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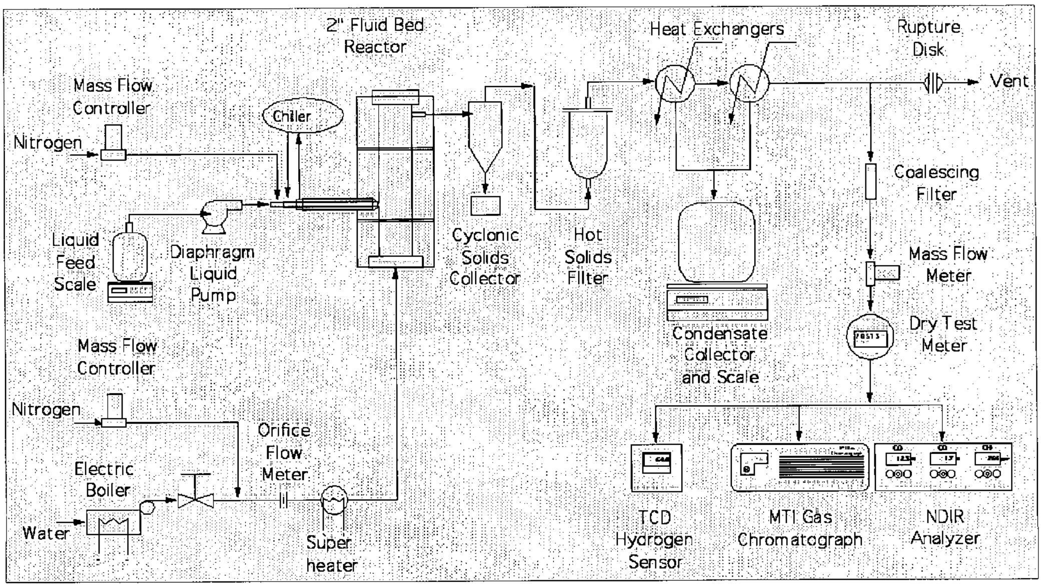
[Continued on next page]

(54) Title: ATTRITION RESISTANT FLUIDIZABLE REFORMING CATALYST



(57) Abstract: A method of preparing a steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, reforming, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, comprising: fabricating the ceramic support particle, coating a ceramic support by adding an aqueous solution of a presursor salt of a metal selected from the group consisting of Ni, Pt, Pd, Ru, Rh, Cr, Co, Mn, Mg, K, La and Fe and mixtures thereof to the ceramic support and calcining the coated ceramic in air to convert the metal salts to metal oxides.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ATTRITION RESISTANT FLUIDIZABLE REFORMING CATALYST

Contractual Origin

The United States Government has rights in this invention under Contract No. DE-AC3699GO10093 between the United States Department of Energy and the National Renewable Energy Laboratory, a division of the Midwest Research Institute.

Background Art

A method of preparing a family of attrition resistant, steam reforming catalyst materials for fluid bed application is presented, and more particularly, a method of utilizing the steam reforming of the product stream from gasified biomass, and the like, to produce a hydrogen-rich product stream.

Description of the Prior Art

Catalytic steam reforming is not new and is typically carried out with relatively "clean" gases and vapors over a fixed bed of catalyst in a flow through reactor arrangement; however, if gases, liquids and particulate matter compose the feed stream to the catalytic reactor, the use of a packed bed system is not practical due to rapid plugging of the interstices between catalyst particles due to solids accumulation.

Commercially available reforming catalysts are designed for use in a fixed bed configuration and are offered as large particles shaped to minimize pressure drop while providing some physical strength to survive normal handling and exposure to severe reaction environments.

Fluidizable versions of these reforming catalysts are not commercially available. Nevertheless, the use of fluid bed type reactors with catalyst particles smaller in size (100s μm range) than for fixed bed applications (mm-cm range) should address this problem.

In the past, catalyst particles for use in laboratory scale fluid bed reactors have been prepared by breaking and grinding down to size, commercial catalyst pellets, and although the resulting material exhibits reactivity while under fluidization conditions, it also readily breaks down by attrition and cannot be contained in the reactor by ordinary means.

Therefore, use of such a friable material at large scale would be unrealistic both practically and economically.

U.S. Patent Application Publication No. 2003/0103893 discloses a reforming process comprising: reforming hydrocarbons in the presence of a catalyst in a reaction zone, the catalyst being Nickel (Ni) catalyst of discrete Ni crystallites formed on the support by a several step incipient wetness process, the Ni crystallites having a maximum dimension measured in any one direction in the range of between 10 and 1000 angstroms and a distribution on the support element of no more than 0.2 of a square meter of nickel exposed metal/square meter of support selected from alumina and zeolite materials, recycling the catalyst to and from the reaction zone, regenerating between 10 and 100% of the catalyst being recycled in a regeneration zone to provide a regenerated catalyst and returning the regenerated catalyst to the reaction zone.

A process for steam reforming of hydrocarbons is disclosed in U.S. Patent 4,233,179, comprising: passing normally liquid hydrocarbons and steam at a ratio of about 1.5 to about 5 moles of steam per mole of carbon in the normally liquid hydrocarbons at a pressure in the range of from about 1 to 50 atmospheres and at a temperature in the range of from 800 to 1800° F over a catalyst comprising catalytically active constituents for the reaction impregnated onto a low surface area refractory support; the improvement in which the catalytically active constituents comprise nickel, expressed as the metal, in a weight concentration of from about five to thirty percent and promotional amounts of the oxides of manganese and iron, in which the ratio of manganese to iron, expressed as the metal, does not exceed 2:1 and in which: the catalytically active constituents are not chemically bound to the refractory support, having been impregnated onto the low surface area refractory support from a solution of their heat decomposable water soluble salts, followed by calcination at a temperature of at least 700°F but not in excess of 1200°F for sufficient time to convert each of the salts to the oxide.

U.S. Patent 5,476,877 discloses particulate solids for catalyst supports and heat transfer materials obtained in a process for production of hydrogen and carbon monoxide from a low molecular weight hydrocarbon by contact with a fluidized bed of catalyst at elevated temperatures in the presence of steam, or oxygen, or both steam and oxygen, wherein the fluidized bed is comprised of: an admixture of a particulate, fluidizable pre-calcined zirconia heat transfer solid which contains from about 0 percent to about 1 percent silica, based on the weight of the zirconia, in concentrations ranging from about 10 percent to about 99.9 percent, based on the total weight of the admixture, wherein the zirconia component of the admixture has a Davison Index measurement of not greater than about 15 and a catalyst constituted of a refractory inorganic oxide support composited with a metal, or metals, component catalytic for the production of hydrogen and carbon monoxide from low molecular weight hydrocarbons, of fluidizable particle size in concentration ranging from about 0.1 percent to about 90 percent, based on the total weight of the admixture.

Steam reforming catalyst and a method of preparing the same is disclosed in U.S. Patent 5,679,614, in which the catalyst include: Ni.Cr/MgO.La_2O_3.Al_2O_3, the method comprising the following steps, wherein weight percentages are expressed as weight percentages per total weight of catalyst:

(a) preparing a catalyst support by mixing about 5% of lanthanum oxide, 10% of magnesium oxide and 65% aluminum oxide;

(b) calcining the resulting mixture; and

(c) adding nickel and chrome to the calcined support obtained in step (b) to complete the approximate chemical composition of the catalyst for steam reforming of hydrocarbons; wherein the catalyst for steam reforming of hydrocarbons includes the following percentages per weight of catalyst: 15% Ni, 10% MgO, 5% Cr, 65% Al_2O_3, 5% La_2O_3; and

(d) shaping the catalyst.

A process for preparation of an improved support catalyst, containing nickel and cobalt, with or without noble metals is disclosed in U.S. Patent 5,744,419. The process consists of deposition of oxides of these transition metals on a sintered low surface area porous catalyst carrier pre-coated with BeO, MgO, CaO or their mixture, useful for the oxidative conversion of methane, natural gas (which comprises mainly methane with smaller amounts of ethane, propane, butane, CO_2 and N_2 and traces of C_5+ hydrocarbons and water) and biogas to syngas involving partial oxidation with oxygen or oxidative steam and/or CO_2 reforming with oxygen of methane or light hydrocarbons.

