electron-donors (Lewis bases), (c) halo-

generating the catalyst-precursor obtained in (b) by contact of said activated support with halogenating agents, (d) titanating the catalyst-precursor obtained in (c) with Ti-tetrahalide in the presence of electron-donors, (e) recovering the solid catalyst-component from the reaction products of step (d). The catalyst component, which is obtained according to the above procedure, may also be used together with Al-trialkyl or Al-alkylhalides and a Lewis base, as a catalyst for the polymerization of olefins.

#### 5739226

##### **Solid catalytic component containing zirconium and cycloalkadienyl groups, process for producing it and process for the polymerization of olefins in its presence**

Spitz Roger; Pasquet Veronique; Dupuy Jerome; Malinge Jean, Serezin, France assigned to Elf Atochem

The solid catalytic component according to the invention is obtained by (a) treatment of a catalytic component support with  $ZrCl_4$  or  $HfCl_4$  in the gas phase, followed by a (b) treatment with a solution or suspension of a compound capable of grafting a group containing the cycloalkadienyl skeleton to the Zr or Hf contained in the support. Polymerization of olefins in the presence of such a catalytic component results in polymers with low polydispersities, which polymers are obtained with high productivities.

#### 5739257

##### **Binary phase transfer/amine catalyst for making aromatic polycarbonates**

Boden Eugene P.; Flowers Larry I.; Phelps Peter D.; Ramsey David L.; Sybert Paul D., Scotia, NY, United States assigned to General Electric

A composition and method is provided for making polycarbonate utilizing an effective amount of a binary catalyst system, comprising a phase transfer catalyst selected from the group consisting of methyltributylammonium halide and hexabutylbutylenediammonium halide and a tertiary organic amine, as a condensation catalyst during the interfacial phosgenation of a bisphenol, such as bisphenol A. Improved phosgene utilization and the substantial elimination of emulsion formation in the interfacial polymerization reactor and the processing units downstream thereof results.

#### 5739367

##### **Cobalt catalyst**

Carr John Frederick; Pakenham Derek Abbeymead, United Kingdom assigned to Rhone-Poulenc Chemicals

PCT No. PCT/GB96/01986 Sec. 371 Date Jul. 21, 1997 Sec. 102(e) Date Jul. 21, 1997 PCT Filed Aug. 14, 1996 PCT Pub. No. WO97/07124 PCT Pub. Date Feb. 27, 1997. A process for preparing a cobalt (III) complex is described which comprises: (i) treating a divalent cobalt salt of formula  $CoIX_2/n$  where  $n$  is the valency of an anion X, with up to 15 molar equivalents of ammonia or an amine; (ii) oxidizing the resulting amine complex; (iii) converting the oxidized complex to the corresponding carboxylate of formula  $(CoIII(NR_3)5R_1-COO)X_2/n$  where each R, which may be the same or different, represents hydrogen or an optionally substituted hydrocarbon group and R1 represents an alkyl or alkenyl group of 1 to 18 carbon atoms, at a pH above 8.5; and optionally (iv) replacing the X ion by a different anion by a metathetical reaction.

#### 5739368

##### **Use of heat treated alumoxanes in preparing supported catalysts**

Krzystowczyk Niomi L.; Diefenbach Steven P.; Burt Edward A., Baton Rouge, LA, United States assigned to Albemarle

Alumoxane, and especially methylalumoxane, which provide supported metallocene and/or transition metal catalyst compositions having increased activity are prepared by heating the alumoxane prior to placing it on the support.

#### 5741868

##### **Olefin polymerization process by using a substituted indenyl containing metallocene catalyst**

Winter Andreas; Kuml uber Frank; Aulbach Michae; Bachmann Bernd; Klein Robert; Kuml uhlein Klaus; Spaleck Walter; Kohlpaintner Christian, Glashutten, Germany assigned to Hoechst Aktiengesellschaft

The present invention relates to a metallocene compound of the formula I (\*See Patent for Chemical Structure\*) (I) which can advantageously be used as catalyst component for olefin polymerization.



