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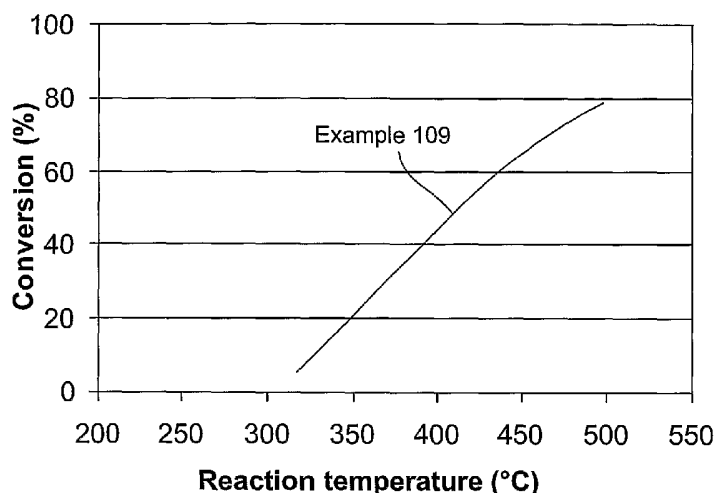
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(54) Title: COMPLEXED NANOCATALYSTS, FUEL COMPOSITIONS INCORPORATING SUCH CATALYSTS, AND METHODS MAKING AND USING SUCH NANOCATALYSTS AND COMPOSITIONS



(57) Abstract: Organically complexed nanocatalyst compositions are applied to or mixed with a carbon-containing fuel (e.g., coal, briquetted charcoal, tobacco, biomass, or a liquid hydrocarbon like fuel oils or gasoline) in order to enhance combustion properties of the fuel. The nanocatalyst compositions include nanocatalyst particles made using a dispersing agent. They can be formed as a stable suspension to facilitate storage, transportation and application of the catalyst nanoparticles to a fuel substrate. Nanocatalyst compositions can be applied to or mixed with a solid fuel substrate in order to reduce the amount of CO, hydrocarbons and soot produced by the fuel during combustion, hi addition, a nanocatalyst composition can be applied to or mixed with coal prior to or upon introducing the coal into a coal burner in order to catalyze the removal of coal nitrogen from the coal and its conversion into nitrogen gas prior to combustion of the coal. This leads to reduced NOx production during coal combustion.

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**COMPLEXED NANOCATALYSTS, FUEL COMPOSITIONS
INCORPORATING SUCH CATALYSTS, AND METHODS MAKING
AND USING SUCH NANOCATALYSTS AND COMPOSITIONS**

5 **The Field of the Invention**

The invention relates to organically complexed nanocatalysts for improving the combustion properties of fuels, modified fuels incorporating such nanocatalysts, and methods for manufacturing and using such nanocatalysts and fuel compositions.

Related Technology

10 Carbon-containing fuels typically yield mainly carbon dioxide and water as products of combustion. Due to incomplete combustion, other more harmful molecules can be formed, such as carbon monoxide (CO), hydrocarbons and soot. Impurities in the fuel can also yield significant quantities of ash, SO_x and NO_x. Due to increased environmental awareness and stricter governmental guidelines, there are
15 ongoing efforts to reduce the release of harmful emissions into the environment.

Coal combustion is major source of energy for the production of electricity throughout the world. Coal is a good source of energy because of its high energy to weight ratio and its great abundance. The use of coal, however, is increasingly under scrutiny because of environmental concerns. Among the known environmental
20 difficulties with coal combustion is the production and emission of NO_x compounds, such as NO, N₂O, and NO₂. NO_x compounds can be harmful to human health and are known to produce undesirable environmental effects such as smog.

Government regulations require emission from coal burning to be monitored and controlled. Controlling NO_x emissions has become increasingly important as
25 government regulations continue to lower the allowable level of NO_x and other pollutants that can be released into the environment. The requirement for reduced pollutants from coal-fired power plants has led to a demand for suitable new technologies.

In a coal fired power plant, there are two principle sources of NO_x formation:
30 fuel NO_x and thermal NO_x. Fuel NO_x is NO_x that forms from nitrogen found in the fuel, whereas thermal NO_x is formed from other sources of nitrogen (*e.g.*, atmospheric nitrogen). About 80% of NO_x emitted from coal combustion are produced from fuel nitrogen.

One method for reducing pollutants during coal combustion is to remove NO_x from power plant flue gas. For example, NO_x emitted in flue gas can be removed using selective catalytic reduction (SCR), which converts NO_x compounds to nitrogen gas (N₂) and water. However, this type of NO_x control method is expensive, in part
5 because of the required capital investment. The cost of these technologies and increasingly stringent government regulations have created a need for less expensive technologies to reduce NO_x emissions from coal combustion.

Another method of reducing NO_x emissions is to remove coal nitrogen from the coal material by converting it to N₂. Recently, researchers have discovered that
10 iron-based catalysts can assist in releasing fuel nitrogen from coal. In work by Ohtsuka and coworkers at Tohoku University (Sendai, Japan), methods have been described for the production of an iron-based catalyst, which, when combined with coal and placed in a pyrolysis environment, causes nitrogen compounds in coal to be released more rapidly, thus causing a decrease in the amount of nitrogen remaining in
15 the char material. Ohtsuka et al., *Energy and Fuels* 7 (1993) 1095; and Ohtsuka et al., *Energy and Fuels* 12 (1998) 1356.

Several features make Ohtsuka's catalyst and methods too expensive and less effective than desired for use in coal fired power plants. First, Ohtsuka teaches precipitating a FeCl₃ solution directly onto coal using Ca(OH)₂, which results in
20 intimate contact between the coal, catalyst precursors, and other reagents used to make the catalyst nanoparticles. To remove chloride and calcium residues, Ohtsuka suggests washing the coal, which would be very costly on an industrial scale. Furthermore, at least some of these chemicals are likely to be adsorbed by the coal and remain even after washing. Substances such as chloride and calcium can have an
25 adverse effect on power plant equipment and can cause pollution themselves.

In addition, precipitating the catalyst onto the coal requires that the catalyst be formed in the same location as the coal. This limitation could require that the catalyst be prepared at a coal mine or power plant, or that the coal material be shipped to a separate facility for catalyst preparation, thereby adding to production costs.

30 Another disadvantage of Ohtsuka's catalyst is that it requires high loading amounts to obtain desired results (e.g., up to 7% by weight of iron). High loading

amounts can increase costs and offset the benefits of using a relatively inexpensive material such as iron. In addition, high iron content contributes to ash formation and/or can alter the ash composition.

Other fuels that emit pollutants into the environment due to incomplete
5 combustion include charcoal, wood, biomass, and liquid petroleum fuels. Typical pollutants include CO and hydrocarbons. Another substance that is a solid fuel is tobacco, which is deliberately combusted in a way so as to yield smoke that is inhaled or puffed into the body. In addition to desired large molecules, such as nicotine, tobacco combustion produces undesired small molecules such as CO and nitric oxide
10 (NO).

What is needed are improved catalysts that can be applied to or combined with solid fuels, such as coal, charcoal, wood, biomass, tobacco, or liquid hydrocarbons to reduce undesired pollutants during combustion, and a method for reducing NO_x emissions during coal combustion.

15 **BRIEF SUMMARY OF THE INVENTION**

The present invention provides nanocatalyst compositions that can be applied to or mixed with a fuel in order to improve the combustion properties of the fuel. The disclosed catalyst compositions more particularly include organically complexed nanocatalyst particles having a size less than 1 micron that can be applied to or mixed
20 with fuels such as coal, briquetted charcoal, wood, biomass, tobacco, and hydrocarbon liquids (*e.g.* jet fuel, diesel, heavy fuel oils, and gasoline) in order to improve the combustion properties of such fuels.

The invention also provides a method for reducing the output of NO_x during coal combustion by increasing the conversion of coal nitrogen (*i.e.*, nitrogen that is
25 bound or fixed within the coal) to nitrogen gas prior to or during combustion. In general, nitrogen that has been fixed within coal can easily oxidize to NO_x during coal combustion. Converting a substantial portion of the coal nitrogen to nitrogen gas at least partially prevents or inhibits the formation of NO_x from the coal nitrogen. That is because nitrogen gas is highly stable and much more resistant to oxidation
30 during combustion than nitrogen bound in the coal.

According to one aspect of the invention, a catalyst complex comprising a plurality of active catalyst atoms complexed with a dispersing agent is formed initially. The catalyst complex may comprise a solution, colloid, or a suspension of nanoparticles. The active catalyst atoms typically include one or more titanium (Ti),
5 vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn), Antimony (Sb), tungsten (W), and osmium (Os). The catalyst atoms may include one or more oxides of the foregoing instead of, or in addition to, ground state catalyst atoms. The dispersing agent typically includes organic molecules that
10 include one or more functional groups selected from the group of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrile, an amino acid, a thiol, a sulfonic acid, an acyl halide, a sulfonyl halide, or a nitrogen with a free lone pair of electrons.

According to one embodiment, the catalyst complex comprises a suspension of organically complexed nanocatalyst particles having a size less than about 1 micron
15 as a suspension within a solvent. The nanocatalyst particles typically have a concentration greater than about 1% by weight of the suspension, preferably greater than about 5% by weight of the suspension, more preferably greater than about 7.5% by weight, and most preferably greater than about 10% by weight of the suspension.

An advantage of providing a suspension of organically complexed
20 nanocatalyst is that the nanocatalyst particles are stable; the suspension can be easily stored and transported without substantial agglomeration of the nanocatalyst particles. This allows a catalyst composition according to the invention to be prepared, stored, and then transported as needed, thus obviating the need to form the catalyst on-site at the time it is applied to a fuel substrate. The catalyst suspension may be applied using
25 simple techniques, such as spraying, which adds negligible to minimal cost to the operation of, *e.g.*, a coal-fired power plant.

In another aspect of the invention, a fuel composition comprises a fuel substrate and a plurality of organically complexed nanocatalyst particles on and/or mixed with the fuel substrate. The fuel substrate may comprise coal, coal briquettes,
30 wood, tobacco, biomass, or a liquid hydrocarbon such as fuel oils, diesel or gasoline. The organically complexed nanocatalyst particles on and/or mixed with the fuel

substrate have a size less than 1 micron. If the fuel is coal, charcoal briquettes, wood, biomass, or liquid hydrocarbon, the nanocatalyst particles are preferably less than about 300 nm in size, more preferably less than about 100 nm, even more preferably less than about 50 nm, and most preferably less than about 10 nm. If the fuel
5 substrate is tobacco, the nanocatalyst particles are preferably less than about 100 nm, more preferably less than about 10 nm, even more preferably less than about 6 nm, and most preferably less than about 4 nm.

Another feature of the inventive fuel compositions is that the dispersing agent binds to at least a portion of the catalyst atoms and prevents or inhibits agglomeration
10 of the nanocatalyst particles during combustion, pyrolysis, or other high temperature conditions to which the fuel compositions may be exposed. Thus, the organically complexed nanocatalyst particles according to the invention have greater stability under extreme temperature conditions compared to conventional metal catalysts. The dispersing agent acts to stabilize the nanocatalyst particles and prevents deactivation.
15 In some cases, the nanocatalyst particles may even be anchored to the fuel substrate, thereby preventing or inhibiting sintering or agglomeration of the catalyst particles during pre-combustion processing, and possibly even during at least a portion of the combustion process itself. Preventing agglomeration of the nanocatalyst particles maintains the benefit of nano-sized catalyst particles for longer periods of time
20 compared to conventional catalysts.