U.S. Patent 6,262,132 discloses a method of reducing Fischer-Tropsch catalyst attrition comprising: reacting a synthesis gas in a high agitation reaction system in the presence of a catalyst comprising a (gamma) γ-alumina support, wherein the γ-alumina support has an internal structure which comprises primarily γ -alumina and includes a controlled amount of a titanium dopant effective for increasing the attrition resistance of the catalyst in the high agitation reaction system.

Sudsakorn et al., in "PREPARATION OF ATTRITION-RESISTANT SPRAY-DRIED FE FISCHER-TROPSCH CATALYSTS USING PRECIPITATED SiO_2", *Ind. Eng. Chem. Res.* 2001, 40, 4778-4784 disclose preparation of attrition-resistant spray-dried Fe Fischer-Tropsch catalysts using precipitated SiO_2.

Z. R. Ismagilov et al., in "SYNTHESIS OF MECHANICALLY STRONG AND THERMALLY STABLE SPHERICAL ALUMINA CATALYST SUPPORTS FOR THE PROCESS OF METHANE DIMERIZATION IN A FLUIDIZED BED", *Catalysis Today* 24 " (1995) 269-271 disclose development of a method of chemical modification for the preparation of thermally stable spherical γ-alumina catalyst supports in the size range of 1 to 3 mm in diameter for the process of methane dimerization in a fluidized bed.

Z. R. Ismagilov et al., in "NEW TECHNOLOGY FOR PRODUCTION OF SPHERICAL ALUMINA SUPPORTS FOR FLUIDIZED BED COMBUSTION" *Catalysis Today* 47 " (1999) 51-71 disclose a technological solution for the synthesis of spherical γ-alumina (1 to 3 mm diameter) with high mechanical strength and thermal stability, in which alumina supports for catalysts operating in moving-or fluidized bed reactors can be prepared via the hydrocarbon-ammonia molding of pseudo-boehmite aluminum hydroxide.

There is a need in the art of catalytic steam reforming to provide a family of attrition resistant catalyst materials for fluid bed applications, and more particularly, the steam reforming of a product stream from gasified biomass, and the like, to produce a hydrogen rich product stream that is closer to being competitive with gasoline.

The foregoing examples of the related art and limitations related therewith are intended to be illustrative and not exclusive. Other limitations of the related art will become apparent to those of skill in the art upon a reading of the specification and a study of the drawings.

Summary

A family of attrition resistant catalyst materials for fluid bed application is disclosed, and more particularly, steam reforming of the liquid and gaseous product streams from gasified biomass is disclosed to produce a hydrogen rich product stream that can be used for producing fuels and chemicals. Other feedstocks successfully reformed to produce a hydrogen rich product stream with this process include vapors from gasified waste grease and plastics mixtures; volatiles from natural gas and petroleum fractions; and volatile compounds containing carbon, hydrogen, and oxygen.

A method of preparing a steam reforming catalyst is disclosed which is characterized by improved resistance to attrition when used for fluidized bed cracking, water gas shift and gasification reactions on feedstock, comprising coating a ceramic support by adding an aqueous solution of a precursor salt of a metal selected from the group consisting of Ni, Pt, Pd, Ru, Rh, Cr, Co, Mn, Mg, K, La and Fe and mixtures thereof to said ceramic support and calcining the coated ceramic in air to convert the metal salts to metal oxides.

Further disclosed is a steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on a feedstock in a fluidized bed reactor, wherein the catalyst comprises less than 30% by weight NiO.

Still further disclosed is a steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, wherein the catalyst comprises: less than 5 weight percent MgO; less than 10 weight percent K_2O; less than 1.0 weight percent Pt; a mixture containing less than 10 weight percent NiO, less than 5 weight percent MgO and less than 10 weight percent K_2O and less than 1.0 weight percent Pt and less than 10 weight percent K_2O.

Yet further disclosed, as one basic component, is a substrate or support composed of a mixture of metal oxides, the primary component comprising α-alumina, formed into particles of small size, relatively spherical in shape, and calcined to yield a hard, porous solid; and minor components in the form of metals and/or metal oxides which may catalytically facilitate chemical reactions for production of a hydrogen rich product stream. The minor catalytic components are, in this description, incorporated throughout the support material and are an integral part of the porous solid particle.

In addition to the exemplary aspects and embodiments described above, further aspects and embodiments will become apparent by reference to the drawings and by study of the following descriptions.

Brief Description of the Drawings and Tables

Exemplary embodiments are illustrated in referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

TABLE.1 Presents physical characteristics and attrition test results for a variety of commercial ball milling media, alumina supports, catalysts, and (ground and sized) commercial catalysts.

TABLE.2 Presents major physical and chemical characteristics of all materials tested for catalyst cracking and reforming activity.

TABLE.3 Presents evidence of catalytic activity of various catalyst materials tested for various types of feed streams at 850°C.

TABLE.4 Presents evidence of catalytic activity of various catalyst materials tested for tar vapor feed streams at 850°C.

FIGURE.1 Is a diagram of the fluidized bed reactor system and apparatus used to evaluate the attrition resistance and/or the catalytic cracking and steam reforming activity of various catalysts and support materials.

Detailed Description of Preferred Embodiment

Commercially available packed bed naptha reforming catalysts, crushed and sized for fluid bed operation, cannot withstand the harsh reaction conditions used in a fluidized bed for 1) reforming biomass-derived pyrolysis liquids to hydrogen, carbon dioxide and carbon monoxide; 2) cracking and reforming tars produced from biomass pyrolysis vapors to hydrogen, carbon dioxide and carbon monoxide; 3) reforming renewable feedstocks (waste grease and oils) to produce H_2, CO and CO_2; and 4) reforming hydrocarbons from natural gas and petroleum derived fractions and volatile compounds containing carbon, oxygen and hydrogen. Fluidization is required to optimize the contact of catalyst with these feedstocks, which tend to form coke instead of being cracked in a conventional fixed bed reactor arrangement.

The fluidizable catalyst particles derived from commercial catalyst pellets, which generally consist of nickel (Ni) coated onto ceramic supports, attrit significantly when fluidized and show consistent attrition rates of 10-20 wt% per day (TABLE.1). Because process economics cannot tolerate such catalyst loss, and because nickel is toxic, there was a need to identify and/or develop attrition-resistant supports and catalysts that could withstand fluidized reforming of varied feedstocks.

TABLE 1

Material Identity	Description	Support Material	Shape[1]	Particle Size	BET Surface Area	Incipient Wetness	Alumina Content (nominal)	Attrition Rate
				[mesh]	[m^2/g]	[ml/g]	[%w]	[%w/48hrs.]
	Potential Support Material							
A	Carbo Ceramic, HPS, mill media	n/a	s	30/60	0.03	–	≥80	0.3
B	CoorsTek, Std. Micro mill media	n/a	s	30/50	0.02	–	≥90	0.6
C	CoorsTek, Std. BG mill media	n/a	s	30/50	0.07	–	≥90	11.0
D	CoorsTek, Exp. 1	n/a	s	35/45	0.2-0.8	0.10-0.18	90	0.6
E	CoorsTek, Exp. 2	n/a	s	40/80	4.9	–	≥90	39.6
F	CoorsTek, Exp. 3	n/a	s	40/80	2.73	–	≥90	3.2
G	CoorsTek, Exp. 4	n/a	s	35/50	0.46	–	90	5.2
H	CoorsTek, Exp. 5	n/a	s	50/80	2.7	–	≥90	0.3
I	CoorsTek, Exp. 6	n/a	s	35/50	1.0-1.8	0.10-0.18	99.5	0.5
	Catalysts							
J	Süd-Chemie, C11NK catalyst	proprietary mixed oxides	g	35/50	8.8-10.6	–	20 - 40	14.8 - 28.8
K	ICI 46-1S catalyst	proprietary mixed oxides	g	35/50	n/a	–	–	33.2
Cat.1	Catalyst Ex. 1	D	s	35/50	1.4	–	90	0.8
Cat.2	Catalyst Ex. 2	I	s	35/50	2.8	–	99.5	0.2

Attrition resistance screening experiments carried out with a variety of potential support materials showed that several ceramic materials could have the necessary strength to withstand fluidizing condition (TABLE.1). Attrition testing is performed in a laboratory scale fluidized bed reactor system.

