NEW PATENTS

ELECTROCHEMISTRY

Electrochemical Synthesis of Ozone

LYNNTECH INC. *U.S. Patent* 5,770,033

Electrochemical synthesis of ozone used in disinfection processes involves supplying a source of O_2 gas through a gas diffusion layer to a catalyst in a cathodic catalyst layer. The latter comprises a proton exchange polymer, PTFE and Pt, Pd, Ir, Au and/or Ni, and has a first surface of an ionically conducting membrane bonded mainly with H_2O and an acid, to an anode in contact with a second surface. Current through the anode, cathode and ionic conducting membrane produces H_2O_2 at the cathode and O_3 at the anode. H_2 is not formed, resulting in lower costs.

ELECTRODEPOSITION AND SURFACE COATINGS

Coating a Superalloy Article

ROLLS-ROYCE PLC *British Appls.* 2,322,382–83A

Coating superalloy single crystal turbine blades or vanes to avoid premature failure involves applying Cr, Ti or Ta and diffusing to form an enriched layer, then forming a Pt aluminide-silicide coating from Pt, Si and Al, via diffusion and heat treatments; layers of Al_2O_3 and a thermal barrier are then added. During the diffusion heating the Al reacts with Pt to form Pt aluminide. Si does not diffuse into the superalloy.

Activation for Electroless Plating

MURATA MFG. CO. LTD. *European Appl.* 861,923A

A hydrophilic activating catalytic solution for electroless plating comprises a lactate, a Pd salt and an alkaline medium, which are applied to a substrate to form a photosensitive film. The film needs only short exposure to radiation to deposit a Pd catalyst on the substrate.

Deposition of Palladium Layer

WHITAKER CORP. *World Appl.* 98/38,351A

A Pd layer is deposited on a substrate by heat decomposition of a Pd precursor on the substrate surface. The precursor has the formula $Pd(OOCR_1)_m$-$(OOCR_2)_n$, such as glyoxilic Pd(II) glycoliate, where R_1 and R_2 are H, alkyl, alkenyl, alkynyl or -R_3COOH; R_3 is 1–5C alkyl substituted with 1–2 hydroxyl group. The Pd films can be deposited on electrical interconnects, flex circuits, multi-chip modules and printed wiring boards in an environmentally-friendly way.

Platinum Alloy Plating Bath

TANAKA KIKINZOKU KOGYO K.K. *Japanese Appl.* 10/212,592

A plating bath with high Mo concentration consists of a Pt compound, molybdenic acid, molybdate and a Fe group transition metal compound. The Pt film has improved ductility and is easily mouldable. It is used for insoluble anodes for electrolysis, sensors, etc.

APPARATUS AND TECHNIQUE

Gas Sensor for Detecting Gas

CTS CORP. *U.S. Patent* 5,779,980

A sensor for measuring gas concentrations in air, for example exhaust gas from I.C.E., has a resistor on an Al_2O_3 substrate, with a catalyst support structure of Al_2O_3 and glass on the resistor which binds them all together, and a Pt-containing catalyst. The sensor is compact, cost effective, durable, and can function in the harsh conditions of a car exhaust system.

Device for Abating Carbon Monoxide

E. I. DU PONT DE NEMOURS & CO. *U.S. Patent* 5,806,886

A device for abating CO generated during vehicle airbag inflation with combustion gases has a catalytic activation system comprising a supported Pd(II) salt in contact with a thermally stable oxidising agent. The device lowers CO and NOx contents in vehicle airbags inflated by pyrotechnic nitrocellulose inflators. The device is small and easily made.

HETEROGENEOUS CATALYSIS

Diesel Engine Catalyst

FORD GLOBAL TECHNOLOGIES INC. *European Appl.* 864,354A

A lean NOx catalyst for reducing the NOx concentration in diesel engine exhaust gases comprises a porous Al_2O_3 support; 5–40 wt.% of 12-tungstophosphoric acid; and ≥ 0.25 wt.% of Pt, Pd and/or Rh. A process for reducing the NOx concentration in the O_2-rich exhaust gas emissions of a diesel I.C.E. is also claimed. The catalyst has high resistance to S poisoning and begins to convert more NOx at a lower temperature, thus reducing cold start emissions.