The organically complexed nanocatalyst compositions according to the invention also increase catalyst efficiency, thereby allowing for lower catalyst loadings within a fuel composition and/or increasing catalyst activity. The dispersion and stability of the nanocatalyst particles increases the activity of the catalyst such
25 that lower amounts of the catalyst can be loaded while still providing a desired level of catalytic activity.

In the case where the organically complexed nanocatalyst composition is used with coal, the stability of the nanocatalyst particles on the coal material and the efficacy with which the catalyst can assist in converting coal nitrogen to N_2 allows the
30 nanocatalyst composition to be mixed with the coal material in significantly lower concentrations than has been accomplished heretofore. The nanocatalyst composition

can be mixed with the coal before or after pulverizing the coal preparatory to combustion. The catalyst complex can be applied to coal or other fuel using low-cost equipment, such as pumps and sprayers. In another embodiment, the organically complexed nanocatalyst is injected into a coal burner together with pulverized coal.

5 In an exemplary embodiment, the nanocatalyst composition is loaded onto the coal material with a catalyst loading of less than about 2.5% by weight of the coal product. In a more preferred embodiment, the catalyst loading is less than about 1.5% by weight. Minimizing catalyst loading significantly reduces the cost of treating the coal and can also reduce the risk of damaging power plant equipment. Minimizing
10 catalyst metal loading can also reduce the risk of adversely affecting commercially valuable byproducts, such as fly ash, produced during coal combustion.

In an exemplary method according to the present invention, a catalyst complex is formed by: (i) providing a plurality of active catalyst atoms; (ii) providing a dispersing agent that includes at least one functional group selected from the group
15 consisting of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrile, nitrogen with a lone pair of electrons, an amino acid, a thiol, a sulfonic acid, sulfonyl halide, and an acyl halide; and (iii) reacting the catalyst atoms and the dispersing agent to form the catalyst complex, which may be in the form of a solution, colloid, or suspension. In one embodiment, the catalyst complex includes a plurality of
20 organically complexed nanocatalyst particles having a size less than 1 micron in suspension within a solvent.

Forming a nanocatalyst suspension from ground state metal atoms instead of an iron salt (*e.g.*, iron chloride or nitrate) can be advantageous because ground state metals are devoid of undesirable anions. A salt form of iron, such as iron chloride or
25 nitrate, can produce a catalyst composition with heteroatoms, such as chloride or nitrate ion, which may need to be removed from the nanocatalyst composition before use. By using a ground state metal as a precursor, use of significant amounts of heteroatoms can be avoided. This feature avoids the expense of subsequent washing of the coal or other fuel and the difficulties of corrosion, fouling, and other side
30 effects of having heteroatoms in the fuel.

Notwithstanding the foregoing, it should be understood that the present invention can be carried out using metal salts, though this is less preferred. Whether the heteroatoms have an adverse effect can depend on the particular system in which the nanocatalyst composition is used and the particular heteroatoms produced in the catalyst preparation process. In addition, those skilled in the art will recognize that a ground state metal may be oxidized during or after formation of the nanocatalyst particles.

The organically complexed nanocatalyst and coal compositions made therewith can be used to reduce NO_x in any type of coal burner. According to one embodiment, they may be used in a low NO_x burner that includes a specially designed low oxygen pyrolysis zone into which pulverized coal is first introduced in order to convert a portion of the coal nitrogen to nitrogen gas. The organically complexed nanocatalyst further catalyzes this process in order to more efficiently convert coal nitrogen into nitrogen gas, thereby further lowering the overall NO_x output during coal combustion.

These and other advantages and features of the present invention will become more fully apparent from the following description and appended claims as set forth hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

To further clarify the above and other advantages and features of the present invention, a more particular description of the invention will be rendered by reference to specific embodiments thereof which are illustrated in the appended drawings. It is appreciated that these drawings depict only typical embodiments of the invention and are therefore not to be considered limiting of its scope. The invention will be described and explained with additional specificity and detail through the use of the accompanying drawings, in which:

Figure 1 is a graph showing carbon monoxide conversion during tobacco combustion in Example 109;

Figure 2 is a graph showing carbon monoxide conversion during tobacco combustion in Examples 110 and 111;

Figure 3 is a graph showing carbon monoxide conversion during tobacco combustion in Examples 112 and 113; and

Figure 4 is a graph showing carbon monoxide conversion during tobacco combustion in Examples 114, 115, 116 and 117.

5 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

I. INTRODUCTION AND DEFINITIONS

 The invention encompasses organically complexed nanocatalyst compositions for use with a fuel in order to improve the combustion properties of the fuel. The combination of organically complexed nanocatalyst particles and a fuel substrate
10 forms a fuel composition within the scope of the invention. The invention also encompasses methods for manufacturing catalyst complexes, organically complexed nanocatalyst particles, and fuel compositions that include such nanocatalyst compositions. The present further relates to methods for reducing the output of NO_x during coal combustion. This is accomplished, at least in part, by applying or mixing
15 an organically complexed nanocatalyst with coal in order to catalyze the release and conversion of coal nitrogen to nitrogen gas prior to or during combustion. Converting a substantial portion of the coal nitrogen to more stable nitrogen gas at least partially prevents or inhibits the formation of NO_x from the coal nitrogen during combustion of the coal.

20 Organically complexed nanocatalyst particles according to the invention have a size less than 1 micron and can be applied to or mixed with carbon-containing fuels such as coal, briquetted charcoal, wood, tobacco, biomass, and liquid hydrocarbons in order to improve the combustion properties of such fuels. In one aspect, the inventive nanocatalyst compositions provide for the conversion of carbon monoxide and nitric
25 oxide to safer substances such as carbon dioxide and nitrogen. In the case of coal, the inventive nanocatalyst compositions may also provide the added benefit of helping to convert coal source nitrogen into nitrogen gas in a low oxygen portion of a coal burner (*e.g.*, in a conventional low NO_x burner).

 For purposes of this disclosure, the term “catalyst” does not exclude atoms,
30 molecules, and/or particles that are consumed in a reaction, such as the degradation of unwanted molecules during combustion of carbon-based fuel, such as coal, briquetted

charcoal, wood, tobacco, biomass, or liquid hydrocarbons. For example, in some embodiments, the catalysts of the present invention may be consumed by reduction or oxidation during combustion or other high temperature operations.

The terms "briquetted charcoal" and "charcoal briquettes" shall refer to solid
5 pieces of charcoal comprising individual charcoal particles that are bonded, compacted, or otherwise held together so as to be something other than a pulverized powder. In general, the terms "briquetted charcoal" and "charcoal briquettes" shall refer to any form of charcoal other than "activated charcoal", "activated carbon" and "carbon black," as those terms are defined in the art.

10 The term "biomass" refers to any plant-derived fuel material from any plant source whatsoever. Examples include waste stocks, leaves, or other materials from grains, husks, shells, or other materials resulting from the harvesting and processing of grains, nuts, fruits, or other edible plant products. It also refers to hemp, grass, leaves, stocks, or other plant materials specifically grown for the purpose of
15 producing biomass fuel. It includes wood chips, sawdust, or other scrap materials resulting from the milling or processing of lumber and other wood products, and the like.

The term "carbon-based fuel" or "fuel substrate" shall refer to any solid, or semi-solid, viscous liquid, or liquid fuel material, but shall exclude forms of carbon
20 that, though possibly flammable or combustible, are not in a form or produced at a sufficiently low cost to make them primarily usable as a fuel (*i.e.*, carbon black, activated charcoal, or activated carbon designed for use as a filtration or scavenging material).

II. ORGANICALLY COMPLEXED CATALYST COMPOSITIONS

25 Organically complexed nanocatalyst compositions include a catalyst complex formed by reacting one or more active catalyst atoms and a dispersing agent and, optionally, a solvent. The catalyst complex may be in the form of nanocatalyst particles or may be a precursor thereto. The organically complexed nanocatalyst compositions may be in the form of a solution, colloid, or suspension when mixed
30 with a solvent, or they may be in the form of a concentrated or dried material upon removal of the solvent. The dried composition can be reconstituted so as to form a

solution, colloid, or suspension upon reintroducing one or more solvents into the composition.

A. Catalyst Complexes

Catalyst complexes according to the invention include one or more different
5 types of active catalyst atoms complexed with one or more different types of
dispersing agents. When so complexed, the catalyst atoms are arranged in such a
manner that the catalyst atoms either (i) form dispersed nanocatalyst particles in
solution or suspension or (ii) that upon contact with a fuel substrate and/or after
undergoing further processing, the catalyst complexes form dispersed nanocatalyst
10 particles. In either case, the dispersing agent can form a catalyst complex to produce
nanoparticles that are dispersed, stable, uniform, and/or desirably sized.

1. Active Catalyst Atoms

The active catalyst atoms useful in practicing the present invention are metal
atoms or elements, such as iron or other metals, that can form nanocatalyst particles
15 capable of catalyzing desired reactions during combustion of the fuel (*e.g.*, the
conversion of NO_x to non-polluting gases such as N₂ in the case of coal and/or the
conversion of CO to CO₂ and NO to N₂ during combustion of any carbon-based fuel,
such as coal, briquetted charcoal, wood, tobacco, biomass, and liquid hydrocarbons).
These include elements or groups of elements that exhibit primary catalytic activity,
20 as well as promoters and modifiers.

As the primary active catalyst component, base transition metals are preferred
due to their valence characteristics and/or their relatively low cost compared to noble
metals and rare earth metals. Examples of base transition metals that exhibit catalytic
activity when mixed with a fuel include one or more of titanium (Ti), vanadium (V),
25 chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu),
zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn),
Antimony (Sb), tungsten (W), and osmium (Os). Among the foregoing, titanium is
less preferred for use in improving combustion characteristics of tobacco, briquetted
charcoal, wood, and biomass. In the case of coal, particularly where it is desired to
30 assist in reducing coal nitrogen to nitrogen gas prior to combustion, preferred catalyst

metals include one or more of iron, nickel, cobalt, manganese, vanadium, copper, and zinc.

The primary catalysts listed above may be used alone or in various combinations with each other or in combination with other elements, such as noble
5 metals, rare earth metals, alkaline metals, alkaline earth metals, or even non-metals, which will typically comprise a minority or the catalyst atoms, if included at all.

In general, the primary active catalyst component will comprise at least about 50% of the active catalyst atoms in the catalyst complex. This percentage measures the actual number of catalyst atoms or their molar ratio. In a preferred embodiment,
10 at least 50% of the active catalyst atoms are iron. Iron is preferred as the primary active catalyst because of its low cost and also because of its electron valence characteristics. The iron catalyst atoms may be provided in the form of iron metal, iron chloride, iron sulfate, iron nitrate, iron oxide, or other iron salts. The iron catalyst precursor may either be insoluble in an aqueous medium, as in the case of
15 iron metal, or it may be soluble, as in the case of iron chloride and other iron salts. In a preferred embodiment, iron metal is used in order to avoid incorporating compounds that include the anion of the iron salt.

The catalyst atoms may also include a minority metal component to modify or promote the catalytic function of the above mentioned metals. Examples of minority
20 metals that can be added to the catalyst composition in addition to the primary catalyst component include ruthenium, palladium, silver, platinum, nickel, cobalt, vanadium, chromium, copper, zinc, molybdenum, tin, manganese, gold, rhodium, zirconium, tungsten, rhenium, osmium, iridium, titanium, cerium and the like. These components can be added in metal form or as a salt.

25 Optionally, non-transition metals can also be included, typically as promoters or modifiers. Suitable non-transition metals include alkali metals and alkali earth metals, such as sodium, potassium, magnesium, calcium, etc., and non-metals such as phosphorus, sulfur, and halides.