System Description: Bench-Scale Thermo-Catalytic Conversion System Acronym List

TCD: thermal conductivity detector

MTI: manufacturer of rapid scanning gas chromatograph

NDIR: non-dispersive infra red analyzer

The bench-scale thermo-catalytic conversion system is shown in FIG. 1. This flexible unit can be used to investigate various thermal and catalytic processes such as pyrolysis, partial oxidation, and catalytic cracking/reforming for a variety of solid, liquid, and gaseous feedstocks. It is comprised of two Inconel, tubular, bubbling fluidized bed reactors. Each reactor is externally heated by a three-zone electric furnace and can operate at temperatures up to 900°C. In the first, a 1.5 inch-diameter reactor, a 3 inch-height silica sand bed (120 g sand of particle size 180-350 μm) is used to transfer heat necessary for thermal decomposition of the natural or synthetic polymers to lower-molecular-weight volatile compounds. In the second, a 2-inch diameter reformer, 4 inch-height catalyst beds (250-300 g catalyst, particle size 350-500 μm) help crack and reform those volatile compounds to produce clean hydrogen-rich product gas. Superheated steam, air or nitrogen at a flow rate of 3-10 standard liters per minute (slm) are used as the fluidizing gas in the reactors. Steam is generated in an electrically heated boiler then superheated to 500-700°C before entering the reactors. The flow rates of steam (2-5 g/min) are measured by orifice flow meters and controlled by pneumatic valves while electronic mass flow controllers are used for nitrogen and air. This system can also be connected to the Thermochemical Process Development Unit (TCPDU) to study catalytic processing of the slip stream gas generated in a larger-scale system.

More particularly, FIG. 1 is a schematic of the thermo-catalytic conversion system.

Solids are fed to the first reactor using a KCL24T20 K-Tron screw feeder that meters ground biomass or synthetic polymers (particle size < 500 μm) to a small lock hopper built of two pneumatically controlled valves. This lock hopper is connected to a centrifugal mixing chamber and a pneumatic transfer line, which is provided with a cooling jacket in its end section to maintain temperature at the inlet to the reactor below the softening point of the plastics. The feed particles are transported at a rate of 1-2 g/min (60-120 g/h) to the reactor by a stream of nitrogen at a flow rate of 2-3 slm. Char and sand entrained in the first reactor are captured in the cyclone and the gases and vapors formed by thermal decomposition of biomass or plastics are transferred to the second reactor through a 0.25-inch diameter heated line whose outlet is placed in the catalyst bed about 0.25 inches above the distribution plate.

The catalytic reactor is also supplied in a side port, located approximately 1 inch above the perforated distribution plate, which is used for feeding liquids or gas/vapor from TCPDU. The liquids are fed to the catalyst bed using a diaphragm pump and a spraying nozzle. TCPDU gas comes through a 0.25-inch heat-traced stainless steel line provided with a sintered metal filter, an orifice flow meter, and a gas distributing sparger. Typical gas flows in the reactor are in the range of 5-10 slm (20-40 l/min in the process conditions) resulting in 0.4-0.8 seconds residence time in the bed. Typical space velocities are 0.1-0.2 g carbon/h/g catalyst, which corresponds to the methane equivalent space velocity $G_{C1}VSV$ of 750-1500 h^{-1}.

Downstream of the catalytic cracker/reformer, a cyclone and a hot-gas filter capture fine catalyst particles and solids generated in the process. Those particles are recovered and weighted after every experiment. The product collection line includes two heat exchangers to condense excess steam and any remaining organic liquids. The condensate is collected in a vessel whose weight is continuously monitored. The dry gas flow rate is measured by a mass flow meter (instantaneous flow rate) and by a dry test meter (flow rate in one-minute intervals).

The concentrations of CO_2, CO, and CH_4 in the reforming gas are continuously monitored by a non-dispersive infra-red analyzer (NDIR Model 300 from California Analytical Instruments) and that of hydrogen by a thermal conductivity monitor (TCM4 from Gerhard Wagner, Germany). In addition, the gas is analyzed every 5 minutes by an on-line MTI gas chromatograph, which provides concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen as a function of time. In addition, the composition of the gas at the entry and at the exit of the catalytic reactor can be analyzed by molecular-beam mass spectrometer (MBMS) which is connected by heat-traced sampling lines to the respective sampling ports. The MBMS analysis allows us to quantify tar content in the gas, which is a fast way to evaluate the efficiency of the catalytic process.

All the temperatures and flows in the bench-scale unit are recorded and controlled by an OPTO data acquisition and control system. The process parameters (temperatures, flow rates, gas composition) as well as mass balance closure calculated based on NDIR analyzer data are displayed on a PC monitor.

As can be seen from FIG. 1, all experimental supports were evaluated for attrition resistance in a two inch fluidized bed reactor cooperated under simulated reforming conditions. Before attrition testing, the supports were mechanically sieved to characterize the particle size distribution and the air classified to remove very fine powders that adhere to the particles during the forming process. After air classification, the supports were evaluated for attrition resistance in the 2" fluidized bed reactor for 48 hours. Simulated reforming conditions were: 850°C, 2.5g/min fluidizing steam and 2.5g/min liquid water injected into the 250g-support bed with nitrogen. Weight losses of these materials were measured after exposure to these conditions and are reported as % loss per day. The material was then recovered from the reactor and again mechanically sieved to determine the post attrition test particle size distribution.

The support materials are produced by CoorsTek Inc. to meet the required particle size, shape, surface area and attrition resistance necessary for fluidization.

The Support Requirements are as follows:

1) Support material must be fluidizable.

    - The preferred size range is approximately 100 to 1000 microns. Tthe support material can be screened to attain the proper size range and distribution.

2) Support material must show good resistance to attrition.

  a. Spherical shape

     Spherical agglomerates can be formed by any one of a number of known forming methods, including pan mixers (pelletizers), pin mixers, fluidized bed agglomeration, immiscible liquids, etc.

  b. Wear resistance

     Wear resistance characteristics are determined by a combination of composition and grain morphology.

     i. It is well known that compositions in the range of 50 to 99.9% alumina show excellent resistance to both erosive and abrasive wear.

     ii. The catalytic support consists of spherical hard agglomerates that are composed of interconnected particles with an open, porous network. To achieve sufficient mechanical strength and wear resistance, the bonding between particles that make up an agglomerate must be uniform and consistent. This is achieved by:

        1. Use of a high and uniform green body density for the spherical agglomerates prior to sintering results in uniform particle-to-particle spacing/contact. This leads to uniform sintering (mass transport) at the particle-to-particle contacts and uniform mechanical properties.

        2. The sintering profile (time and temperature) is precisely controlled in order to control the bonding between particles and the resulting mechanical properties of the agglomerates.

3) Chemical components of the support must be compatible with the catalyst and promote catalytic reactions themselves. These components include but are not limited to:

  a. Alumina
  b. Silica
  c. Magnesia
  d. Calcia

4) Sufficient surface area and surface morphology is required to support the catalyst. The surface area of the catalytic support is preferably in the range of 0.1 to 10 m^2/g. This is controlled through a combination of:

The starting particle size of the raw material used to fabricate the agglomerates. Typically the un-fired agglomerates are composed of particles with an average size in the range of 0.3 to 10 microns, preferably in the range of 0.9 to 5 microns.

   a. Uniform green body density.
   b. Controlled sintering time/temperature profile.

Preferred Composition

- The support composition is incorporated substantially through the bulk of the support material, and will consist of:
  - 55 to 99.5% alumina
  - 0.2 to 40% silica
  - 0.15 to 8% magnesia
  - 0.05 to 5% calcia by weight
- The preferred primary phase is alpha-alumina (α-Al_2O_3) or mullite ($3Al_2O_3 \cdot SiO_2$)

Substrate Example

- A 90% alumina composition was fabricated into a fluidizable catalytic support.
- The typical minor phase composition, based on the simple oxides, of this formulation included:
  - 4-8% silica
  - 1.5 to 3% magnesia
  - 0.5 to 2% calcia
- An aqueous ceramic slip was created using traditional ball milling techniques. The average particle size was between 2 and 4 microns.
- Organic binders were dispersed in the ceramic slip.
- The ceramic slip was spray dried.
- Spherical agglomerates were created from the spray dried powder using a pan agglomeration technique. Agglomeration was achieved through the use of water.

- Agglomerates were screened to between 30 and 50 mesh.
- 30 to 50 mesh agglomerates were sintered at 1,275°C for 1 hour in alumina refractory.
    - The tap density of the resulting catalytic support was determined to be 1.54 g/cc.

The surface area of the resulting catalytic support was determined to be 0.4617 m^2/g by the BET method.