**5744414****Process for preparing an olefin polymerisation catalyst**

Jenny Charles, Lavera, France assigned to BP Chemicals

The present invention relates to a process for the preparation of a solid catalytic component of a catalyst of Ziegler–Natta type, comprising contacting (i) at least one compound (A) of a transition metal (TM) with (ii) a solid product (B) comprising a magnesium compound and having a reducing power for the transition metal (TM), in the presence of (iii) at least one olefin under conditions such that the olefin at least partially polymerizes during the contacting. The solid catalytic component is particularly useful for producing ethylene (co-)polymers in a gas phase process and for improving the statistical distribution of the comonomer in the copolymer structure.

**5744415****Rare earth metal catalyst for olefin polymerization**

Wenzel Timothy Todd, Charleston, WV, United States assigned to Union Carbide Chemicals and Plastics Technology

A catalyst composition comprising: (a) (i) a catalyst containing at least one cycloalkadienyl ligand substituted with at least one electron donor residue and coordinated with a metal selected from the group consisting of scandium, yttrium, and lanthanide metals; or (ii) a catalyst containing two cycloalkadienyl ligands coordinated with a metal selected from the group consisting of scandium, yttrium, and lanthanide metals, said cycloalkadienyl ligands connected by a bridging group comprising at least one Group IVA element and at least one electron donor residue; and (b) an activating cocatalyst of the formula  $R_xM'$ , wherein R is alkyl, aryl, or hydride;  $M'$  is a Group I, II, or IIIA metal or a Group I, II, or IIIA metal complexed with oxygen, nitrogen, or a halide; and  $x$  is equal to the valence of  $M'$ .

**5744416****Catalyst system for polycarbonate manufacture**

Flowers Larry I.; Sybert Paul; Ramsey David L., Evansville, IN, United States assigned to General Electric

A method is provided for making polycarbonates utilizing an effective amount of a binary phase transfer catalyst, such as tetrabutylammonium bromide and a methyl tertiary amine as a condensation catalyst during the interfacial phosgenation of a bisphenol, such as bisphenol A. Improved phosgene utilization is achieved.

**5744418****Redox catalyst system for the initiation of emulsion polymerization**

Jakob Marti, Kelkheim, Germany assigned to Clariant

A redoxcatalyst system capable of being used for free-radical emulsion polymerization of ethylenically unsaturated compounds, comprising at least one oxidizing agent and at least one reducing agent, said reducing agent comprising an at least bifunctional aldehyde having at least 3 carbon atoms which is completely masked as a bisulfite adduct.

**5744556****Gas phase polymerization employing unsupported catalysts**

Keller George Ernest; Carmichael Keith Ernest; Copley Jean Bowman; Larsen Eldon Ronald; Ramamurthy Arakalud Venkatapathi; Smale Mark Wilton; Wenzel Timothy Todd; Williams Clark Curtis, South Charleston, WV, United States assigned to Union Carbide Chemicals and Plastics Technology

A process for the gas-phase polymerization of polymers which allows for the introduction of an unsupported polymerization catalyst system into the gas-phase reactor, wherein the unsupported polymerization catalyst system comprises (i) a non-volatile materials fraction containing a polymerization catalyst; (ii) a solvent fraction which is at least partially miscible with the non-volatile materials fraction and which is sufficiently volatile to allow for the formation of polymerization catalyst particles when the mixture of the solvent fraction and the non-volatile materials fraction is sprayed into the reactor; (iii) a compressed fluid; and (iv) optionally a slowly vaporizing solvent.

**5744571****Production of particular polyesters using a novel catalyst system**

Hilbert Samuel D.; Davis Thomas, Jonesborough, TN, United States assigned to Eastman Chemical

This invention relates to a process of producing a moldable polyethylene terephthalate or modified polyethylene terephthalate having an inherent viscosity greater than 0.6 dL/g comprising reacting the diacid component with the diol component such that a combination of a titanium-based catalyst and a phosphorus-based catalyst is used during the polycondensation steps.