2. Dispersing Agents

30 In addition to catalyst atoms, the catalyst complexes of the present invention include one or more dispersing agents. The dispersing agent is selected to promote

the formation of nanocatalyst particles that have a desired stability, size and/or uniformity. Dispersing agents within the scope of the invention include a variety of small organic molecules, polymers and oligomers. The dispersing agent is able to interact and bond with catalyst atoms dissolved or dispersed within an appropriate solvent or carrier through various mechanisms, including ionic bonding, covalent bonding, Van der Waals interaction/bonding, lone pair electron bonding, or hydrogen bonding.

To provide bonding between the dispersing agent and the catalyst atoms, the dispersing agent includes one or more appropriate functional groups. In one embodiment, the functional group(s) comprise a carbon atom bonded to at least one electron-rich atom that is more electronegative than the carbon atom and that is able to donate one or more electrons so as to form a bond or attraction with a catalyst atom. Preferred dispersing agents include functional groups which have either a charge or one or more lone pairs of electrons that can be used to complex a metal catalyst atom, or which can form other types of bonding such as hydrogen bonding. These functional groups allow the dispersing agent to have a strong binding interaction with the catalyst atoms.

The dispersing agent may be a natural or synthetic compound. Where the catalyst atoms are metal and the dispersing agent is an organic compound, the catalyst complex so formed may be an organometallic complex.

In an exemplary embodiment, the functional groups of the dispersing agent comprise one or more members selected from the group of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrile, a nitrogen with a free lone pair of electrons, an amino acid, a thiol, a sulfonic acid, a sulfonyl halide, and an acyl halide. The dispersing agent can be monofunctional, bifunctional, or polyfunctional.

Examples of suitable monofunctional dispersing agents include alcohols such as ethanol and propanol and carboxylic acids such as formic acid and acetic acid. Useful bifunctional dispersing agents include diacids such as oxalic acid, malic acid, malonic acid, maleic acid, succinic acid, and the like; dialcohols such as ethylene glycol, propylene glycol, 1,3-propanediol, and the like; hydroxy acids such as glycolic acid, lactic acid, and the like. Useful polyfunctional dispersing agents include sugars

such as glucose, polyfunctional carboxylic acids such as citric acid, pectins, cellulose, and the like. Other useful dispersing agents include ethanolamine, mercaptoethanol, 2-mercaptoacetate, amino acids, such as glycine, and sulfonic acids, such as sulfobenzyl alcohol, sulfobenzoic acid, sulfobenzyl thiol, and sulfobenzyl amine. The dispersing agent may even include an inorganic component (*e.g.*, silicon-based).

Suitable polymers and oligomers within the scope of the invention include, but are not limited to, polyacrylates, polyvinylbenzoates, polyvinyl sulfate, polyvinyl sulfonates including sulfonated styrene, polybisphenol carbonates, polybenzimidazoles, polypyridine, sulfonated polyethylene terephthalate. Other suitable polymers include polyvinyl alcohol, polyethylene glycol, polypropylene glycol, and the like.

In addition to the characteristics of the dispersing agent, it can also be advantageous to control the molar ratio of dispersing agent to the catalyst atoms in a catalyst suspension. A more useful measurement is the molar ratio between dispersing agent functional groups and catalyst atoms. For example, in the case of a divalent metal ion two molar equivalents of a monovalent functional group would be necessary to provide the theoretical stoichiometric ratio. In the case where the fuel is coal, charcoal, wood, biomass, or a liquid hydrocarbon, the molar ratio of dispersing agent functional groups to catalyst atoms is preferably in a range of about 0.001:1 to about 50:1, more preferably in a range of about 0.005:1 to about 10:1, and most preferably in a range of about 0.01:1 to 1:1. In the case where the fuel is tobacco, the molar ratio of dispersing agent functional groups to catalyst atoms is preferably in a range of about 0.01:1 to about 40:1, more preferably in a range of about 0.1:1 to about 30:1, and most preferably in a range of about 0.5:1 to about 20:1.

The dispersing agents of the present invention allow for the formation of very small and uniform nanoparticles. In general, the nanocatalyst particles formed in the presence of the dispersing agent are less than 1 micron in size. In the case where the fuel composition includes coal, briquetted charcoal, wood, biomass, or a liquid hydrocarbon, the nanocatalyst particles are preferably less than about 300 nm in size, more preferably less than about 100 nm, even more preferably less than about 50 nm, and most preferably less than about 10 nm. In the case where the nanocatalyst

composition is used within a tobacco fuel composition, the nanocatalyst particles are preferably less than about 100 nm, more preferably less than about 10 nm, even more preferably less than about 6 nm, and most preferably less than about 4 nm. In some cases, the nanocatalyst particles may approach the atomic scale.

5 Finally, depending on the desired stability of the nanocatalyst particles within the fuel composition, the dispersing agent can be selected in order to act as an anchor between the nanocatalyst particles and the fuel substrate. While the dispersing agent has the ability to inhibit agglomeration of the nanocatalyst particles in the absence of anchoring, chemically bonding the nanocatalyst particles to the fuel substrate surface
10 by means of the dispersing agent is an additional and particularly effective mechanism for preventing agglomeration.

 During thermal degradation and combustion of the fuel composition, the dispersing agent can inhibit deactivation of the nanocatalyst particles. This ability to inhibit deactivation can increase the temperature at which the nanocatalysts can
15 perform and/or increase the useful life of the nanocatalyst in the extreme conditions of combustion, *e.g.*, in a coal burner, an industrial burner, backyard barbeque, campfire, or cigarette. Even if including the dispersing agent only preserves catalytic activity for a few additional milliseconds, or even microseconds, the increased duration of the nanocatalyst can be very beneficial at high temperatures, given the dynamics of fuel
20 combustion and pollution formation.

 Depending on the type of fuel composition and/or the manner in which the fuel composition is to be utilized, the organically complexed nanocatalyst particles may be applied or anchored to a support material apart from the fuel substrate. The use of a support material may be advantageous in order to more fully and completely
25 disperse the organically complexed nanocatalyst particles throughout the fuel material. The support material may result in a more active nanocatalyst particle by providing more active sites per unit of catalyst material.

B. Solvents and Other Additives

 The liquid medium in which the organically complexed nanocatalyst
30 composition is prepared may contain one or more solvents, including water and organic solvents. Solvents participate in catalyst formation by providing a solution

for the interaction of catalyst atoms and dispersing agent. In some cases, the solvent may act as a secondary dispersing agent in combination with a primary dispersing agent that is not acting as a solvent. In one embodiment, the solvent also allows the nanoparticles to form a suspension, as described more fully below. Suitable solvents
5 include water, methanol, ethanol, n-propanol, isopropyl alcohol, acetonitrile, acetone, tetrahydrofuran, ethylene glycol, dimethylformamide, dimethylsulfoxide, methylene chloride, and the like, including mixtures thereof.

The selection of a particular solvent is often dictated by cost. While there may in some instances be certain advantages in the use of organic solvents, the cost of
10 either recovering the organic solvent or allowing the organic solvent to be consumed with the catalyst during combustion of the coal may result in a significant economic disadvantage for the use of organic solvents. Therefore, liquids which contain mostly or entirely water are the preferred solvents for the present invention. However, if an organic solvent is used, the solvent can be recovered using known methods such as
15 distillation. Alternatively, if the organic solvent is not recovered, it can provide some fuel value when consumed during coal combustion.

The catalyst composition can also include additives to assist in the formation of the nanocatalyst particles. For example, mineral acids and basic compounds can be added, preferably in small quantities (*e.g.*, less than 5 wt%). Examples of mineral
20 acids that can be used include hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, and the like. Examples of basic compounds include sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, and similar compounds.

It is also possible to add solid materials to assist in nanoparticle formation.
25 For example, ion exchange resins may be added to the solution during catalyst formation. Ion exchange resins can be substituted for the acids or bases mentioned above. Solid materials can be easily separated from the final iron catalyst solution or suspension using simple techniques such as centrifugation and filtration. Solid materials can also be added to remove unwanted byproducts. For example, activated
30 carbon is a relatively inexpensive material that can be used to remove some unwanted by-products formed during catalyst preparation.

C. Supports and Support Materials

Organically complexed nanocatalyst particles can be isolated on a support surface if desired. In an exemplary embodiment, the nanocatalyst particles are supported by the fuel substrate itself. According to one embodiment, the fuel
5 substrate may include functional groups to which the dispersing agent can bond.

Alternatively, the organically complexed nanocatalyst particles can be formed on a separate solid support. The support may be organic or inorganic. It may be chemically inert, or it may serve a catalytic function complementary to the nanocatalyst. The support may be in a variety of physical forms. It may be porous or
10 nonporous. It may be a three-dimensional structure, such as a powder, granule, tablet, or extrudate. The support may be a two-dimensional structure such as a film, membrane, or coating. It may be a one-dimensional structure such as a narrow fiber. In the case of a cigarette, the solid support may be a filter attached to and forming part of the cigarette, or it may be some other part of the cigarette such as the paper which
15 forms the outer wrapping.

One class of support materials includes porous, inorganic materials, such as alumina, silica, titania, kieselguhr, diatomaceous earth, bentonite, clay, zirconia, magnesia, metal oxides, zeolites, and calcium carbonate. Another useful class of supports includes carbon-based materials, such as carbon black, activated carbon,
20 graphite, fluoridated carbon, and the like. Other supports include polymers and other inorganic solids, metals, and metal alloys. Organic supports are advantageous in the case where it is desired for the support to burn up with the fuel substrate.

In the case where the nanocatalyst particles are attached to a support, they may be deposited within a wide range of loadings on the support material. The loading can
25 range from about 0.01% to about 70 wt% of the supported nanocatalyst particles exclusive of the fuel substrate, more preferably in a range of about 0.1% to about 25%. In the case where the support material is porous, it is preferable for the surface area to be at least 20 m²/g, more preferably greater than 50 m²/g.

III. METHODS OF MAKING NANOCATALYST COMPOSITIONS AND PARTICLE SUSPENSIONS

The process for manufacturing organically complexed nanocatalyst particles can be broadly summarized as follows. First, one or more types of catalyst atoms and one or more types of dispersing agents are selected. Second, the catalyst atoms (*e.g.*, in the form of a ground state metal or metal salt) and dispersing agent (*e.g.*, in the form of a carboxylic acid salt) are reacted or combined together to form a catalyst complex. The catalyst complex is generally formed by first dissolving the catalyst atoms and dispersing agent in an appropriate solvent or carrier and then allowing the catalyst atoms to recombine as the catalyst complex so as to form a solution, colloid, or suspension. The various components may be combined or mixed in any sequence or combination. In addition, a subset of the components can be premixed prior to addition of other components, or all components may be simultaneously combined.

In one aspect of the invention, the catalyst complex may be considered to be the complexed catalyst atoms and dispersing agent, exclusive of the surrounding solvent or carrier. Indeed, it is within the scope of the invention to create a catalyst complex in a solution, a colloid, or a suspension, and then remove the solvent or carrier so as to yield a dried catalyst complex. The dried catalyst complex can be applied to and/or mixed with a fuel substrate in such a form, or can be reconstituted as a solution, colloid, or suspension by adding an appropriate solvent.

In an exemplary embodiment, the components are mixed for a period of about 1 hour to about 5 days. This mixing is typically conducted at temperatures ranging from 0 °C to 200 °C. Preferably the temperature does not exceed 100 °C. The preparation of the catalyst complex is typically exothermic, so provisions for cooling may be used to control the temperature. The temperature can be held at a constant value throughout the mixing step, or it can be programmed to change during the mixing period.