Support materials (D) and (I) exhibited the best combination of attrition resistance and other physical properties. Invention catalyst formulations described herein incorporate one or the other of these two types of support materials. The particle size range of interest is from 80 μm to 1000 μm (≈ 18 to 170 mesh), preferably 150 μm to 800 μm and most preferably from 300 μm to 500 μm. Particles should be spherical in shape to minimize abrasion effects and favor stable fluidization behavior.

A first catalyst (Cat.1), prepared (Example 1) with support (D) was subjected to the attrition testing procedure to show that the catalyst preparation process had no detrimental effect on the attrition resistance of the underlying support.

Catalysts were formulated incorporating these two support materials and evaluated at several temperatures for cracking and reforming activity with a variety of feed stream compositions in the same apparatus as used for attrition testing. The reactant feed to the reactor was either 1) biomass pyrolysis or gasification derived liquids (whole or aqueous extract); or 2) liquid trap grease; or 3) biomass pyrolysis derived tar vapors.

Cracking and reforming ability on all feed types were benchmarked with the commercial C11NK catalyst, material (J). Ni-based catalysts, which may contain one to two orders of magnitude less Ni than material (J) performed similarly at 850°C. The virgin support materials (D and I) alone also exhibit some thermal cracking ability.

Feedstock Fluidized Bed Operations

For attrition testing, the reactor shown in FIG.1 is supplied with an adequate stream of mixed gases and liquids to maintain vigorous ebullating conditions in the fluidized catalyst (or support) material at a temperature of 850°C. Flow conditions are maintained for 24 to 48 hours. The composition of the typical feed mixture for attrition testing contains 2.5 grams per minute of 10% w MeOH in water, 2.5 grams per minute of DI water as steam, 2.25 SLPM N_2

gas and 0.5 SLPM H_2 gas. The typical catalyst or support material charge for a test is ≈ 250 grams.

For catalytic activity testing, the same reactor system (FIG.1) is used and is supplied with an appropriate amount of hydrocarbon mixture in addition to the nitrogen and steam streams. The hydrocarbon feed can be composed of one of the following biomass derived mixtures:

a) Water soluble extract of the liquid oil mixture from pyrolysis of hard and/or soft woods, with a characteristic composition of C: 10.1 %w, H_2: 10.4 %w, O_2: 79.5 %w. The feed contains ≈ 80%w water, a steam to carbon ratio S/C of 7 – 9, and is supplied to the reactor at a gas hourly space velocity based on all carbon expressed as methane $G_{C1}HSV$: 700 – 1000 h^{-1}.

b) Whole oil mixture from pyrolysis of hard and/or soft woods, with a characteristic composition of C: 36.5 %w, H_2: 8.4 %w, O_2: 55 %w. The feed has a steam to carbon ratio S/C of 8.5, and is supplied to the reactor at a gas hourly space velocity based on all carbon expressed as methane $G_{C1}HSV$: 1000 h^{-1}.

c) Water washed trap grease liquids (fatty acids and associated glycerides) from food processing with a characteristic composition of C: 76.2 %w, H_2: 11.8 %w, O_2: 12.6 %w. This feed has a steam to carbon ratio S/C of 5, and is supplied to the reactor at a gas hourly space velocity based on all carbon expressed as methane $G_{C1}HSV$: 1100 h^{-1}.

d) Tar containing vapor and gas stream derived from either the pyrolysis or gasification of woods followed by thermal cracking, with typical composition (dry, tar free gas basis) of CO_2: 27.7 %w, CO: 13.9 %w, CH4: 12.1 %w, C_2H4: 2.5 %w, C_2-C4: 1.0 %w, H_2: 33.6 %w, O_2: 0 %w, N_2: 7.8 %w, He: 0.8 %w. The tar content of the stream represents 15%w of all the carbon present. The feed has a steam to carbon ratio S/C of ≈ 7.5, and is supplied to the reactor at a gas hourly space velocity based on all carbon expressed as methane $G_{C1}HSV$: 420 - 460 h^{-1}. The stream is supplemented with ≈ 4 SLPM of N_2 to fluidize the catalyst.

Catalyst Preparation and Evaluation

The two support materials of choice for attrition resistance and physical properties are materials (D) and (I) described in TABLE.1. These experimental materials are fabricated by CoorsTek Inc. of Golden, Colorado. Various means of forming the particles can be utilized as practiced in the art. Formed particles are heat treated to yield the desired hardness, porosity, surface area, and density in the finished product. The metal oxide composition of the support particles can be made to include one or more components that show catalytic or stabilizing properties (TABLE.2).

TABLE 2

Material Identity	Description	Support Material	NiO	MgO	K_2O	Other Metal	BET Surface Area	Example No.
			[%w]	[%w]	[%w]	[%w]	[m2/g]	
J	Süd-Chemie, C11NK Catalyst	proprietary mixed oxides	20	15	6.6	–	8.8 - 10.6	–
Cat.1	Catalyst 1	D	2.4	3.5	<0.02	–	1.4	1
Cat.2	Catalyst 2	I	3.6	3.3	<0.02	–	2.8	2
Cat.9	Catalyst 9	I	0.25	0.08	0.05	–	na	3
Cat.14	Catalyst 14	D	1.1	2.7	0.39	–	0.88	4
Cat.17	Catalyst 17	D	0.0	0.0	0.08	0.2 (Pt)	na	5
Cat.18	Catalyst 18	D	3.0	2.7	0.64	–	0.69	6
Cat.19	Catalyst 19	D	1.4	2.1	0.39	2.5 (La_2O_3)	1.03	7
Cat.26	Catalyst 26	D	5.6	2.7	4.0	–	0.68	8
D	CoorsTek Support, Exp.1	self	0.0	1 - 2.5	0.01	–	0.5	–
I	CoorsTek Support, Exp. 6	self	0.0	0.0	0.0	–	1.0	–

These support materials were used to prepare catalysts described herein. The catalytic components added to the support particles comprise mixtures of some or all of Ni-, Cr-, La-, Mg-, K-, and Pt. Resulting catalysts are evaluated for both cracking and reforming activity with one or more of the feedstocks described above. Active components were deposited onto the solid support as an aqueous solution of soluble salts by the method of incipient wetness. The wet solids are then dried and thermally treated at 650°C to decompose the metal salt(s) into the corresponding metal oxide. Components such as MgO, K_2O, La_2O_3, remain as oxides on the surface and act as promoters or stability enhancers. Other compounds such as Cr and Ni oxides will reduce to catalytic metal species on the surface of the solid in the presence of hydrogen. Precursor salts include 99% $Ni(NO_3)_2{\circ}6H_2O$, $Cr(NO_3)_3{\circ}9H_2O$, $La(NO_3)_3{\circ}6H_2O$, and $Mg(NO_3)_2{\circ}6H_2O$ (Alfa Aesar); 99% KNO_3 (Aldrich); and 99.9% $H_2PtCl_6{\cdot}6H_2O$ (Johnson Mathey). Other metals that can be used include Pd, Fe, Ru, Rh, Mn, Cu, and Co. In general, Mg is used to stabilize Ni crystallite size and K is used to reduce coke deposition on the catalyst surface. Nickel itself functions as both a hydrogenation and a methanation catalyst and Pt is a powerful hydrogenation catalyst. The other metals function as support modifiers (La, Mn) or as reforming catalysts (Co, Cu, Fe, Cr, Rh, Ru, Pd).

Fluidized Bed Reactor System and Apparatus

The reactor system schematic is presented in FIG.1. The fluidized bed portion consists of a tubular two-inch-diameter Inconel reactor with a perforated gas distribution plate in the lower section and is externally heated by a three-zone electric furnace. The reactor can hold 250g of either support or catalyst. Before tar cracking or reforming, support or catalyst in the reactor was activated in a H_2/N_2 stream for 2 hours. The reactor solids were then fluidized using superheated steam at 750°C. A slipstream of biomass-derived vapors was supplied to the fluidized catalyst bed through a side-mounted nozzle. Liquid feedstocks were sprayed into the fluidized bed via the same nozzle. The product collection line included a cyclone and a hot-gas filter to capture fine catalyst particles and char generated in the reactor. The system also contained two heat exchangers to condense excess steam, which was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter.