Selective Hydrogenation Catalyst

NISSAN GIRDLER CATALYST CO. LTD. *World Appl.* 98/10,863A

A catalyst for selective hydrogenation of highly unsaturated hydrocarbon compounds contained in olefin compounds comprises Pd/Al_2O_3, in which the exposed faces of the Pd crystallites are mainly (100) or (110). The catalyst does not hydrogenate the olefin as a side reaction nor is there precipitation of carbonaceous material. It gives highly pure olefinic compounds and finds use in the petrochemical industry.

Conversion of Mixed Aromatic Hydrocarbons

MITSUBISHI OIL CO. *World Appl.* 98/12,159A

Mixed aromatic hydrocarbons containing ≥ 20 mol.% 9C alkyl substituted aromatics are converted to a product rich in toluene and/or xylene by contact with Pd on a dealuminated mordenite support with a Si:Al ratio of 12–30, and 10–50 wt.% SiO_2 binder, in the presence of H_2. The process gives high yields of toluene and/or xylenes in a stable operation with minimal coking and catalyst deactivation and low H_2 consumption.

Reduction of Nitrogen Oxides

GAZ DE FRANCE *World Appl.* 98/15,339A

A catalyst for the reduction of NOx to N_2 in the presence of CH_4 comprises a mordenite small pore (< 5 Å) zeolite exchanged with Pd alone, with 0.4–0.6% Pd^{2+} or/and 1.2–3.2% Co^{2+}, all relative to total catalyst weight. The zeolite is the Na or ammonium form, with a molar ratio Si:Al of 5.5. The process avoids the use of NH_3 as a reducing agent and allows high conversion rates of NOx of ≤ 70% in 10% O_2.

Supported Palladium-Gold Catalysts

MILLENNIUM PETROCHEMICALS INC. *World Appl.* 98/18,553A

A catalyst for vinyl acetate production comprises an inert support impregnated with Pd and Au salts, and calcined in a non-reducing atmosphere at 100–600°C to decompose ≥ 10% of the Pd and Au salts before reducing the Pd and Au to the metallic state. The catalyst can be tailored to have high selectivity at the higher calcination temperature and high activity at the lower temperature. Increased selectivity and activity for vinyl acetate production is achieved in the vapour-phase reaction of C_2H_4, CH_3COOH and O_2.

Reforming Hydrocarbons

CHEVRON CHEM. CO. LLC *World Appls.* 98/30,656–57A

A catalytic reforming process using a halide-Pt L-zeolite catalyst in a metal-coated reactor system involves removing volatile acidic halide prior to loading and reforming the catalyst. The system containing the reactive metal, usually Sn, is contacted with a getter to produce movable metal, and then fixing the movable metal and/or the getter. Catalytic reforming of hydrocarbons to aromatics can then take place. The process reduces catalytic contamination from a freshly metal-coated reactor system, and when replacing a conventional catalyst with a halide catalyst.

Composition for Gasoline Engine

CLEAN DIESEL TECHNOLOGIES INC. *World Appl.* 98/33,871A

A composition to add to gasoline to maintain or improve the performance of a three-way catalytic converter comprises a blend of Rh acetylacetonate and a fuel-soluble organo-Pt compound. The composition is fed to the combustion chamber where the organic parts of the Rh and Pt compounds are oxidised to give the metal active catalyst species. Exhaust gases are then passed to the catalytic converter, where the Rh and Pt are deposited. Emissions of NOx, HCs and CO are reduced while the performance of the three-way catalytic converter is maintained or improved.

Catalytic Composition

PHILLIPS PETROLEUM CO. *World Appl.* 98/37,966A

A composition used for the selective catalytic hydrogenation of unsaturated hydrocarbons comprises Pd, a selectivity enhancer, such as Pb, Bi, Th, Ir, Sn, Sb, Ge, As, Cd and/or Hg, and an inorganic support. The support is SiO_2, Al_2O_3 and/or spinel. Diolefins can be selectively hydrogenated to monoolefins.