The preparation of the catalyst complex can evolve hydrogen gas, which can require provisions for handling the gas pressure. Normally, the mixing step will be conducted at or near atmospheric pressure, although elevated pressure may be needed in cases where the mixing is conducted at elevated temperature, especially those

exceeding the normal boiling point of the liquid solvent. In one embodiment, an inert gas flow may be provided to safely purge any evolved gases from the mixing apparatus.

According to one currently preferred embodiment, the catalyst atoms used to
5 form nanocatalyst particles comprise iron metal. Using iron metal can be advantageous because iron metal does not form an anion by-product. After mixing with the dispersing agents and optional additives, the iron metal is converted to an active catalyst form and becomes dissolved or suspended in the solvent. The only significant by-product of the catalyst preparation using iron metal is hydrogen gas,
10 which is evolved during the mixing procedure.

In another embodiment, the catalyst atoms are provided as precursors in the form of an iron salt such as iron chloride, iron nitrate, iron sulfate, and the like. These compounds are soluble in an aqueous solvent. However, formation of the catalyst nanoparticles leads to the formation of additional by-products from the release of the
15 anion in the iron salt.

The anion-containing by-product may remain in the catalyst mixture; however, it is usually beneficial to remove the by-product to prevent the heteroatoms from having deleterious effects on equipment used in coal combustion. In the case where the byproduct is in solid form, it may be removed by filtration, centrifugation, or the
20 like. In the case where the byproduct is in liquid form, the byproduct can be removed by distillation, absorption, adsorption, extraction, ion exchange, membrane separation, or the like.

In an exemplary embodiment, the nanocatalyst particles are in an active form once the mixing step is complete. In a preferred embodiment, the nanocatalyst
25 particles are formed as a suspension of stable active iron nanocatalyst particles. The stability of the nanocatalyst particles prevents the particles from agglomerating together and maintains them in suspension. Even where some or all of the nanocatalyst particles settle out of suspension over time, the nanocatalyst particles can be easily re-suspended by mixing. The stable suspension is particularly
30 advantageous because it can be shipped, stored, transported, and easily applied to a

fuel substrate (e.g., a coal stream, briquetted charcoal, wood, tobacco, biomass, or a liquid hydrocarbon).

Because of strong price pressures on energy production, cost effective production and application of the nanocatalyst compositions to a fuel substrate may be important in maintaining the economic viability of their use. In one embodiment, the low cost of iron-based precursors, solvent, and dispersing agents are particularly beneficial for minimizing cost.

In one embodiment of the present invention, the concentration of metal catalyst in the suspension may be increased to reduce shipping costs, to more easily apply the catalyst composition to a fuel substrate, and/or improve catalyst performance. Typically, the nanocatalyst solution colloid or suspension contains at least about 1% by weight active catalyst atoms. In a preferred embodiment, the final catalyst solution or suspension contains at least about 5% by weight of active catalyst atoms, more preferably at least about 7.5% active catalyst atoms by weight, and most preferably at least about 10% active catalyst atoms by weight. In one embodiment, the nanocatalyst composition is dried and then reconstituted prior to use, as discussed above.

The catalyst compositions as described herein provide catalyst nanoparticles that are particularly advantageous for converting coal nitrogen to non-polluting gases such as N_2 . The effectiveness of the catalyst of the present invention occurs in part because of the small size of the particles, often below 100 nm, the uniform dispersion of the metal catalyst on or within the coal, and the surface structure of the catalyst nanoparticles.

IV. FUEL COMPOSITIONS AND RELATED METHODS

Fuel compositions according to the invention include at least one type of carbon-containing fuel substrate and at least one type of organically complexed nanocatalyst applied on or mixed with the fuel substrate. Exemplary fuel substrates include coal, briquetted charcoal, wood, tobacco, biomass, and liquid hydrocarbons, such as diesel, jet fuel, heavy fuel oils, and gasoline. The complexed nanocatalyst particles can be applied to or mixed with a fuel substrate using any desired method, including dipping, spraying, mixing, compacting, etc.

The organically complexed nanocatalyst particles improve one or more burn properties or characteristics of the fuel, *e.g.*, reducing CO, NO, and unburned hydrocarbons and soot in any fuel. In the case of coal, the organically complexed nanocatalyst particles may also assist in removing and converting coal nitrogen to
5 nitrogen gas prior to combustion in a low oxygen zone of a burner (*e.g.*, within a conventional low NO_x burner).

A. Coal Compositions

The catalyst compositions of the present invention can be combined with coal to make a modified coal composition having improved burn properties. In one
10 embodiment, complexed nanocatalyst particles applied to or mixed with coal can assist in reducing the emission of NO_x during combustion. The catalyst compositions can be combined with almost any type of coal material. Suitable coal materials include anthracite, bituminous, subbituminous, and lignite coals.

Any method can be used to apply the catalyst composition to the coal material.
15 The complexed nanocatalyst particles can be applied to or mixed with a coal substrate using any desired method, including dipping, spraying, mixing, compacting, etc. Complexed nanocatalyst nanoparticles in the form of a suspension are particularly easy to apply using a spraying technique.

The amount of catalyst applied to coal may be expressed in terms of weight
20 percent of the metal catalyst (*e.g.*, iron) by weight of the overall coal composition. Coal compositions typically include a catalyst metal loading of between about 0.01% and about 10% by weight of the overall coal composition. In a preferred embodiment, the catalyst metal (*e.g.*, iron) loading is preferably less than about 5% by weight of the coal composition, more preferably less than about 2.5% by weight, and most
25 preferably less than about 1.5% by weight.

The complexed nanocatalyst compositions of the invention have sufficient catalytic activity that catalyst loadings can be limited sufficiently to avoid problems with high metal concentrations. For example, high quantities of metal can present potential deposition problems in a boiler due to the fluxing abilities of the metal. The
30 fly ash chemistry can also change with high metal loading. High metal loadings may also have an effect on corrosion of coal combustion equipment. By limiting the metal

loading in the coal compositions of the present invention, the risks of these potential problems is reduced.

Coal compositions within the scope of the invention are designed to be used in combination with low NO_x burners and over fire air ports. These technologies create
5 a fuel-rich pyrolysis zone within a boiler that provides favorable conditions for the catalytic conversion of fuel nitrogen to harmless nitrogen gas. While not being limited to any particular theory, it is currently believed that the inventive organically complexed nanocatalyst compositions promote the increase of nitrogen release rates within high volatile eastern bituminous coal during the devolatilization stage of a low
10 NO_x burner. This fuel-rich zone promotes the conversion of fuel nitrogen to nitrogen gas. Once converted to nitrogen gas, the nitrogen becomes more resistant to oxidation to form NO_x. Therefore, when the pyrolyzed coal mixture passes into the combustion zone, nitrogen is much less likely to be converted to NO_x compounds than the original coal compounds would be. This substantially reduces the overall generation
15 of NO_x during coal combustion.

Coal burners are typically designed to burn coal that has been pulverized. Those skilled in the art are readily familiar with coal burners, pulverizers, and related systems used to burn coal. According to one method of the present invention, a catalyst composition as described above is applied directly to the coal prior to
20 pulverization. In this embodiment, applying the catalyst composition to the coal is very simple because the coal can be readily accessed. For example, the catalyst composition can be applied to coal on a conveyor. The nanocatalyst compositions may be applied to coal prior to combustion by "direct injection" or "mixing". In "direct injection", the catalyst is applied to the vertical coal stream located between
25 the pulverizer and the burners. In "mixing", the catalyst is sprayed on the coal as it is conveyed prior to entering the pulverizer.

In an alternative embodiment, the catalyst composition is applied after the pulverizer but before the coal stream reaches the coal burner. Applying the catalyst composition to the coal stream can be somewhat more difficult after pulverization
30 because there is more limited access to the pulverized coal.

In one embodiment, injectors are installed into the tubing of the coal feedstream and the catalyst composition is sprayed into the pulverized coal feedstream. Applying the catalyst composition directly into the pulverized feedstream can be advantageous because the catalyst composition can be better mixed initially since
5 the coal has a small particle size.

In yet another embodiment, the catalyst composition and the pulverized coal material are injected individually into an oxygen depleted portion of a coal burner. In an exemplary embodiment, the catalyst material is sprayed into the burner with the coal material such that the catalyst nanoparticles and the pulverized coal material are
10 sufficiently mixed such that the catalyst nanoparticles can catalyze the removal of coal nitrogen from the coal material within the oxygen depleted portion.

C. Other Fuel Compositions

The foregoing discussion of coal compositions can be extended to other carbon-containing fuels such as briquetted charcoal, wood, biomass, and liquid
15 hydrocarbons. Catalyst loadings in such fuels will typically be similar to those discussed above with respect to coal. Organically complexed nanocatalyst particles can be also combined with tobacco to make enhanced tobacco compositions and articles, such as cigarettes and cigars. The complexed nanocatalyst particles are associated with the tobacco such that upon combustion and/or pyrolysis of the
20 tobacco, the smoke produced therefrom comes into contact with the nanocatalyst particles. The nanocatalyst particles help degrade the undesirable small molecules (*e.g.*, CO and NO) before the smoke is inhaled by a user.

The complexed nanocatalyst particles of the present invention can be placed anywhere in or on a smoking article so long as smoke can come into contact with the
25 nanoparticles during use. In an exemplary embodiment, supported and/or unsupported complexed nanocatalyst particles are associated with a tobacco material by positioning them sufficiently close to gasses in tobacco smoke that the nanocatalyst can perform its catalytic function. The complexed nanocatalyst particles can be directly mixed with the tobacco material or they can be associated with the
30 tobacco material by being deposited between the tobacco material and the filter of a

cigarette. The complexed nanocatalyst particles can be disposed within the filter or be present in or on tobacco paper used to make a cigarette.

Because the complexed nanocatalyst particles are stable and highly active, catalyst loadings applied to the tobacco and/or filter can be significantly lower than catalyst loadings in the prior art. In an exemplary embodiment, the complexed nanocatalyst particles comprise iron mixed with a tobacco material with a metal loading less than about 30% by weight of the tobacco composition, more preferably less than about 15% by weight, and most preferably less than about 5% by weight.

In one embodiment, it is possible for the complexed nanocatalyst particles, at elevated temperatures, to be consumed in a redox reaction. In yet another embodiment, the complexed nanocatalyst particles can perform a catalytic function at one temperature and an oxidative and/or reductive function at another temperature.

Temperatures in a burning cigarette can reach temperatures between 200°C and 900°C. At such temperatures, traditional catalyst particles can sinter and agglomerate to form larger particles, which can deactivate the catalyst particles by reducing the surface area available for catalysis and/or oxidation or reduction. In contrast, the nanocatalyst particles of the present invention are complexed with an organic complexing agent, such as glycolic acid, which help prevent or at least delay agglomeration and catalyst deactivation sufficiently as to be effective to increase combustion efficiency.

The dispersing agent allows the nanocatalyst particles to operate at a higher temperature, which can have significant benefits. Higher operating temperatures can increase catalytic activity, thus reducing the amount of required catalyst. In some cases, proper catalytic activity can only be obtained at higher temperatures. Thus, higher operating temperatures can provide opportunities for using new catalysts. Alternatively, the dispersing agent increases the length of time before the nanocatalyst particles are destroyed in combustion or pyrolysis. In this embodiment, the ability of the dispersing agent to inhibit deactivation allows the nanocatalyst particles sufficient time to degrade undesirable small molecules before being consumed.