**5747404****Polysiloxane supported metallocene catalysts**

Nagy Sandor; Tyrell John A., Grand Island, NY, United States assigned to Lyondell Petrochemical

Disclosed is a catalyst having the formula (\*See Patent for Chemical Structure\*) where each R is independently selected from aliphatic from C1 to C6 and aromatic from C6 to C10, each R5 is independently selected from H, R, and L', each L' is independently selected from LM'L<sub>r</sub>X<sub>3-r</sub> or two L' groups form the bridge -LM'X<sub>2</sub>-rL<sub>r</sub>-, each L is independently selected from cyclopentadienyl, indenyl, and fluorenyl, X is chlorine or bromine, M' is zirconium, titanium, or hafnium, n is 5 to 500, the ratio of R to H + L in R5 is 0 to 100, the ratio of H to L' in R5 is 0 to 4, and r is 0 or 1.

**5747405****Catalyst compositions and process for preparing polyolefins**

Little Ian Raymond; McNally John Paul, Hampton, United Kingdom assigned to BP Chemicals

Catalyst compositions comprising both metallocene complexes having polymerisable groups and polymerization catalysts, e.g., Ziegler-Natta may be used for the preparation of polyolefins. The catalyst compositions may comprise the metallocene complex in the form of a polymer and may suitably be supported on inorganic supports. Polymers having a wide range of molecular weights and comonomer distributions may be

prepared by use of the catalyst compositions. Preferred metallocene complexes are zirconium complexes in which the polymerisable group is vinyl.

**5747406****Catalyst composition for the production of olefin polymers**

Reichle Walter Thomas; Yang Xinmin; Karol Frederick John, Warren, NJ, United States assigned to Union Carbide Chemicals and Plastics Technology

A catalyst composition comprising the reaction product of (a) a monocycloalkadienyl catalyst precursor; (b) an activity enhancing cycloalkadiene; and (c) an activating cocatalyst is disclosed, which has high activity in the polymerization of olefins.

**5747407****Method of making a ziegler-natta olefin polymerization catalyst**

Martin Joel, Bartlesville, OK, United States assigned to Phillips Petroleum

A composition which can be used in, for example, slurry polymerization of an olefin such as, for example, ethylene is produced by a process comprising: (1) combining a first transition metal compound and a metal halide to form a solution; (2) contacting the solution with a precipitating agent to form a solid catalyst intermediate; (3) contacting the solid catalyst intermediate with a second transition metal compound to produce a catalyst composition; and optionally (4) depositing a prepolymer onto the catalyst composition. The precipitating agent comprises a sufficient amount of both a Lewis acid and an ether to effect the precipitation of a solid. Also disclosed is the use of the composition in polymerization of an olefin.

**5747595****Catalyst for the polymerization of olefines and processes for the polymerization of olefines using the same**

Saito Toshiya; Taki Takayuki; Nakajima Masashi; Imanishi Kunihiko; Murata Masahide; Ozaki Hiroyuki; Aiba Kazukiyo; Ookura Masatoshi; Ueki Satoshi, Saitama ken, Japan assigned to Tonen

A catalyst for the polymerization of olefines comprises a solid catalytic component obtained by pre-polymerizing propylene in the presence of (A) a solid component containing magnesium, titanium, halogen and an electron-donating compound, (B) an organoaluminum compound, and (C) an alkylalkoxysilane represented by the formula,  $R_1Si(OR_2)(OCH_3)_2$ , wherein  $R_1$  represents a branched or cyclic alkyl group having 3 to 6 carbon atoms, and  $R_2$  represents a branched alkyl, alkenyl or alkinyl group having 3 to 6 carbon atoms; (B) an organoaluminum compound; and (D) an alkyltri-alkoxysilane represented by the formula,  $R_3Si(OR_4)_2(OCH_3)$ , wherein  $R_3$  represents a linear alkyl group having 3 to 6 carbon atoms, and  $R_4$  represents a branched alkyl, alkenyl or alkinyl group having 3 to 5 carbon atoms.