In both tar cracking and reforming modes, the concentrations of CO_2, CO, and CH_4 in the reforming gas were continuously monitored by a non-dispersive infrared analyzer (NDIR Model 300 from California Analytical Instruments), The concentration of hydrogen is measured by a thermal conductivity monitor (TCM4 from Gerhard Wagner, Germany). In addition, the gas was analyzed every 5 minutes by an on-line MTI gas chromatograph for hydrogen, carbon monoxide, carbon dioxide, methane, C_{2-4} hydrocarbons, benzene, and nitrogen content as a function of time. System temperatures and gas flows were recorded and controlled by an OPTO data acquisition and control system. Total and elemental balances were calculated as well as the yield of hydrogen generated from the feed. In all runs, catalyst remaining in the reactor, cyclone, and filter was recovered and weighed to measure attrition loss from the reactor.

For attrition testing alone, complex hydrocarbon feed is not essential and could be replaced by a combination of methanol, water, nitrogen and hydrogen as specified earlier. An attrition test consists of quantifying the amount of particulate fines carried out of the reactor and trapped in the cyclone and filter after 48 hours of real or simulated fluidized reforming reaction. The percent weight loss (%wt) used to characterize attrition losses in TABLE.1 is the amount of catalyst fines entrained divided by the amount of catalyst originally put into the reactor x 100.

Hydrocarbon Cracking and Reforming Operations

Each batch of catalyst material was evaluated at one or more temperatures between 750 to 850° C in individual experiments that generated at least 6 hours of steady state data for cracking biomass derived vapors and/or liquids. Single or multiple run could be performed on any one batch of material. After each run in a multi run session, the catalyst bed was regenerated using a temperature ramp and air to remove carbon. Activity after regeneration was tested before the next run by checking the methane reforming activity. If methane was reformed with less than 95% efficiency, the catalyst was regenerated again until appropriate methane activity was attained. Several catalyst compositions were investigated by varying metal and metal oxide contents and proportions. Catalyst activity experiments were conducted with fresh, regenerated or partially deactivated catalyst batches. Performance data was generated for experiments lasting from 6 hours to 200 hours.

Example 1

Catalyst (Cat.1) is prepared by sequential incipient wetness impregnation of the dry support material followed by drying and calcination of the impregnated material to decompose the metal precursor salt and form the metal oxide. Two aqueous solutions were prepared for this purpose. A Ni salt solution was prepared by combining 240.1 grams of $Ni(NO3)_2•6H_2O$ salt with 150.09 grams of deionized water (DI). A Mg salt solution was prepared separately by combining 104.41 grams of $Mg(NO3)_2•6H_2O$ salt with 100.52 grams of DI water. 374.99 grams of support material (D) with a loss–on–ignition (LOI) value of 1.1% by weight was placed in a rotating drum contactor.

The first of two incipient wetness impregnations of the solid was accomplished by adding 55.07 grams of the Mg salt solution, drop wise, to the tumbling solids in the rotating drum apparatus. The moist solids were then dried and calcined, in air, in an electric muffle furnace. The temperature program consisted in ramping the temperature from room conditions to 200°C at a rate of 25°C per minute; dwelling at 200°C for 90 minutes; ramping to 650°C at a rate of 50°C per minute; dwelling at 650°C for 240 minutes; cutting off the power and letting the furnace and contents cool down naturally to below 100°C prior to handling the solids. The (dry basis) weight difference between the original support and the material recovered post calcination is directly related to the amount of MgO deposited on the solid. In this case this corresponds to 1.2 % by weight.

The second of the two incipient wetness impregnations of the solid was accomplished by adding 61.57 grams of the Ni salt solution, drop wise, to 362.32 grams of tumbling solids (containing 1.2 %w MgO) in the rotating drum apparatus. The moist solids were then dried and calcined, in air, in an electric muffle furnace following the same temperature program described earlier. The weight difference in this step is attributed to NiO and corresponds to 2.7 %w dry basis of the initial virgin support material. The virgin support is used throughout these examples as the dry basis reference for the deposited oxide concentrations.

This catalyst (Cat.1) was tested for attrition resistance and catalytic activity as reported in TABLE.1 and TABLE.3.

Example 2

Catalyst (Cat.2) was prepared by multiple and sequential impregnations of the solids in a similar manner as (Cat.1) in example 1. The support material (I) was used in this case. Three successive additions of Mg salt solution were followed by two successive additions of Ni salt solution. Each solution addition was separated by drying and calcinations of the moist solids as described in Example 1 (five complete cycles). Based on dry basis weight differences, the final composition of (Cat.2) was approximately 3.25% w MgO and 4.12% w NiO with respect to the virgin support.

This catalyst (Cat.2) was tested for attrition resistance and catalytic activity as reported in TABLE.1 and TABLE.3.

TABLE 3

Catalyst Identity	Reactant Feed Stream	H_2 Yield	CO_2/CO	H_2/CH_4	Tar Cracking
		[%]	[mole ratio]	[mole ratio]	[%]
	Water Extracted Pyro. Oil				
J		88	3.7	27.1	NA
Cat.1		83	0.7	24.6	NA
Cat.2		55	2.1	54.7	NA
Cat.9		52	1.8	84.4	NA
	Whole Pyro. Oil				
J		94	76	2.5	NA
Cat.19		88	48	1	NA
Cat.26		91	59	1.2	NA
	Trap Grease				
J		87	43	1.7	NA
Cat.18		80	36	0.8	NA
	Tar Vapors	H2/CH4 in	CO2/CO in	H2/CH4 out	CO2/CO out
J		1.8	1	10	2.6
Cat.14		1.8	0.9	7	1.5
Cat.17		1.6	0.8	4.1	1.4
D		1.9	1	3.5	1.7

nominal reaction temperature: 850 °C

Example 3

Catalyst (Cat.9) was prepared using 586.45 grams of support material (I) with an LOI of 0.35% w, a surface area of 1.0 m^2/g, and an incipient wetness of 0.16 ml/g. All the metal salts solutions were combined into one single solution containing the required amounts of each metal. The solution volume is adjusted to the required incipient wetness volume for the mass of support material used. The (Cat.9) formulation is made with one impregnation of the solids followed by drying and calcinations.

Three stock solutions were prepared to yield a) a Ni salt solution containing the equivalent of 0.218 grams NiO per gram of solution; b) a Mg salt solution containing the equivalent of 0.082 grams of MgO per gram of solution; c) a K salt solution containing the equivalent 0.155 grams of K_2O per gram of solution. All solutions were prepared from the nitrate salts. The mixed salt solution is obtained by combining 6.79 grams of the Ni solution with 5.82 grams of Mg solution, 1.97 grams of K solution, and 80.04 grams of DI water. The solution is added to the tumbling solids as in previous examples. The moist solids are then dried and calcined following the same temperature program described in Example 1. The (Cat.9) formulation represents a low concentration of catalytic metal and promoters deposited by a one step impregnation. The composition of this preparation is 0.25% w NiO, 0.08% w MgO, and 0.05% w K_2O. This catalyst (Cat.9) was tested for catalytic activity as reported in TABLE.3.

Example 4

A large batch of catalyst (Cat.14) was prepared using 51000 grams of support material (D) with an LOI of 0.15% w, a surface area of 0.53 m^2/g, and an incipient wetness of 0.13 ml/g. Impregnation of the solids was done in one step with a salt mixture solution containing 3600.7 grams of $Ni(NO3)_2{\bullet}6H_2O$, 602.0 grams of $Mg(NO3)_2{\bullet}6H_2O$, 399.3 grams of KNO3, and 4415.95 grams of DI water. The solution was added to the tumbling solids in a cement mixer via a peristaltic pump. A 500 gram sample of moist solids was dried and calcined in the laboratory following the temperature program of example 1. Catalytic activity data is presented for this sample in TABLE.4. The balance of the moist solids was dried and calcined in a continuous rotary kiln operating at 650°C with a retention time of approximately 2 hours.

This material represents an average composition catalyst well suited for pyrolysis oil liquids cracking and reforming.

TABLE.4

Catalyst Identity	Reactant Feed Stream	H_2/CH_4 in	CO_2/CO in	H_2/CH_4 out	CO_2/CO out
		[mole ratio]	[mole ratio]	[mole ratio]	[mole ratio]
	Tar Vapors				
J		1.8	1	10	2.6
Cat.14		1.8	0.9	7	1.5
Cat.17		1.6	0.8	4.1	1.4
D		1.9	1	3.5	1.7

nominal reaction temperature: 850 °C

Example 5

Catalyst (Cat.17) was prepared using 510 grams of support material (D) with an LOI of 0.15% w, a surface area of 0.53 m^2/g, and an incipient wetness of 0.13 ml/g. Impregnation of the solids was done in one step with a salt mixture solution containing 3.19 grams of a H_2PtCl_6 solution containing 30% w Pt, and 8.77 grams of a KNO_3 solution containing 0.046 grams K_2O per gram of solution. Impregnation, drying and calcination follow the same procedure as in previous examples. The resulting composition of (Cat.17) is approximately 0.2% w Pt and 0.08% w K_2O. Catalytic activity of this material for tar vapor cracking and reforming is presented in TABLE.4.