An organically complexed catalyst composition in a suspension can be sprayed or otherwise directly mixed with a tobacco material. Likewise, if the

complexed nanocatalyst particles are supported on a support surface, the support material can be mixed with the tobacco. Tobacco compositions within the scope of the invention may further comprise one or more flavorants or other additives (e.g., burn additives, combustion modifying agents, coloring agents, binders, etc.) known in the art.

V. EXAMPLES OF FUEL COMPOSITIONS FOR USE IN REDUCING POLLUTANTS DURING COMBUSTION

The following are various examples of inventive fuel compositions made using inventive organically complexed nanocatalyst compositions according to the invention. Examples stated in the past tense are actual examples of catalyst and fuel compositions that have been manufactured and/or used according to the invention. Examples recited in the present tense are hypothetical examples of catalyst and fuel compositions that could be manufactured and/or used according to the invention. Some examples may even include both actual and hypothetical aspects. Even though an example may be hypothetical in nature, or include a hypothetical portion, it should be understood that all examples are based on or extrapolated from actual compositions that have been made and/or tested.

Example 1

The following components were combined in a glass jar: 10 g iron metal powder, 3.3 g of a 70 wt.% aqueous solution of glycolic acid, 1.9 g of citric acid, 0.25 g of hydrochloric acid, 0.7 g of nitric acid, and 34.2 g of water. The mixture was placed on a shaker table and agitated for 5 days. At the completion of this process, the iron metal was fully dispersed to yield an organically complexed iron nanocatalyst composition. The mixture was stable and did not settle upon standing for several days.

Example 2

The following components were combined and formed into a catalyst as in Example 1: 5 g iron metal powder, 3.3 g of a 70 wt.% aqueous solution of glycolic acid, 1.9 g of citric acid, 0.25 g of hydrochloric acid, and 39.55 g of water.

Example 3

The following components were combined and formed into a catalyst as in Example 1: 5.6 g iron metal powder, 33 g of a 70 wt.% aqueous solution of glycolic acid, 19.2 g of citric acid, 55.6 g of a 0.01 wt% aqueous solution of hexachloroplatinic acid, and 200 g of water. This yielded an organically complexed iron-platinum nanocatalyst composition.

Example 4

The following components were combined and formed into a catalyst as in Example 1: 5 g iron powder, 3.3 g of a 70 wt.% aqueous solution of glycolic acid, 1.9 g of citric acid, 5 g of a 0.01 wt.% aqueous solution of hexachloroplatinic acid, 0.125 g of hydrochloric acid, 0.35 g of nitric acid, and 34.675 g of water. This yielded an organically complexed iron-platinum nanocatalyst composition.

Examples 5-8

The organically complexed iron nanocatalyst composition of Examples 1 and 2 were applied to River Hill coal to yield a coal composition according to the Examples 5 and 6 having an iron catalyst loading of 1.5 wt.%. The organically complexed iron-platinum nanocatalyst compositions of Example 3 and 4 were applied to River Hill coal to yield coal compositions according to Examples 7 and 8 having an iron catalyst loading of 1.6 wt% and 1.5 wt%, respectively. The coal compositions were designed to assist in removing coal nitrogen as nitrogen gas in the low oxygen zone of a coal burner in order to reduce overall NO_x production during combustion. In addition, the coal composition may also have superior combustion properties compared to untreated coal (e.g., in terms of possible reductions in CO, hydrocarbons and/or soot).

Examples 9-49

Organically complexed nanocatalyst compositions were made by combining and agitating the components set forth in Table I until the metal(s) was/were fully dissolved (i.e., there was no settling when agitation was stopped). The complexed metal nanocatalyst compositions can be applied to or mixed with a coal substrate to reduce NO_x when combusted in a coal burner by removing coal nitrogen as nitrogen gas in the low oxygen zone of the burner. They can also be used to improved

combustion properties of any fuel, such as decreasing the formation of CO and/or NOx. Unless otherwise specified, the iron was in the form of iron powder, the solvent was water, the glycolic acid was a 70 wt% solution in water, the polyacrylic acid ("PAA") was a 45 wt% in water. "AcAc" is shorthand for acetylacetonate.

5

TABLE I

Example	COMPONENTS (g)							
	Iron	Solvent	Glycolic Acid	Citric Acid	PAA	Sodium AcAc	Other Organic	Other Metal
9	5.6 ¹	300	33	0	0	0	0	0
10	5.6	300	33	0	0	0	0	0
11	5.6	300	33	19.2	21	0	0	0
12	5.6	300	0	19.2	0	14	0	0
13	5.6	200	0	19.2	7.2 ²	0	0	0
14	5.6	300	0	19.2	21	0	0	0
15	5.6	200	33	19.2	0	0	0	0
16	5.6	300	33	0	0	14	0	0
17	5.6	200	0	0	0	0	111.66 ³	0
18	5.6	200	0	0	0	0	37.2 ³	0
19	5.6	200	33	19.2	0	0	0	55.6 ⁴
20	26.6 ¹	200	33	0	0	0	0	55.6 ⁴
21	35 ⁵	200 ⁶	0	0	0	0	0	0
22	35 ⁵	200 ⁶	0	0	0	0	0	55.6 ⁴
23	5.6	200	0	19.21	0	0	3.96 ⁷	55.6 ⁴
24	5.6	200	0	19.21	0	0	3.96 ⁷	0
25	5.6	200	0	19.2	0	2.8	0	0
26	5.6	200	0	19.2	0	2.8	0	55.6 ⁴
27	5.6	200	33	19.2	4.2	0	0	0
28	5.6	200	33	19.2	4.2	0	0	55.6 ⁴
29	5.6	200	0	19.2	0	2.8	0	55.6 ⁴
30	5.6	200	33	19.2	4.2	0	0	55.6 ⁴
31	5.6	200	33	19.2	0	0	0	55.6 ⁴
32	5.56	200	33	4.8	0	0	0	0.265 ⁸
33	5.56	200	33	4.8	0	0	0	0.250 ⁹
34	5.56	200	33	4.8	0	0	0	0.182 ¹⁰
35	5.56	200	33	4.8	0	0	0	0.190 ¹¹
36	5.56	200	33	4.8	0	0	0	0.248 ¹²
37	5.56	200	33	4.8	0	0	0	0.190 ¹¹ 0.182 ¹⁰ 0.245 ¹²
38	5.56	200	33	4.8	0	0	0	0.25 ⁹ 0.265 ⁸
39	5.56	200	33	4.8	0	0	0	0

40	10	34.55 0.25 ¹³ 0.35 ¹⁴	3.3	1.9	0	0	0	0
41	5	39.675 0.125 ¹³ 0.35 ¹⁴	3.3	1.9	0	0	0	0
42	10	34.55 0.7 ¹⁴	3.3	1.9	0	0	0	0
43	5	39.625 0.525 ¹⁴	3.3	1.9	0	0	0	0
44	10	34.20 0.25 ¹³ 0.7 ¹⁴	3.3	1.9	0	0	0	0
45	10	34.3 0.5 ¹³	3.3	1.9	0	0	0	0
46	5	39.55 0.25 ¹³	3.3	1.9	0	0	0	0
47	10	34.1 0.7 ¹³	3.3	1.9	0	0	0	0
48	5	39.45 0.35 ¹⁴	3.3	1.9	0	0	0	0
49	10	33.6 0.5 ¹³ 0.7 ¹⁵	3.3	1.9	0	0	0	0

¹ Iron (III) Citrate

² Polyacrylic Acid (MW 2020)

³ EDTA (disodium salt)

⁴ Aqueous Hexachloroplatinic Acid (0.01 wt% Platinum)

5 ⁵ Iron (III) Acetyl Acetate

⁶ Methanol

⁷ Dextrose

⁸ Vanadyl Acetyl Acetate

⁹ Tungstic Acid

10 ¹⁰ Copper (II) Acetate

¹¹ Lanthanum Hydroxide

¹² Manganese (II) Acetate

¹³ Aqueous Hydrochloric Acid (37 wt%)

¹⁴ Aqueous Nitric Acid (70 wt%)

15 ¹⁵ Concentrated Nitric Acid

After dissolving the components of Example 12, the mixture was heated at 100°C for 10 minutes.

Examples 50-87

20 Examples 50-87 describe a number of organically complexed nanocatalyst compositions that can be applied to or mixed with a coal substrate in order to assist in

reducing NO_x when combusted in a coal burner by removing coal nitrogen as nitrogen gas in the low oxygen zone of the burner.

The organically complexed nanocatalyst compositions were made according to the following procedure: a metal complexing solution was made by mixing together
 5 mineral acid components (*i.e.*, aqueous hydrochloric acid (37%) and/or aqueous nitric acid (70%), dispersing agents (*i.e.*, aqueous glycolic acid (70%) and/or citric acid, and/or ethylene glycol), and 5 wt.% of the de-ionized water in a first container. The remaining de-ionized water was placed into a high shear mixing vessel and the mixer
 10 ramped up to 5400 RPM. The iron powder was gradually added to the mixing vessel with continued mixing. The complexing solution was slowly added to the mixing vessel over the course of five minutes to inhibit foaming and rapid temperature increase. Mixing was maintained for 60 hours for each of Examples 50-80 and 86 (4, 2, 2, 6, 6 and 6 hours, respectively, for each of Examples 81-85 and 87), while
 15 purging the vessel with nitrogen, to form the organically complexed nanocatalyst compositions.

The components and the amounts of each component measured in grams used to form the organically complexed nanocatalyst compositions of Examples 50-87 are set forth in Table II below:

TABLE II

Example	COMPONENTS (g)						
	Iron	HCl	HNO ₃	Glycolic Acid	Citric Acid	Ethylene Glycol	Deionized Water
50	1500	38	105	165	285	0	5408
51	1500	75	105	165	285	0	5370
52	1500	38	105	165	0	0	5693
53	1500	38	105	0	285	0	5573
54	1500	38	105	660	285	0	4913
55	3000	75	210	495	195	0	3525
56	1500	38	105	54	143	0	5561
57	1500	45	105	0	285	0	5565
58	1500	38	113	0	285	0	5565
59	1500	45	105	108	0	0	5742
60	1500	38	113	108	0	0	5742
61	1500	38	113	54	0	0	5654
62	2250	56	169	0	428	0	4598

63	2250	60	158	0	428	0	4605
64	1500	38	113	81	143	0	5627
65	1500	38	113	54	210	0	5586
66	1500	38	113	0	0	225	5625
67	1500	38	105	0	0	113	5745
68	1500	0	38	0	0	150	5813
69	1500	0	38	8	15	150	5790
70	2250	56	169	162	0	0	4863
71	2250	56	169	81	214	0	4730
72	2250	0	56	2	11	225	4955
73	3000	75	210	0	570	0	3645
74	3750	0	113	0	0	450	3188
75	3750	94	281	270	0	0	3105
76	4500	113	338	162	428	0	3461
77	3200	80	240	230	0	0	4250
78	3200	80	240	115	304	0	4061
79	3200	80	240	0	608	0	3872
80	3600	90	270	259	0	0	4781
81	5100	136	357	0	969	0	10438
82	6400	160	480	0	1216	0	7744
83	6400	160	480	461	0	0	8499
84	8000	120	360	346	0	0	7174
85	6000	150	450	432	0	0	7968
86	3600	90	270	259	0	0	4781
87	6400	160	480	461	0	0	8499

Examples 88-94

Examples 88-94 describe a number of organically complexed nanocatalyst compositions that can be applied to or mixed with a coal substrate in order to assist in reducing NO_x when combusted in a coal burner by removing coal nitrogen as nitrogen gas in the low oxygen zone of the burner.