#### 5747612

##### Process for transitioning between incompatible polymerization catalysts

Agapiou Agapios Kyriacos; Muhle Michael Elroy; Renola Gary Thomas, Humble, TX, United States assigned to Exxon Chemical Patents

This invention relates to a process for transitioning between incompatible polymerization catalyst systems. Particularly, the invention relates to a process for transitioning from an olefin polymerization reaction utilizing a traditional Ziegler–Natta catalyst system to a metal-locene–olefin polymerization reaction.

#### 5747614

##### Catalyst for producing styrenic polymer and process for producing styrenic polymer by using same

Takeuchi Mizutomo; Shouzaki Hajime; Tomotsu Norio, Ichihara, Japan assigned to Idemitsu Kosan

PCT No. PCT/JP94/01078 Sec. 371 Date Jan. 2, 1996 Sec. 102(e) Date Jan. 2, 1996 PCT Filed Jul. 1, 1994 PCT Pub. No. WO95/01328 PCT Pub. Date Jan. 12, 1995. A catalyst for producing a styrenic polymer which comprises an (A) transition metal compound having one and only one pi-ligand comprising only one indenyl group, said indenyl group bearing a substituent group at at least the 1-, 2-, or 3-positions of the indenyl ring, and wherein the transition metal is preferably a

least one metal selected from the group consisting of titanium, zirconium, hafnium, niobium and tantalum, and optionally (B) at least one compound selected from the group consisting of 1 an aluminoxane and 2 an ionic compound comprising an anion that does not coordinate to the transition metal compound of component (A) in its cationic form, and a cation, and further optionally (C) a Lewis acid; and a process for producing a styrenic polymer using the catalyst.

#### Catalysts Preparation

#### 5736483

##### Niobium or tantalum promoted silver catalyst

Rizkalla Nabil, Riverdale, NJ, United States assigned to Scientific Design

A rhenium free silver catalyst for ethylene oxidation to ethylene oxide is provided containing a promoter combination consisting of an alkali metal component a niobium or tantalum component, and a sulfur component.

#### 5736484

##### Nickel-containing hydrogenation catalysts

Polanek Peter; Schwahn Harald; Irgang Matthias; Erdbruml ugger Cristina Freire, Weinheim, Germany assigned to BASF Aktiengesellschaft

PCT No. PCT/EP95/00809 Sec. 371 Date Sep. 12, 1996 Sec. 102(e) Date Sep. 12, 1996 PCT Filed Mar. 4, 1995 PCT Pub. No. WO95/24964 PCT Pub. Date Sep. 21, 1995. A catalyst suitable for hydrogenating organic compounds, essentially containing from 65 to 80% of nickel, calculated as nickel oxide, from 10 to 25% of silicon, calculated as silicon dioxide, from 2 to 10% of zirconium, calculated as zirconium oxide, and from 0 to 10% of aluminum, calculated as aluminum oxide, with the proviso that the sum of the content of silicon dioxide and aluminum oxide is at least 15% (percentages in % by weight, based on the total weight of the catalyst), obtainable by addition of an acidic aqueous solution of nickel, zirconium and, if desired, aluminum salts to a basic aqueous solution or suspension of silicon compounds and if desired aluminum compounds, the pH of the mixture thus obtained being

decreased to at least 6.5 and then adjusted to from 7 to 8 by addition of further basic solution, isolation of the solid thus precipitated, drying, shaping and calcining, furthermore a process for preparing the catalysts and their use for preparing medicinal white oil, highly pure medicinal paraffins and low-boiling aromatic-free hydrocarbon mixtures.