Emission Control System

JOHNSON MATTHEY PLC *World Appl.* 98/40,153A

An emission control system for lean-burn I.C.E. comprises a first catalyst system (I) of Pt, and/or Pd and/or Rh, which gives a percentage conversion ratio of NOx:hydrocarbon of ≥ 0.2, at 230°C, space velocity of 25,000 h^{-1} and hydrocarbon:NOx input ratio of 3:1, with the hydrocarbon being counted as equivalent to propane. A second catalyst system (II) has a hydrocarbon conversion of > 80% and CO conversion of > 70%. Exhaust gases from the engine pass over (I) then over (II). The system controls NOx emissions with high selectivity for NOx reduction. (I) has low space velocity, while (II) has high oxidation activity.

Gasoline Catalysts

GENERAL MOTORS CORP. *U.S. Patent* 5,753,581

A catalyst comprises a substrate with a washcoat of Al_2O_3, CeO_2 and NiO, impregnated with a Pt solution at pH 9.5–10.5, so that the Pt is associated with CeO_2 and Al_2O_3. A Rh solution is then impregnated into the washcoat at a pH 6.5–7.5, so that the Rh is associated with the CeO_2. This provides a low cost effective method to alter the association of Pt group metal catalysts with specific support oxides.

Purification of Terephthalic Acid

AMOCO CORP. *U.S. Patent* 5,756,833

Terephthalic acid (TPA) is produced by liquid phase oxidation of *p*-xylene with an O_2-containing gas at 120–240°C in the presence of an oxidation catalyst of Co, Mn and Br components and a 1–6C monocarboxylic aliphatic acid solvent system containing H_2O. The impure TPA solution is purified with catalysts of Pt group metal/TiO_2 and Pd/C. The TPA has low levels of impurities and good colour.

Upgrading Naphtha to Gasoline

UOP *U.S. Patent* 5,770,042

A process for selectively upgrading a naphtha feedstock, composed of paraffins and naphthenes, to obtain a product with increased isoparaffin content comprises contacting the feedstock and a paraffinic intermediate with a solid Pt group metal isomerisation catalyst in an isomerisation zone at 40–250°C. The cyclics concentrate produced is converted using a non-acidic catalyst (1) of Pt group metal(s) on a metal oxide or molecular sieve support at 100–550°C. (1) is effective at ring cleavage and gives improved octane values when combined with paraffin isomerisation.

Platinum and/or Ruthenium Catalysts

CSIR COUNCIL SCI. IND. RES. *U.S. Patent* 5,792,875

Butyrolactone (1) or tetrahydrofuran (2) is prepared by hydrogenation of an alkyl ester of succinic or maleic acid at an elevated temperature in the presence of a bimetallic catalyst. The catalyst is obtained by impregnation of Al_2O_3 with an aqueous solution of Pt and/or Ru salts, followed by treatment with Sn salts. The Pt group metal:Sn ratio is 1:5–1:20. The support is then treated with an alkali solution followed by a B-containing solution. The process shows a high selectivity towards (1) and (2) at milder conditions.

Production of 4-*tert*-Butylcyclohexyl Acetate

SUMITOMO CHEM. CO. LTD. *Japanese Appl.* 10/195,020

The production of 4-*tert*-butylcyclohexyl acetate (1) comprises hydrogenating 4-*tert*-butylphenol with a Rh/C catalyst and a solvent in the presence of at least one of HCl, anhydric H_2SO_4 and perchloric acid and acetylating the obtained 4-*tert*-butylcyclohexanol. The hydrogenation takes place at 20–100°C. (1) is used as a perfume for cosmetics and soaps and can be obtained in ≥ 90% yield and ≥ 80% as the *cis*-isomer.

Hydrocracking of Gas Oil

COSMO OIL CO. LTD. *Japanese Appl.* 10/195,457

A method for hydrocracking various raw gas oils containing high S contents uses a mixture of catalysts. One catalyst contains 0.01–10 wt.% of Pt group metal carried on inorganic oxides, another comprises metals of Groups VI and VIII carried on inorganic oxides, at 300–380°C, 3.0–8.0 MPa and a liquid space velocity of 1.0–5 h^{-1} for a H_2:oil volume ratio of 250–1500. The method produces deep desulphurisation and hydrocracking of raw oils having ≥ 1000 ppm S without increasing the reaction pressure. It produces fuels with fewer pollutants in the exhaust gas.