The organically complexed nanocatalyst compositions were made according to the following procedure: a metal complexing solution was made by mixing together mineral acid components (*i.e.*, aqueous hydrochloric acid (37%) and/or aqueous nitric acid (70%)), aqueous glycolic acid (70%), and de-ionized water in a high shear mixer at 100 RPM. A mixture of iron powder and citric acid powder was added to the mixing vessel with continued mixing. Mixing continued between 200 and 4000 RPM, while purging the vessel with nitrogen, to form the organically complexed nanocatalyst compositions.

The components, the amounts of each component measured in weight percent, and the mixing times used to form the organically complexed nanocatalyst compositions of Examples 88-94 were as follows, as set forth in Table III:

TABLE III

Example	COMPONENTS (wt.%)						
	Iron	HCl	HNO ₃	Glycolic Acid	Citric Acid	Deionized Water	Mixing Time
88	10	0.25	0.70	6.60	3.80	78.65	99
89	20	0.25	0.70	6.60	3.80	68.65	96
90	20	0.25	0.70	6.60	3.80	68.65	168
91	20	0.5	1.40	6.60	3.80	67.70	125
92	10	0.5	1.40	6.60	3.80	77.70	53
93	20	0.5	1.40	6.60	3.80	67.70	54
94	20	0.5	1.40	6.60	3.80	67.70	32

5

Example 95

Any of the foregoing nanocatalyst compositions is modified by substituting or augmenting the iron component with one or more of titanium, vanadium, chromium, manganese cobalt, nickel, copper, zinc, yttrium, zirconium, niobium, molybdenum, tin, antimony, tungsten, and osmium, thereby yielding an organically complexed nanocatalyst suitable for application to or mixing with a coal substrate to be burned in a coal burner so as to reduce formation of NO_x.

The following examples show results from a bench-scale pre-combustion test that was performed in order to preliminarily test the concept that applying or mixing an organically complexed nanocatalyst composition with coal would assist in the removal of coal nitrogen in a low oxygen zone of a conventional coal burner. The examples demonstrate that complexed nanocatalysts according to the invention were useful in increasing coal nitrogen removal at high temperature and low oxygen relative to untreated coal.

The pre-combustion test apparatus was a LECO TGA-601 analyzer, which included four major parts: 1) a coal feeder, 2) a combustion chamber, 3) an electric furnace, and 4) off gas analyzers. The combustion chamber utilized a ceramic vessel that fit inside a protective outer stainless steel chamber to act as a liner to eliminate

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the catalytic effects of stainless steel. Sweep gas, made up of air and argon, was metered and swept past the end of a coal auger from which coal entered the gas mixture. The mixture of coal, air and argon were then dropped into the ceramic combustion chamber located inside the electric furnace. A thermocouple inserted into
5 the ceramic chamber recorded the temperature.

As the mixture of air, argon and coal entered the heated combustion chamber, the coal ignited. As the coal devolatilized, the heavier ash particles fell to the bottom of the chamber and were collected after the experiment ended. The off gases, with any entrained ash particles, passed from the ceramic chamber to a particulate trap to
10 remove the ash material. The clean gases flowed through a series of moisture traps designed to remove any water vapors and tars. After removing these substances, the gas flowed to a gas analyzer to measure NO_x.

Examples 96-99

Examples 96-99 show the results of the pre-combustion study relative to the
15 organically complexed nanocatalyst compositions of Examples 1-4, which were used to make the coal compositions of Examples 5-8. The catalyst compositions of Examples 1-4 were applied to coal in pulverized form to form the coal compositions of Examples 5-8.

Approximately 2.5 grams of a pulverized coal/catalyst mixture made using the
20 nanocatalyst compositions of Examples 1-4 were loaded into the LECO TGA-601 apparatus and heated to 107°C for 30 minutes in an argon environment. The apparatus was programmed to ramp at 43°C per minute up to 950°C and then hold that temperature for 60 minutes, all in an argon environment. After subsequent cooling, the coal char samples were recovered from the apparatus and analyzed in a
25 CHN analyzer. This allows the percentage of coal nitrogen released during pyrolysis to be determined.

Comparative Example 1

In order to provide a baseline from which to analyze the effect of applying an organically complexed nanocatalyst material to coal (*i.e.*, River Hill coal), untreated
30 River Hill coal (a Pittsburgh 8 bituminous coal) was tested using the LECO TGA-601

analyzer according to the method described above. CHN analysis of the coal char material indicated that 30.67% of the coal nitrogen was released to gaseous products.

Example 96

The coal composition of Example 5 was tested using the LECO TGA-601
5 analyzer according to the method described above. CHN analysis of the coal char indicated that 41.2% of the coal nitrogen was released to gaseous products. This is an increase in nitrogen release of 34.3% relative to Comparative Example 1.

Example 97

The coal composition of Example 6 was tested using the LECO TGA-601
10 analyzer according to the method described above. CHN analysis of the coal char indicated that 42.6% of the coal nitrogen was released to gaseous products. This is an increase in nitrogen release of 38.9% relative to Comparative Example 1.

Example 98

The coal composition of Example 7 was tested using the LECO TGA-601
15 analyzer according to the method described above. CHN analysis of the char indicated that 44.1% of the coal nitrogen was released to gaseous products. This is an increase in nitrogen release of 43.8% relative to Comparative Example 1.

Example 99

The coal composition of Example 8 was tested using the LECO TGA-601
20 analyzer according to the method described above. CHN analysis of the coal char indicated that 43.2% of the coal nitrogen was released to gaseous products. This is an increase in nitrogen release of 40.8% relative to Comparative Example 1.

The results of the pre-combustion test indicate that the four nanocatalyst compositions described in Examples 96-99 were effective in substantially increasing
25 the release of coal nitrogen from coal in a low oxygen pre-combustion setting. This suggests that coal treated using such nanocatalyst compositions would be expected to increase the release of coal nitrogen within the low oxygen, pre-combustion zone of a coal burner.

Even though most of the exemplary organically complexed nanocatalyst
30 compositions set forth in the examples were not rigorously tested to determine if they would definitively work to reduce NO_x production during coal combustion in a coal

burner, one of skill in the art will readily understand that many, if not most, of such compositions might be expected to work in this manner. Moreover, many, if not all, of the exemplary catalyst compositions would be expected to enhance at least some aspect of combustion of coal or other fuels (*e.g.*, in increasing combustion efficiency in order to reduce the amount of CO, hydrocarbons and/or soot that is produced during combustion of a nanocatalyst treated coal or fuel composition).

Examples 100-108 describe supported nanocatalyst compositions that can be used with a fuel substrate to improve burn properties (*e.g.*, a tobacco material to reduce undesirable small molecules in tobacco smoke). Examples 109-117 describe test results that illustrate the ability of the nanocatalyst compositions of Examples 100-108, respectively, to convert carbon monoxide to carbon dioxide.

Example 100

A precursor liquid was prepared by mixing together 0.56 g of iron powder, 1.8 g of dextrose, 1.92 g of citric acid, and 100 g of water. The components were mixed until all solids were dissolved. The precursor liquid was added to 5.0 g of gamma-alumina with a BET surface area of 83 m²/g while stirring. The mixture of liquid and solid was heated to 90 °C while stirring until the slurry volume was reduced to about 30 ml by evaporation. The supported iron nanocatalyst sample was placed in a rotating drier under a heat lamp until dry. The solid material was further dried in an oven at 80 °C for 2 hrs. The supported nanocatalyst, which comprised 6% iron on an alumina support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 101

A precursor liquid was prepared by mixing 0.112 g of iron powder, 1.114 g of a 0.010 wt. % Pt solution (prepared by mixing 0.2614 g of H₂PtCl₆ in 1000 ml water), 0.36 g of dextrose, 0.384 g of citric acid, and 100 g of water. The catalyst of this example was prepared according to the process of Example 1, except that the dried powder was also reduced under hydrogen flow for 6 hours at 300 °C. The supported nanocatalyst, which comprised 0.2% iron and 22 ppm platinum on an alumina support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 102

The catalyst of this example was prepared using the same procedure as Example 2, except that the alumina support was substituted with calcium carbonate having a surface area of $6 \text{ m}^2/\text{g}$. The supported nanocatalyst, which comprised 0.2% iron and 22 ppm platinum on a calcium carbonate support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 103

A precursor liquid was prepared by mixing 0.56 g of iron powder, 5.57 g of the 0.010 wt. % platinum solution used in Example 2, 1.8 g of dextrose, 1.92 g of citric acid, and 100 g of water. The catalyst was prepared according to the process of Example 2. The supported nanocatalyst, which comprised 6% iron and 60 ppm platinum on an alumina support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 104

The catalyst of this example was prepared using the same procedure employed in Example 4, except that the alumina support material was substituted with 5.0 g of calcium carbonate of the same type used in Example 3. The supported nanocatalyst, which comprised 6% iron and 60 ppm platinum on a calcium carbonate support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 105

0.80 g NaOH was dissolved in 40 ml of ethylene glycol to form a first solution, and 0.72 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 10 ml ethylene glycol to form a second solution. The two solutions were mixed together. 1.54 g of CaCO_3 of the type used in Example 3 was added to the resulting mixture. 50 ml of a 1.0 M aqueous NH_4NO_3 solution was added to the above solution, and the mixture of liquids was aged for 2 hours to form a precursor composition. The precursor composition was filtered and the precipitate washed 3 times with water. The precipitate was dried at 70°C in a vacuum oven for 3 hours, followed by further drying at 80°C in a drying oven for 2 hours. The supported nanocatalyst, which comprised 6% iron on a calcium

carbonate support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 106

A precursor liquid was created by mixing 75 ml of a first solution (prepared by mixing 1.3339 g PdCl₂ in 4.76 g HCl and then diluting to 1000 ml using water), 12 ml of a second solution (prepared by mixing 0.2614 g of H₂PtCl₆ with 1000 ml of water), and 10 ml of a third solution (prepared by diluting 15 g of 45% polyacrylate sodium salt solution (MW=1200) to a total mass of 100 g with water). The precursor liquid was diluted to 500 ml with water and stirred in a vessel fitted with a gas inlet, to which nitrogen is fed for 1 hour, followed by hydrogen for 20 minutes.

0.167 g of the above precursor liquid was diluted to 16.67 g with water. The diluted liquid was mixed with 0.20 g of the 6% Fe on CaCO₃ catalyst of Example 6. The mixture of liquid and solid was heated to 80°C with stirring until dry. The solid was further dried at 80°C in a drying oven for 2 hours. The supported nanocatalyst, which comprised 6% iron and 1 ppm palladium on a calcium carbonate support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 107

1.67 g of the precursor liquid in Example 7 was diluted to 16.7 g with water and added to 0.20 g of the 6% Fe on CaCO₃ catalyst of Example 6. The mixture of liquid and solid was heated to about 80°C with stirring until dry. The solid was further dried at 80°C in a drying oven for 2 hours. The supported nanocatalyst, which comprised 6% iron and 10 ppm palladium on a calcium carbonate support, can be applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Example 108

16.67 g of the precursor liquid in Example 7 was added, without further dilution, to 0.20 g of the 6% Fe on CaCO₃ catalyst of Example 6. The mixture of liquid and solid was heated to about 80°C with stirring until dry. The solid was further dried at 80°C in a drying oven for 2 hours. The supported nanocatalyst, which comprised 6% iron and 100 ppm palladium on a calcium carbonate support, can be

applied to or mixed with any fuel substrate and was found to be useful when mixed or associated with tobacco.