Example 6

Catalyst (Cat.18) was prepared using 501.1 grams of support material (D) with an LOI of 0.15% w, a surface area of 0.53 m^2/g, and an incipient wetness of 0.13 ml/g. Impregnation of the solids was done in one step with a salt mixture solution containing 83.11 grams of a Ni salt solution containing 0.218 grams of NiO per gram of solution, 24.69 grams of a K solution containing 0.155 grams K_2O per gram of solution, and 12.75 grams of $Mg(NO3)_2 \cdot 6H_2O$ salt. Impregnation, drying and calcination follow the same procedure as in previous examples. The resulting composition of (Cat.18) is approximately 3.6% w NiO, 0.4% w MgO and 0.8% w K_2O. Catalytic activity of this material for trap grease cracking and reforming is presented in TABLE.3.

Example 7

Catalyst (Cat.19) was prepared using 502.5 grams of support material (D) with an LOI of 0.15% w, a surface area of 0.53 m^2/g, and an incipient wetness of 0.13 ml/g. Impregnation of the solids was done in one step with a salt mixture solution containing 40.16 grams of a Ni salt solution containing 0.218 grams of NiO per gram of solution, 12.20 grams of a K solution containing 0.155 grams K_2O per gram of solution, 42.52 grams of La solution containing 0.226 grams La_2O_3 per gram of solution, and 6.16 grams of $Mg(NO_3)_2 \bullet 6H_2O$ salt. Impregnation, drying and calcination follow the same procedure as in previous examples. The resulting composition of (Cat.19) is approximately 1.74% w NiO, 0.2% w MgO and 0.4% w K_2O and 1.9% w La_2O_3. Catalytic activity of this material for whole pyrolysis oil cracking and reforming is presented in TABLE.3.

Example 8

Catalyst (Cat.26) was prepared using 501.4 grams of support material (D) with an LOI of 0.15% w, a surface area of 0.53 m2/g, and an incipient wetness of 0.13 ml/g. Impregnation of the solids was done in two consecutive steps separated by drying and calcination following the temperature program outlined in the other examples. The first impregnation was done with a mixed solution containing 69.95 grams of $Ni(NO_3)_2 \bullet 6H_2O$ salt, 13.13 grams of $Mg(NO_3)_2 \bullet 6H_2O$ salt, 28.36 grams of KNO_3, and 33.84 grams of DI water. The second impregnation used a similar solution containing 69.45 grams of $Ni(NO_3)_2 \bullet 6H_2O$ salt, 13.12 grams of $Mg(NO_3)_2 \bullet 6H_2O$ salt, 28.45 grams of KNO_3, and 33.42 grams of DI water. The resulting composition of (Cat.26) is approximately 6.9% w NiO, 0.8% w MgO and 5.3% w K_2O. Catalytic activity of this material for whole pyrolysis oil cracking and reforming is presented in TABLE.3.

Results and Discussion

Results for attrition resistance tests and physical properties and characteristics of potential support materials, crushed and sized commercial catalysts and invention supports and catalysts are summarized in TABLE.1.

Both commercial catalysts (J) and (K) were used for 48 hours, reforming a feed of pyrolysis oil extract and attrition losses ranged from 28-33% of the original catalyst charge. The corundum material (A) and most of the alumina samples (B, D, F, H, I) exhibited acceptable attrition resistance after 48 hours of simulated reforming. Samples (D and I) had the best combination of attrition resistance, surface area, incipient wetness volume and particle size distribution. Screen sieve analysis, performed before and after attrition tests for all materials, showed loss of material from the reactor (as recovered in the cyclone and filter) and any changes in particle size distribution. A $Ni/MgO/Al_2O_3$ catalyst (Cat.1) made with support material (D) was used for 48 hours of methanol reforming and showed a loss of < 0.5 %wt /day from the reactor, essentially the same loss as the support alone. This catalyst was further used for reforming pyrolysis oil for 48 hours. Attrition losses were similar to the methanol experiment (<0.5% per day). This result shows that catalyst preparation does not change support attrition resistance and that the catalyst is re-useable.

A second $Ni/MgO/Al_2O_3$ catalyst (Cat.2) made with support material (I) was prepared in a similar fashion to (Cat.1). Preparation involved multiple and sequential impregnations of the support with metal salt solutions (Examples 1 and 2). These two materials demonstrate that the attrition resistance of the catalyst is similar to that of the support alone. Furthermore, catalytic activity for both materials is also demonstrated.

The one step impregnation of the support with a mixture of metal salts in solution is introduced and demonstrated in Example 3 for the preparation of catalyst (Cat.9). A similar procedure is followed in the remaining five examples (#4-8). In Example 8 for the preparation of catalyst (Cat.26) the procedure is repeated to increase the concentration of active species. Catalytic activity for (Cat.9) material is demonstrated on aqueous pyrolysis oil extract and for (Cat.26) on whole pyrolysis oil liquids. These two materials illustrate the range in concentration of active metals and promoters of the invention.

Example 4 describes the preparation of a large batch of catalyst (Cat.14) for pilot scale testing. Its catalytic activity for tar vapor reforming is presented in TABLE.4.

Example 5 describes a formulation (Cat.17) containing Pt as the active species. Other metals that can provide cracking activity include Co, Cr, Cu, Fe, Pd, Rh, and Ru. This Pt containing material was also tested with tar vapors.

Example 6 describes a catalyst (Cat.18) similar to Cat.14 with a three-fold increase in active Ni. This material was tested on a trap grease feed.

Example 7 describes a formulation (Cat.19) incorporating some lanthanum oxide in addition to the Ni, Mg and K oxides. This material was tested on whole pyrolysis oil.

The various examples cover variations in support materials, impregnation types, composition and concentration in metals and metal oxides deposited onto the solid or incorporated within, and catalytic activity with various biomass derived feed types. Catalyst compositions are summarized in TABLE.2. Catalysts performance for cracking and reforming biomass derived vapors and liquids, tars and waste trap grease are summarized in TABLE.3 and TABLE.4. Performance parameters (hydrogen formed, and/or critical product gas ratios) are presented in support of catalytic activity at 850°C for the various materials tested. All concentrations are representative of steady state conditions. The H_2/CH_4 ratio measures catalyst reforming activity and selectivity for hydrogen production and CO_2/CO indicates water gas shift activity. The tar cracking efficiency is reported as the change in gas ratios between inlet and outlet. Hydrogen yield is the factor increase in outlet to inlet hydrogen concentration.

While a number of exemplary aspects and embodiments have been discussed above, those of skill in the art will recognize certain modifications, permutations, additions and sub combinations thereof. It is therefore intended that the following appended claims and claims hereafter introduced are interpreted to include all such modifications, permutations, additions and sub-combinations as are within their true spirit and scope.

CLAIMS

What is claimed is:

1. A method of preparing a steam reforming catalyst characterized by improved resistance to attrition when used for fluidized bed cracking, water gas shift and gasification reactions on feedstock, comprising:

coating a ceramic support by adding an aqueous solution of a precursor salt of a metal selected from the group consisting of Ni, Pt, Pd, Ru, Rh, Cr, Co, Mn, Mg, K, La and Fe and mixtures thereof to said ceramic support and calcining the coated ceramic in air to convert the metal salts to metal oxides.

2. The method of claim 1 wherein the metal is Ni.

3. The method of claim 2 wherein the salt is $Ni(NO_3)_2 \bullet 6H_2O$.

4. The method of claim 1 wherein the metal is Pt.

5. The method of claim 4 wherein the salt is $H_2PtCl_6 \bullet 6\ H_2O$.

6. The method of claim 1 wherein the metal is Mg.

7. The method of claim 6 wherein the salt is $Mg\ (NO_3)_2 \bullet 6\ H_2O$.

8. The method of claim 1 wherein the metal is K.

9. The method of claim 8 wherein the salt is KNO_3.

10. The method of claim 1 wherein the metal is a mixture of Ni, Pt, Mg and K.

11. The method of claim 10 wherein the salt is a mixture of $Ni(NO_3)_2 \bullet 6H_2O$, $H_2PtCl_6 \bullet 6\ H_2O$, $Mg\ (NO_3)_2 \bullet 6\ H_2O$ and KNO_3.

12. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, said catalyst comprises less than 30% by weight NiO.

13. The steam reforming catalyst of claim 12, wherein said catalyst comprises less than 10% by weight NiO.

14. The steam reforming catalyst of claim 12, wherein said catalyst comprises less than 2% by weight NiO.

15. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, said catalyst comprising less than 5 weight percent MgO.

16. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, said catalyst comprising less than 10 weight percent K_2O.

17. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, said catalyst comprising less than 1.0 weight percent Pt.

18. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, wherein said catalyst comprises a mixture containing less than 10 weight percent NiO, less than 5 weight percent MgO and less than 10 weight percent K_2O.

19. A steam reforming catalyst characterized by improved resistance to attrition loss when used for cracking, water gas shift and gasification reactions on feedstock in a fluidized bed reactor, said catalyst comprising less than 1.0 weight percent Pt and less than 10 weight percent K_2O.

20. The method of claim 1 wherein said ceramic support is selected from the group consisting of olivine, ceria, zirconia, lanthanum and tin oxides.

21. The method of claim 1 wherein said ceramic support is alumina-based.

22. The steam reforming catalyst of claim 12 on a ceramic support is selected from the group consisting olivine, ceria, zirconia, lanthanum and tin oxide.

23. The steam reforming catalyst of claim 15 on an alumina-based ceramic support.

24. The steam reforming catalyst of claim 16 on an alumina-based ceramic support.

25. The steam reforming catalyst of claim 17 on an alumina-based ceramic support.

26. The steam reforming catalyst of claim 18 on an alumina-based ceramic support.

27. The steam reforming catalyst of claim 19 on an alumina-based ceramic support.

AMENDED CLAIMS
received by the International Bureau on 16 February 2007 (16.02.2007)
+ STATEMENT

WE CLAIM:

1. A prosthetic foot comprising a forefoot portion, a midfoot portion and a hindfoot portion, said hindfoot portion including an ankle joint permitting closed kinetic chain motion of the prosthetic foot in gait, said ankle joint having a joint axis oriented with the medial more anterior than the lateral for permitting motion of said hindfoot portion about said ankle joint axis such that said motion is in the sagittal and frontal planes, said ankle joint being formed integrally with said hindfoot portion by a strut of resilient material of said hindfoot portion, the strut having an anterior side surface and a posterior side surface which are anterior facing convexly curved, wherein a hole extends through said hindfoot portion with the periphery of the hole forming an anterior side surface of said strut, wherein the hindfoot portion anterior to said hole includes a gap to permit said motion of said hindfoot portion about said ankle joint axis, and wherein said hole as seen in a cross section of the prosthetic foot in the sagittal plane is elongated upwardly such that said strut is upstanding.

2. The prosthetic foot according to claim 1, wherein said strut extends in the direction of the human ankle joint axis.

4. The prosthetic foot according to claim 1, wherein the height of said gap is selected so that a lower surface of said hindfoot portion defining said gap acts as a stop against an opposing upper surface defining said gap to limit the amount of said motion of said hindfoot portion about said ankle joint axis in dorsiflexion.

5. The prosthetic foot according to claim 1, wherein said hole extends in a direction parallel to said joint axis of said ankle joint.

6. The prosthetic foot according to claim 1, further comprising an adapter connected to the prosthetic foot above the ankle joint, the adapter having a socket for receiving a member to detachably connect the prosthetic foot to an amputee's leg stump.

7. The prosthetic foot according to claim 6, wherein said adapter includes a member containing said socket, a base underlying said member and a releasable fastener connecting said member on said base to permit relative rotation of the member and the base.

8. The prosthetic foot according to claim 7, wherein said relative rotation of the socket containing member on the base of the adapter is in the transverse plane.

9. The prosthetic foot according to claim 6, wherein said adapter includes a plurality of adjustable fasteners for changing the position said member is received in said socket.

10. The prosthetic foot according to claim 9, wherein said adapter with socket and adjustable fasteners permit anterior-posterior, medial-lateral and tilt adjustments of the member and prosthetic foot.

11. A prosthesis comprising:

a foot;

an ankle;

wherein the foot and ankle are monolithically formed as a resilient member including a strut which is oriented so that the medial side is more anterior than the lateral side, the strut forming an ankle joint permitting closed kinetic chain motion of the prosthesis in gait about an ankle joint axis oriented such that said motion is in the sagittal and frontal planes , wherein a hole extends through said resilient member with the periphery of the hole forming an anterior side surface of said strut, wherein said resilient member anterior to said hole includes a gap to permit said motion about said ankle joint axis, and wherein the anterior side surface of said strut and a posterior side surface of said strut are anterior facing convexly curved.

13. The prosthesis according to claim 11, wherein said hole as seen in a cross section of the resilient member in the sagittal plane is elongated upwardly such that said strut is upstanding.

14. The prosthesis according to claim 11, wherein said strut extends in the direction of the human ankle joint axis.

16. The prosthesis according to claim 11, wherein the height of said gap is selected so that a lower surface of said member defining said gap acts as a stop against an opposing upper surface defining said gap to limit the amount of said motion about said ankle joint axis in dorsiflexion.

17. The prosthesis according to claim 11, wherein said hole extends in a direction parallel to said joint axis of said ankle joint.

18. The prosthesis according to claim 11, further comprising an adapter connected to the prosthesis above the ankle joint, the adapter having a socket for receiving a member to detachably connect the prosthesis to an amputee's leg stump.

19. The prosthesis according to claim 18, wherein said adapter includes a member containing said socket, a base underlying said member, and a releasable fastener connecting said member on said base to permit relative rotation of the member and the base.

20. The prosthesis according to claim 19, wherein said relative rotation of the socket containing member on the base of the adapter is in the transverse plane.

21. The prosthesis according to claim 18, wherein said adapter includes a plurality of adjustable fasteners for changing the position said member is received in said socket.

22. The prosthesis according to claim 21, wherein said adapter with socket and adjustable fasteners permit anterior-posterior, medial-lateral, and tilt adjustments of the member and prosthesis.

23. A prosthetic foot comprising a forefoot portion, a midfoot portion and a hindfoot portion, said hindfoot portion including an ankle joint permitting closed kinetic chain motion of the prosthetic foot in gait, said ankle joint having a joint axis oriented with a medial side which is more anterior than a lateral side for permitting motion of said hindfoot portion about said ankle joint axis which is in the sagittal and frontal planes , said ankle joint being formed integrally with said hindfoot portion by a strut of resilient material of said hindfoot portion, wherein a hole extends through said hindfoot portion with the periphery of the hole forming an anterior side surface of said strut, wherein the hindfoot portion anterior to said hole includes a gap to permit said motion of said hindfoot portion about said ankle joint axis, and wherein said strut and said hole are configured such that the anterior side surface and a posterior side surface of said strut are anterior facing convexly curved.

24. A prosthesis comprising:

a foot;

an ankle;

wherein the foot and ankle are monolithically formed as a resilient member including a strut which has a medial side which is more anterior than a lateral side and which forms an ankle joint permitting closed kinetic chain motion of the prosthesis in gait about an ankle joint axis oriented such that said motion is in the sagittal and frontal planes, wherein a hole extends through said resilient member with the periphery of the hole forming an anterior side surface of said strut, wherein said resilient member anterior to said hole includes a gap to permit said motion about said ankle joint axis, and wherein said hole is elongated upwardly such that said strut is upstanding, and wherein said anterior side surface and a posterior side surface of said strut are anterior facing convexly curved.

STATEMENT UNDER ARTICLE 19(I)

(PCT Rule 46)

A preferred feature of the prosthetic foot and prosthesis of the present invention is that the ankle joint axis is externally rotated an angle of 8° to 30° with the medial more anterior than the lateral as shown in Figures 4, 29 and 30 and as explained on page 6 of the specification. As a result of this feature, motion of the hindfoot portion about the ankle joint axis is in the sagittal and frontal planes to closely mimic human foot ankle joint motion. This feature of the invention has been recited in each of the independent claims as amended, e.g. claims 1, 11, 23 and 24.

A further feature of the invention is that in the species of Figures 29 and 31, for example, the strut of resilient material of the hindfoot portion forming the ankle joint has an anterior side surface and a posterior side surface which are anterior facing convexly curved. This feature has also been recited in the independent claims as amended. As referred to on pages 22 and 23 of the specification, the anterior convexly curved strut advantageously provides differential properties in compression and expansion of the strut in gait and, together with the upwardly arched resilient foot of the prosthesis contributes to a dynamic response of the prosthesis having horizontal and vertical directional components for improved efficiency of the prosthesis in use.