#### **5744026**

##### **Catalyst system and process for benzyl ether fragmentation and coal liquefaction**

Zoeller Joseph Rober, Kingsport, TN, United States assigned to Eastman Chemical

Dibenzyl ether can be readily cleaved to form primarily benzaldehyde and toluene as products, along with minor amounts of bibenzyl and benzyl benzoate, in the presence of a catalyst system comprising a Group 6 metal, preferably molybdenum, a salt, and an organic halide. Although useful synthetically for the cleavage of benzyl ethers, this cleavage also represents a key model reaction for the liquefaction of coal; thus this catalyst system and process should be useful in coal liquefaction with the advantage of operating at significantly lower temperatures and pressures.

### **Refinery Processes**

#### **5733518**

##### **Process and catalyst for dehydrogenation of organic compounds**

Durante Vincent A.; Resasco Daniel E.; Walker Darrell W.; Haller Gary L.; Coggins Eugene L., West Chester, PA, United States assigned to Sun (R & M)

The invention comprises a process for selectively oxidizing hydrogen in a mixture with other gaseous materials by contacting the hydrogen containing gas under oxidation conditions with a catalyst comprising a phosphate of a metal wherein the metal is selected from the group consisting of germanium, tin, lead, arsenic, antimony and bismuth.

#### **5736478**

##### **Catalyst to dehydrogenate paraffin hydrocarbons**

Cortright Randy D.; Dumesic James, Madison, WI, United States assigned to Wisconsin Alumni Research Foundation

A new catalyst for the selective conversion of isobutane to isobutylene. This catalyst also could be applied to the selective dehydrogenation of other light paraffins such as propane and *n*-butane. The catalyst is comprised of platinum, tin, and potassium supported on K–L-zeolite. This catalyst exhibits greater than 98% selectivity for conversion of isobutane to isobutylene at isobutane conversion levels greater than 50%. In addition, this catalyst exhibits excellent stability. The preferred catalyst would have an atomic ratio of Sn to Pt greater than 1.0 as well as an atomic ratio of K to Pt greater than 1.0.

#### **5739072**

##### **Process for improving the physical and catalytic properties of a fluid cracking catalyst**

Shi Joseph C.; Albers Edwin; Wilson Geoffrey R., Bartow, GA, United States assigned to Thiele Kaolin

A process for significantly improving the physical and catalytic properties of fluid cracking catalysts (FCC) is disclosed. The invention is a process for manufacturing a fluid cracking catalyst. The process includes adding an effective amount of an acid stable surfactant or an alkaline stable surfactant to a slurry of clay particles and sodium silicate particles. The process then includes forming a sol binder and spray drying the particles. Forming of the dried particles into a catalyst product then occurs.

#### **5739074**

##### **Metal cation-modified alkylation catalysts**

Kocal Joseph A.; Oroskar Anil R., Gurnee, IL, United States assigned to UOP

A catalytic composite of a refractory inorganic oxide whose bound surface hydroxyl group has reacted with a Friedel–Crafts type metal halide and whose acidity has been modified by the deposition of a monovalent metal cation, especially an alkali metal cation, or alkaline earth metal cation shows superior selectivity and a significantly decreased cracking tendency relative to similar catalysts without the monovalent metal or alkaline earth metal cation. The resulting alkylate from an isobutane–butene feedstock shows a substantial increase in research octane number relative to the alkylate formed by a similar catalyst which has not been so modified by an alkali or alkaline earth metal cation.

**5744645****Two-stage process for producing diisopropyl ether using catalytic distillation**

Marker Terry L.; Funk Gregory A.; Barger Paul T.; Hammershaimb Harold U., Warrenville, IL, United States assigned to UOP

A process for the efficient production of diisopropyl ether where catalytic distillation is used to increase the yield of product beyond thermodynamic equilibrium limitations has been developed. In a hydration zone the propylene in a feedstock is reacted with water in the presence of a catalyst to effect hydration to produce an effluent stream containing at least water, unreacted propylene, and isopropyl alcohol, and then, in an etherification zone, at least a portion of the effluent stream is further reacted by catalytic distillation in the presence of a catalyst to effect reaction of propylene and isopropyl alcohol to form diisopropyl ether while concurrently separating an organic portion containing the diisopropyl ether and an aqueous portion, and collecting the organic portion containing the diisopropyl ether.