Examples 109-117

The catalysts of Examples 100-108 were tested for CO oxidation activity in
 5 Examples 109-117, respectively. Each of Examples 109-117 were conducted identically. In each case, 100 mg of supported nanocatalyst was mixed with quartz wool and then packed into a quartz flow tube. The flow tube was placed in a tubular furnace, and subjected to a flow of gas containing 2.94% by volume of carbon monoxide, 21% by volume oxygen, and the balance nitrogen at a total flow rate of
 10 1000 sccm. A thermocouple was placed in the catalyst zone to continuously monitor the reaction temperature. The reactor temperature was ramped at a rate of 12°C per minute.

The exiting gas was periodically sampled and tested by gas chromatography to determine the amount of carbon monoxide remaining at a series of temperatures
 15 spanning the temperature range of the experiment. The carbon monoxide fractional conversion at each temperature was calculated as the molar amount of carbon monoxide consumed divided by the molar amount of carbon monoxide in the feed gas. This was then converted to a percent conversion by multiplying by 100.

The results of Examples 109-117 are summarized in Table IV below:

20

Table IV

Example 109		Example 110		Example 111		Example 112		Example 113	
Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)
317	5	363	0	368	2	318	3	323	0
345	18	388	1	394	6	349	20	348	6
374	32	414	9	430	41	387	49	376	21
402	46	460	84	473	86	421	71	405	51
428	57	482	100	495	90	448	81	436	65
453	66					472	86	462	75
474	73					493	89	487	82
498	79							513	100

Example 114		Example 115		Example 116		Example 117	
Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)	Temp. (°C)	Conv. (%)
288	16	278	10	279	10	272	7

317	24	304	17	312	32	339	90
345	32	333	26	359	64	384	95
371	39	359	33	389	74		
397	45	387	41	415	77		
422	49	413	46	438	78		
448	55	436	50	463	78		
471	59	483	60	484	79		
496	63	508	65				

Figures 1-4 are graphs that illustrate the results of Examples 109-117. Figures 1-4 show the conversion of carbon monoxide to carbon dioxide at various temperatures. Figure 1 shows conversion for an iron catalyst on an alumina support. Figure 2 illustrates the difference in conversion of carbon monoxide as the support is changed from alumina (Example 110) to calcium carbonate (Example 111). Figure 3 illustrates the difference between using an alumina support (Example 112) and a calcium carbonate support (Example 113) with an iron-platinum catalyst. Figure 4 compares an iron catalyst (Example 114) with an iron-palladium catalyst with palladium increasing in concentration from 1 ppm (Example 115) to 10 ppm (Example 116) and 100 ppm (Example 117).

The test data plainly show that the ability to convert CO to CO₂ increases dramatically with increasing temperature. This suggests that maintaining good catalytic activity at higher temperatures would greatly improve the ability of a catalyst to perform its intended catalytic function. The organically complexed nanocatalyst compositions of the present invention have increased stability compared to conventional nanocatalysts and would therefore be expected to provide superior combustion properties, particularly at the higher temperatures associated with most forms of combustion, compared to conventional nanocatalysts.

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Example 118

Any of the fuel compositions of Examples 100-108 is modified by applying the supported nanocatalyst a fuel substrate other than tobacco, including one or more of coal, briquetted charcoal, wood, biomass, and liquid hydrocarbons.

Example 119

25

Any of the supported nanocatalysts of Examples 100-108 and 118 is modified by omitting the solid alumina or calcium carbonate support, thereby yielding an

organically complexed nanocatalyst suitable for application to a desired fuel substrate, including one or more of coal, briquetted charcoal, wood, tobacco, biomass, and liquid hydrocarbons.

Example 120

5 Any of the nanocatalyst compositions of Examples 100-108, 118 and 119 is modified by substituting or augmenting the iron component with one or more of chromium, manganese, cobalt, nickel, copper, zirconium, tin, zinc, tungsten, titanium, molybdenum, and vanadium, thereby yielding an organically complexed nanocatalyst suitable for application to a desired fuel substrate, including one or more of coal,
10 briquetted charcoal, wood, tobacco, biomass, and liquid hydrocarbons.

 The present invention may be embodied in other specific forms without departing from its spirit or essential characteristics. The described embodiments are to be considered in all respects only as illustrative and not restrictive. The scope of the invention is, therefore, indicated by the appended claims rather than by the
15 foregoing description. All changes which come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

1. A composition in the form of a catalyst complex suitable for application to a fuel substrate in order to form a nanoparticle combustion catalyst thereon and thereby modify combustion properties of the fuel substrate, comprising:

a plurality of active catalyst atoms, at least about 50% of which comprise one or more types of primary catalyst atoms selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn), Antimony (Sb), tungsten (W), and osmium (Os); and

a dispersing agent comprising a plurality of organic molecules complexed with at least a portion of said active catalyst atoms,

each of said organic molecules having one or more functional groups capable of bonding to said active catalyst atoms,

said one or more functional groups being selected from the group consisting of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrile, a nitrogen having a free lone pair of electrons, an amino acid, an amine, a thiol, a sulfonic acid, a sulfonyl halide, and an acyl halide.

2. A composition as defined in claim 1, said primary catalyst atoms being selected from the group consisting of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zirconium (Zr), tin (Sn), zinc (Zn), tungsten (W), molybdenum (Mo), and vanadium (V).

3. A composition as defined in claim 1, said active catalyst atoms being in the form of organically complexed nanocatalyst particles having a size less than about 1 micron.

4. A composition as defined in claim 3, said organically complexed nanocatalyst particles being dispersed in a solvent so as to form a nanocatalyst suspension.

5. A composition as defined in claim 4, said solvent comprising water, said nanoparticle suspension having a nanoparticle concentration greater than about 5% by weight of said suspension.

6. A composition as defined in claim 4, wherein said nanoparticle suspension is stable such that it can be stored and transported without substantial agglomeration of said organically complexed nanocatalyst particles prior to application to a fuel substrate.

7. A fuel composition comprising the catalyst complex of claim 1 on and/or mixed with at least one fuel substrate selected from the group consisting of coal, briquetted charcoal, wood, tobacco, biomass, fuel oil, diesel, jet fuel, gasoline, and liquid hydrocarbons.

8. Use of the fuel composition of claim 7 by combusting said fuel composition in the presence of oxygen so that the active catalyst atoms catalyze more efficient and/or thorough combustion of said fuel substrate.

9. A fuel composition having modified combustion properties, comprising:
a fuel substrate;
a plurality of organically complexed nanocatalyst particles on and/or mixed with said fuel substrate, said nanocatalyst particles having a size less than 1 micron and being comprised of:

a plurality of active catalyst atoms, at least about 50% of which comprise one or more types of primary catalyst atoms selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn), Antimony (Sb), tungsten (W), and osmium (Os); and

a dispersing agent comprising a plurality of organic molecules complexed with at least a portion of said active catalyst atoms of said nanocatalyst particles, each of said organic molecules having one or more functional groups capable of bonding to said active catalyst atoms.

10. A composition as defined in claim 9, said fuel substrate comprising coal so as to yield a coal composition.

11. A composition as defined in claim 9, said fuel substrate comprising: at least one member selected from the group consisting of briquetted charcoal, wood, tobacco, biomass, fuel oil, diesel, jet fuel, gasoline, and liquid hydrocarbons.

12. A composition as defined in claims 3 or 9, said nanocatalyst particles having a size less than about 300 nm.

13. A composition as defined in claims 3 or 9, said nanocatalyst particles having a size less than about 100 nm.

14. A composition as defined in claim 9, said nanocatalyst particles comprising less than about 2.5% by weight of the fuel composition.

15. A composition as defined in claims 3 or 9, said active catalyst atoms of said organically complexed nanocatalyst particles further comprising one or more types of minority catalyst atoms, different from said primary catalyst atoms, selected from the group consisting of ruthenium (Ru), palladium (Pd), silver (Ag), platinum (Pt), nickel (Ni), cobalt (Co), vanadium (V), chromium (Cr), copper (Cu), zinc (Zn), molybdenum (Mo), tin (Sn), manganese (Mn), gold (Au), rhodium (Rh), zirconium (Zr), tungsten (W), rhenium (Rh), osmium (Os), iridium (Ir), titanium (Ti), and cerium (Ce).

16. A composition as defined in claim 9, said one or more functional groups being selected from the group consisting of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrogen having a free lone pair of electrons, an amino acid, a thiol, a sulfonic acid, a sulfonyl halide, and an acyl halide.

17. A composition as defined in claims 1 or 9, said dispersing agent comprising at least one member selected from the group consisting of ethanol, propanol, formic acid, acetic acid, oxalic acid, malonic acid, ethylene glycol, polyethylene glycol, propylene glycol, polypropylene glycol, glycolic acid, glucose, citric acid, glycine, ethanolamine, mercaptoethanol, 2-mercaptoacetate, sulfobenzyl alcohol, sulfobenzoic acid, sulfobenzyl thiol, and sulfobenzyl amine.

18. A method of making an organically complexed iron-based nanocatalyst for use in modifying combustion properties of a fuel, comprising:

mixing together iron, a solvent, and a dispersing agent comprising a plurality of organic molecules, each having one or more functional groups capable of bonding to said iron;

reacting said iron with said dispersing agent to yield an iron catalyst complex; and

causing or allowing said iron catalyst complex to form organically complexed iron-based nanocatalyst particles having a size less than about 1 micron.

19. A method as defined in claim 18, further comprising removing at least a portion of said solvent to yield a concentrated or dried organically complexed iron-based nanocatalyst.

20. A method as defined in claim 19, further comprising mixing said concentrated or dried organically complexed iron-based nanocatalyst with additional solvent.

21. A method of manufacturing a fuel composition having modified combustion properties, comprising:

mixing together a plurality of active catalyst atoms and a dispersing agent to yield an intermediate catalyst complex;

at least about 50% of said active catalyst atoms comprising one or more types of primary catalyst atoms selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn), Antimony (Sb), tungsten (W), and osmium (Os),

said dispersing agent comprising a plurality of organic molecules complexed with at least a portion of said active catalyst atoms, each of said organic molecules having one or more functional groups capable of bonding to said active catalyst atoms, and

combining said catalyst complex with a fuel substrate so as to form the fuel composition,

the fuel composition comprising a plurality of organically complexed nanocatalyst particles having a size less than about 1 micron on and/or mixed with said fuel substrate.

22. A method as defined in claim 21, said intermediate catalyst complex being formed in an aqueous solution.

23. A method as defined in claim 22, said aqueous solution further comprising at least one of a mineral acid, a base, or ion exchange resin.

24. A method as defined in claim 21, said fuel comprising coal.

25. A method of reducing NO_x during combustion of coal within a burner, comprising,

providing a coal substrate;

providing an organically complexed nanocatalyst composition, the nanocatalyst composition comprising,

a plurality of catalyst nanoparticles having a size less than about 1 micron and including at least one type of metal; and

a dispersing agent comprising a plurality of organic molecules, each having at least one functional group capable of bonding to at least one metal atom of the catalyst nanoparticles;

introducing the coal substrate and the organically complexed nanocatalyst composition into a coal burner; and

causing or allowing the catalyst nanoparticles to catalyze one or more reactions that reduce the amount of NO_x produced during combustion of the coal substrate.

26. A method as defined in claim 25, the organically complexed nanocatalyst composition being applied to and/or mixed with the coal substrate prior to being introduced into the coal burner.

27. A method as defined in claim 26, further comprising pulverizing the coal prior to introducing it into the coal burner, the organically complexed nanocatalyst composition being applied to the coal substrate prior to pulverization.