Because of this curvature, the strut is moved more easily into plantarflexion at the initial phase of ground contact and gait wherein the curvature is compressed, and is moved with more difficultly into expansion in a later phase in gait during dorsiflexion. This relationship is consistent with the forces which occur in the human foot in gait, which offers more flexibility in initial ground contact for plantarflexion while necessarily offering more resistance as the foot moves into dorsiflexion where higher forces must be resiliently absorbed and resisted as compared with plantarflexion in normal gait.

Neither the patent to Gabourie, U.S. Patent 6,197,066, nor the patent to Cooper, U.S. Patent No. 4,728,336, referred to in the Written Opinion of the International Searching Authority teach or suggest a prosthetic foot or prosthesis having either of the aforementioned significant features of the present invention which contribute to the prosthesis mimicking the human foot in gait. The integral spring 20-20' in Gabourie, and the resilient ankle joint axis, is normal to the long axis of the foot. Motion about the ankle joint axis in Gabourie is strictly in the sagittal plane. In the example in Gabourie, Figure 1, the prosthesis is relatively stiff in plantarflexion and compliant in dorsiflexion, which is the opposite of Applicant's strut, see column 4, lines 34-36.

In view of the amendments, it is respectfully submitted that the claims as amended are novel under PCT Article 33(2) and represent an inventive step under PCT Article 33(3).

Respectfully submitted,

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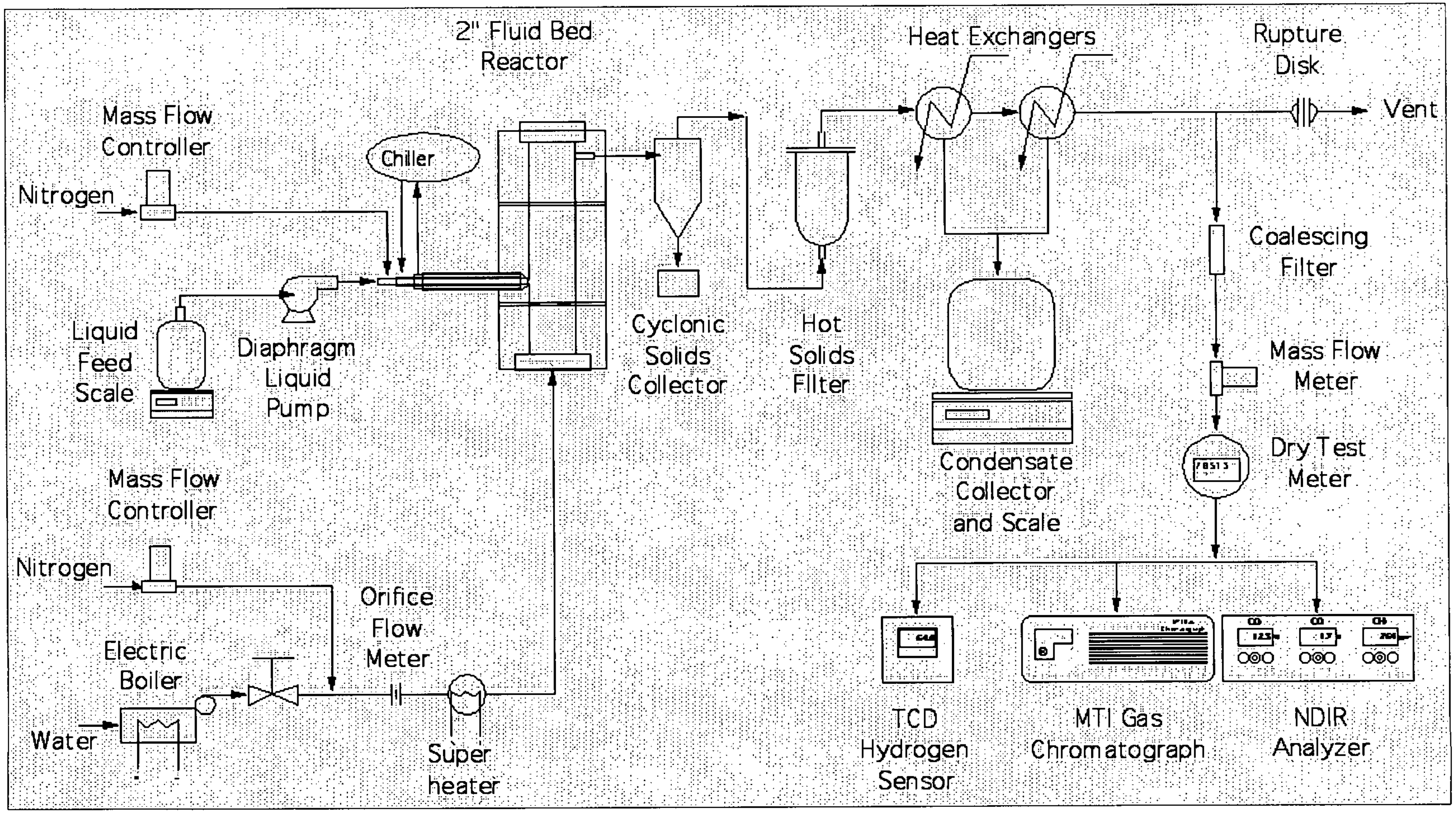
Ronald J. Shore
Attorney/Agent of Record


2" Fluid Bed Reactor
Heat Exchangers
Rupture Disk
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Liquid Feed Scale
Diaphragm Liquid Pump
Cyclonic Solids Collector
Hot Solids Filter
Condensate Collector and Scale
Coalescing Filter
Mass Flow Meter
Dry Test Meter
Mass Flow Controller
Nitrogen
Orifice Flow Meter
Electric Boiler
Water
Super heater
TCD Hydrogen Sensor
MTI Gas Chromatograph
NDIR Analyzer

FIGURE 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US05/36588

A. CLASSIFICATION OF SUBJECT MATTER

IPC: **B01J 23/00**(2007.01),**23/02**(2007.01),**23/04**(2007.01),**23/06**(2007.01),**23/32**(2007.01),**23/40**(2007.01),**23/42**(2007.01),**23/44**(2007.01),**23/56**(2007.01),**23/58**(2007.01),**23/60**(2007.01),**23/70**(2007.01),**23/72**(2007.01),**23/74**(2007.01),**20/00**(2007.01),**21/04**(2007.01)

USPC: Please See Continuation Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : Please See Continuation Sheet

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/0177628 A1 (GAFFNEY et al) 28 November 2002 (28.11.2002), see entire document.	1-3, 6-7, 12-15, & 20-23
X --- Y	US 2003/0180215 A1 (NIU et al) 25 September 2003 (25.09.2003), see entire document.	1-11 & 20-21 ----------- 12-19 & 22-27
X	US 2003/0165424 A1 (RAMANI et al) 04 September 2003 (04.09.2003), see entire document.	1-7, 12-13, 15, 17, 20-23, & 25
X	US 2005/0096215 A1 (ESPINOZA et al) 05 May 2005 (05.05.2005), see entire document.	1-7 & 20-21
Y	US 2003/0149120 A1 (WANG et al) 07 August 2003 (07.08.2003), see entire document.	1-27
Y	US 2002/0035036 A1 (FIGUEROA et al) 21 March 2002 (21.03.2002), see entire document.	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search
14 December 2006 (14.12.2006)

Date of mailing of the international search report
16 FEB 2007

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C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/0054738 A1 (FRAENKEL) 10 March 2005 (10.03.2005), see entire document.	1-27
A	US 2004/0265225 A1 (WATSON et al) 30 December 2004 (30.12.2004), see entire document.	1-27
A	US 2004/0052725 A1 (NIU et al) 18 March 2004 (18.03.2004), see entire document.	1-27
A	US 2002/0131915 A1 (SHORE et al) 19 September 2002 (19.09.2002), see entire document.	1-27

Continuation of B. FIELDS SEARCHED Item 1:
502/303, 304, 305, 308, 310, 313, 314, 315, 316, 317, 319, 320, 324, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 344, 349, 352, 355, 415, 439

Continuation of USPC:
502/303,304,305,308,310,313,314,315,316,317,319,320,324,326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341,344,349,352,355,415,439