HOMOGENEOUS CATALYSIS

One-Pot Process

CERESTAR HOLDING BV *European Appl.* 867,446A

A one-pot process for producing 2-keto-D-gluconic acid (1) from D-glucose comprises oxidation with O_2 in the presence of a Pt based catalyst doped with Pb or Bi. The pH of the reaction medium is kept at 7–10 until all the alkali is consumed; the oxidation is continued to allow the pH to drop to < 6. The (1) may be converted to iso-ascorbic acid. The process shows high selectivity.

Methacrylic and Acrylic Ester Production

ASAHI KASEI KOGYO K.K. *World Appl.* 98/11,050A

Methacrylic and acrylic esters are produced by reacting methacrolein or acrolein with an alcohol and O_2 in the presence of a Pd-containing catalyst while removing H_2 through a membrane, such as A-type zeolite, which is selectively permeable to H_2O. The selectivity and synthesis rate of the methacrylic and acrylic ester is increased by continually removing H_2O. The productivity is high and there is no need for H_2O absorbent regeneration.

Pentenoic Acid Derivative

DSM NV *World Appl.* 98/38,151A

Alkyl or aryl pentenoates are prepared by contacting alkoxy- or aryloxy-butene with CO in the presence of a catalytic system of Pd, a P ligand and an acid promoter. The molar ratio of 3-alkoxy-1-butene:1-alkoxy-2-butene, or 3-aryloxy-1-butene:1-aryloxy-2-butene is > 4. The reaction can be performed at a lower temperature than before and the rate of P ligand consumption/kg of pentenoic acid derivative is also lower. Methyl and ethyl pentenoates are used as precursors in ε-caprolactam and adipic acid preparations.

Liquid Phase Carbonylation of Ethylene

IMPERIAL CHEM. INC. PLC *World Appl.* 98/41,495A

Liquid phase carbonylation of C_2H_4 involves forming a gaseous phase from an C_2H_4 feed stream and a CO feed stream; then contacting the gaseous phase with a catalyst system of a Pd compound in a liquid phase containing a source of hydroxyl groups, a P ligand and a source of anions. The feed streams provide a molar ratio of C_2H_4:CO >1:1, but the activity and life of the catalyst are improved by using molar ratios of 3:1 to at least 5:1. The process is useful for the preparation of methyl propionate. Turnover numbers of 88,667 (mol. of methyl propionate/mol. Pd) are obtained.

FUEL CELLS

Platinum-Based Catalyst

ILLINOIS INST. TECH. *World Appl.* 98/40,161A

A catalyst for use in electrochemical reactors and direct-oxidation fuel cells (as the anode) comprises Pt, Ru and Os, and has a single phase crystal structure comprising a f.c.c. unit cell. The catalyst is useful in the construction of fuel cells operating at ≤ 200°C. The Pt catalyst can adsorb and dehydrogenate MeOH molecules without poisoning by adsorbed intermediates, such as CO, to give a better performance than conventional catalysts.

Fuel Cell Electrode Catalytic Coating

SOUTHWEST RES. INST. *U.S. Patent* 5,795,672

A fuel cell electrode has an electrocatalytic coating, 1 μm thick, comprising a thin film of diamond-like C having a finely dispersed catalytic agent, preferably Pt or Pt/Ru. The electrode is made of Nafion or an ionomeric material. Coatings are produced at low temperature and the method may be scaled up as a reel-to-reel process.

ELECTRICAL AND ELECTRONIC ENGINEERING

Soft Magnetic Thin Films

DAIDO TOKUSHUKO K.K. *Japanese Appl.* 10/208,937

Soft magnetic thin film, $Co_{(100-x-y-z)}Pd_{(x)}M_{(y)}O_{(z)}$, where M is Si, Zr, Al, x = 10–30, y = 2–5, z = 4–15, has unidirectional anisotropy, with effective component > 40. The film is used for inductors in integrated circuits, has improved high frequency characteristics and can be used at a frequency of ~ 1 GHz.

Magnetic Recording Medium

FUJITSU LTD. *Japanese Appl.* 10/228,621

The magnetic recording medium of a magnetic disk unit has a recording film formed upon a foundation film of Cr and Mo, which is formed upon a non-magnetic substrate. The recording film is made of 56–78% Co, 14–22% Cr, 4–20% Pt and 0.5–4% Nb. The medium has improved S:N ratio and enables high density recordings with high coercive force to be made.

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