28. A method as defined in claim 26, further comprising pulverizing the coal prior to introducing it into the coal burner, the organically complexed nanocatalyst composition being applied to and/or mixed with the coal substrate subsequent to pulverization.

29. A method as defined in claim 25, further comprising pulverizing the coal prior to introducing it into the coal burner, the organically complexed nanocatalyst composition being injected into the coal burner together with the pulverized coal.

30. A method as defined in claim 25, at least a portion of the organically complexed nanocatalyst composition forming a bond with the coal substrate prior to being introduced into the coal burner.

31. A method as defined in claim 25, the coal substrate and organically complexed nanocatalyst composition being introduced into a low oxygen zone of a coal burner.

32. A method as defined in claim 25, the coal burner being a low NO_x burner.

33. A method as defined in claim 25, the coal substrate comprising at least one member selected from the group consisting of anthracite coal, bituminous coal, subbituminous coal, and lignite coal.

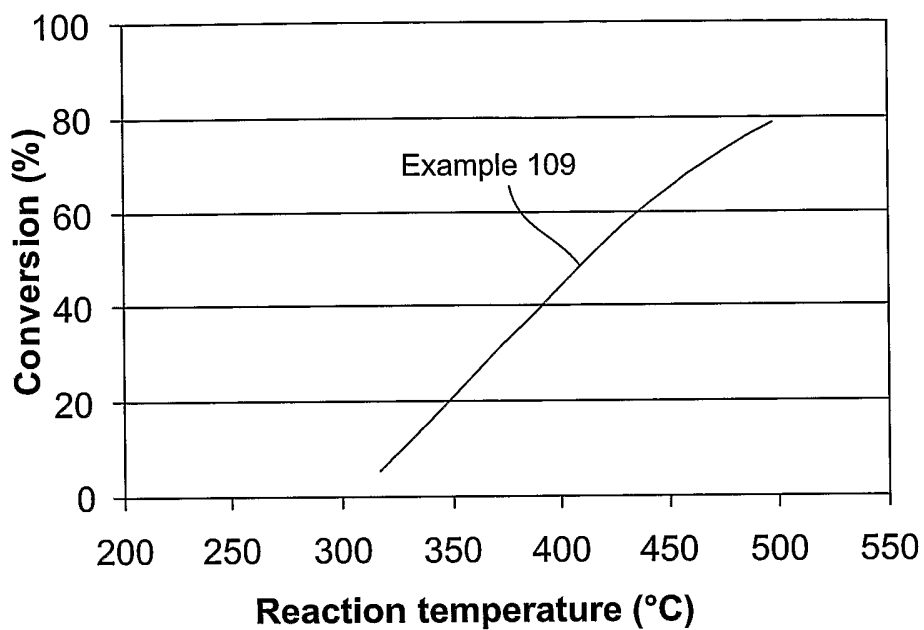
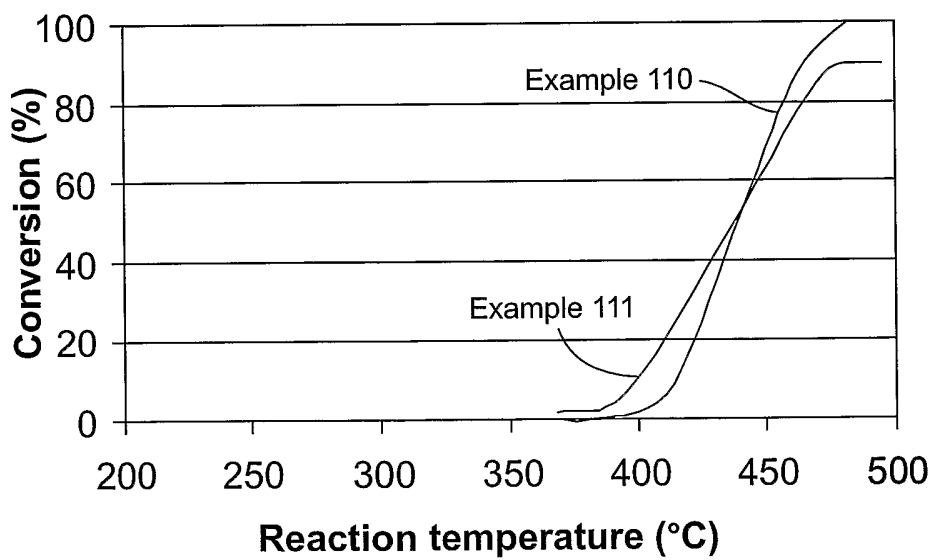
34. A method as defined in claim 25, the metal within the catalyst nanoparticles comprising at least one member selected from the group consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), Yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tin (Sn), Antimony (Sb), tungsten (W), and osmium (Os).

35. A method as defined in claim 34, the catalyst nanoparticles further comprising at least one member selected from the group consisting of noble metals, rare earth metals, alkaline metals, alkaline earth metals, and non-metals.

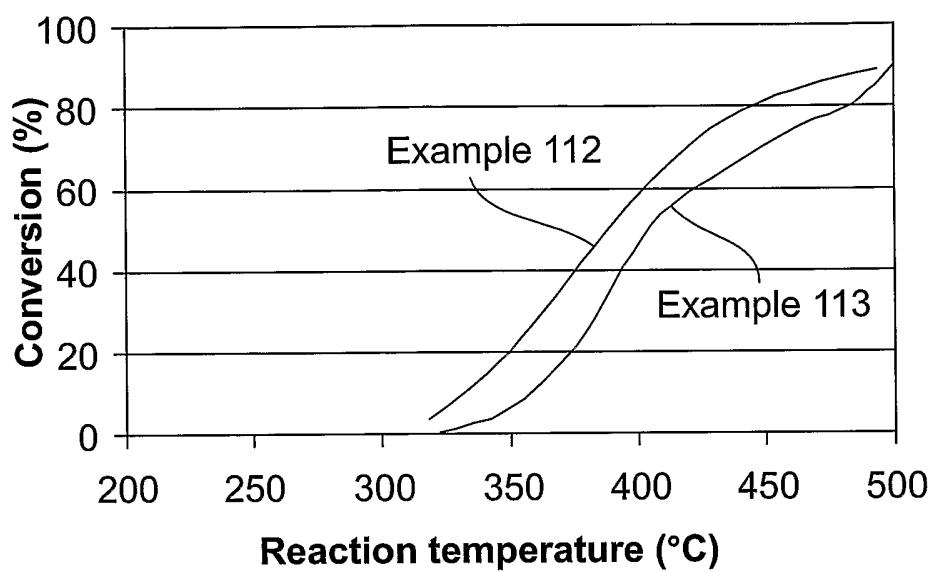
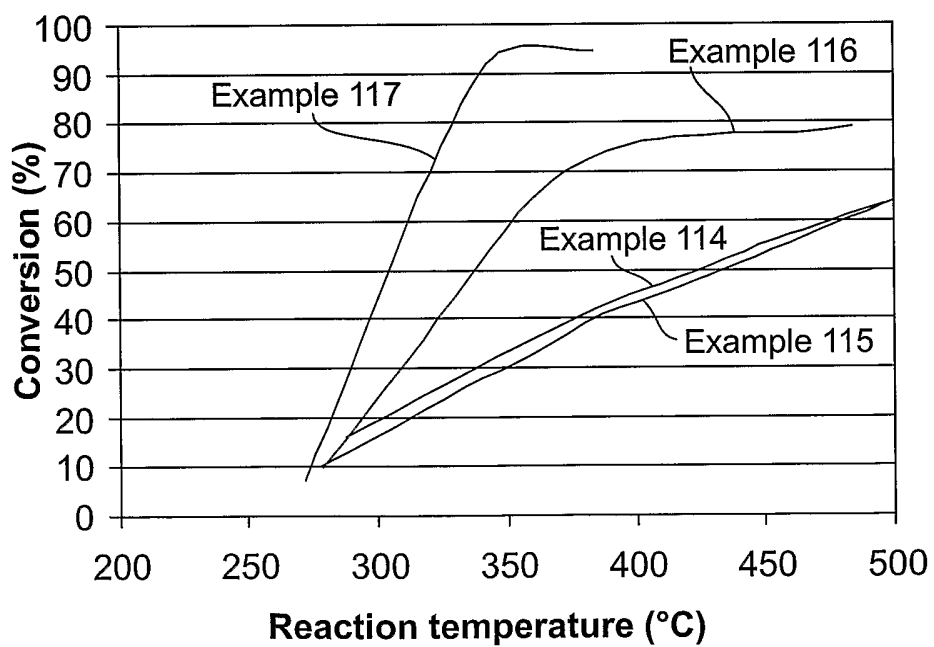
36. A method as defined in claim 25, the functional group capable of bonding to at least one metal atom comprising at least one member selected from the group consisting of a hydroxyl, a carboxyl, a carbonyl, an amine, an amide, a nitrile, a nitrogen having a free lone pair of electrons, an amino acid, a thiol, a sulfonic acid, a sulfonyl halide, and an acyl halide.

37. A method as defined in claim 25, the dispersing agent comprising at least one member selected from the group consisting of alcohols, dialcohols, carboxylic acids, dicarboxylic acids, hydroxy acids, sugars, polyfunctional carboxylic acids, amino acids, sulfonic acids, and silicon-based compounds.

38. A method as defined in claim 25, the catalyst nanoparticles having a size less than about 300 nm.

1 / 2**Fig. 1****Fig. 2**

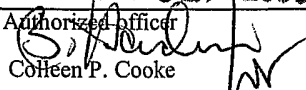
2 / 2

**Fig. 3****Fig. 4**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US06/09387

A. CLASSIFICATION OF SUBJECT MATTER IPC: B01D 53/56 (2006.01), 53/86 (2006.01); B01J 8/00 (2006.01), 23/00 (2006.01), 23/32 (2006.01), 23/02 (2006.01), 23/06 (2006.01) USPC: 423/235,237,239.1;502/302,305,324,325,340,344,349,353 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. : 423/235,237,239.1; 502/302,305,324,325,340,344,349,353 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 <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A,P</td> <td>US 20050109356 A1 (REDDY et al.) 26 May 2005 (26.05.2005), entire document.</td> <td>1-38</td> </tr> <tr> <td>A,P</td> <td>US 2005/0108925 A1 (Jurung et al.) 26 May 2005 (26.05.2005), entire document.</td> <td>1-38</td> </tr> <tr> <td>A</td> <td>US 6716525 B1 (YADAV et al.) 06 April 2004 (06.05.2004), entire document.</td> <td>1-38</td> </tr> <tr> <td>A,P</td> <td>US 6,746,597 B2 (ZHOU et al.) 08 June 2004 (08.06.2004), entire document.</td> <td>1-38</td> </tr> </tbody> </table>			Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A,P	US 20050109356 A1 (REDDY et al.) 26 May 2005 (26.05.2005), entire document.	1-38	A,P	US 2005/0108925 A1 (Jurung et al.) 26 May 2005 (26.05.2005), entire document.	1-38	A	US 6716525 B1 (YADAV et al.) 06 April 2004 (06.05.2004), entire document.	1-38	A,P	US 6,746,597 B2 (ZHOU et al.) 08 June 2004 (08.06.2004), entire document.	1-38
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<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																	
<table border="0"> <tr> <td> * 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 </td> <td> "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 "&" document member of the same patent family </td> </tr> </table>			* 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 "&" document member of the same patent family													
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Date of the actual completion of the international search 20 July 2006 (20.07.2006)		Date of mailing of the international search report 18 SEP 2006															
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