**5744674****Catalyst and process for the conversion of heavy aromatics to light aromatics**

Gui Shouxi; Hao Yuzhi; Li Yanqing; Jing Zhenhua; Gu Haohui; Liang Zhanqiao; Cheng Baoyu, Beijing, China assigned to China Petrochemical; Research Institute of Petroleum Processing

A catalyst for the preparation of benzene, toluene and xylene from C<sub>9</sub> + heavy aromatics consists of zeolite ZSM-5 and gamma- or eta-Al<sub>2</sub>O<sub>3</sub> as carrier, Re, Sn and Pt or Pd supported on the carrier. Under the conditions of 350°–450°C, 0.5–3.5 MPa, a WHSV of 1–5 h<sup>-1</sup> and a H<sub>2</sub>/HC ratio (v/v) of 500–1200, the catalyst achieves high activity and stability as well as low hydrogen consumption.

**5744678****Oligomerization catalysts and process using the same for the production of olefinic oligomers**

Aida Fuyuki; Nakano Takashi; Tajima Yoshio; Matsura Kazuo, Yokohama, Japan assigned to Nippon Oil

PCT No. PCT/JP96/00532 Sec. 371 Date Nov. 1, 1996 Sec. 102(e) Date Nov. 1, 1996 PCT Filed Mar. 6, 1996 PCT Pub. No. WO96/27440 PCT Pub. Date Sep. 12, 1996. An oligomerization catalyst according to the invention comprises a nickel compound (A); an organophosphoric compound (B); an organoaluminum compound (C); and a compound of the group consisting of carbon-halogen bond-containing compounds, oxoacid and salts thereof, sulfonic acid and derivatives thereof, and compounds of any of the formulae QX<sub>4n</sub>, QR<sub>n</sub>, QR'<sub>n</sub>, QX<sub>41Rm</sub>, QX<sub>41R'm</sub>, QR<sub>1R'm</sub>, Q1(BR<sub>4</sub>)<sub>p</sub> and R''(BR<sub>4</sub>) wherein Q is an element of the group consisting of Mg, Ti, Zr, B and Sn, Q1 is an element of the group consisting of Li, Na, K, Ca and Zn, X<sub>4</sub> is a halogen or hydrogen atom, R is a C<sub>1</sub>–C<sub>12</sub> hydrocarbon group, R' is a C<sub>1</sub>–C<sub>12</sub> oxygen-containing hydrocarbon group, R'' is a C<sub>1</sub>–C<sub>20</sub> hydrocarbon group or an ammonium group, n is a valence of Q, l, m is a natural member that satisfied  $n = l + m$ , and p is a valence of Q1. This catalyst is useful for the production of alpha-olefinic oligomers.

**Syngas Catalysis****5744419****Process for the preparation of an improved supported catalyst, containing nickel and cobalt, with or without noble metals, useful for the oxidative conversion of methane, natural gas and biogas to syngas**

Choudhary Vasant Ramchandra; Uphade Balu Shivaji; Mamman Ajit Singh; Rajput Amarjeet Munshiram, Maharashtra, India assigned to Council of Scientific And Industrial Research

A supported catalyst is prepared by depositing oxides of nickel and cobalt, with or without noble metals, on a sintered low surface area porous inert support, surface of which is precoated with an oxide of Be, Mg, Ca or a mixture thereof so that a protective layer of the alkaline earth oxide is formed between the oxides of nickel and cobalt, with or without noble metal, and the support and hence direct chemical interactions between the oxides of the group VIII transition metals and the reactive components of support, which leads to the formation of catalytically inactive binary oxide phases are avoided.