Nanoparticles For Soot Reduction [Div]

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ABSTRACT

Novel nano-sized rare earth metal oxide prepared from aqueous reverse micelles is provided. The engineered nanoparticles have large surface area to volume ratios, and sufficient oxygen vacancies on the surface of each particle, so that when mixed with carbon-containing combustible fuels, the particles remain suspended indefinitely; there is a significant reduction in soot and other by-products of combustion, an increase in engine efficiency and less fuel consumed per mile traveled in various vehicles, such as, but not limited to, automobiles, defense vehicles, airplanes, ships and other surface or air-bearing vehicles.

8 Claims, 10 Drawing Sheets
Nucleation

Growth

Fig. 2
Fig. 4
Fig. 5
Fig. 6

$C_7H_8 + O_2 (\phi = 5), 98\% \text{ Ar}$

$1903 \text{ K}$

$0.82 \text{ atm}$

Reflected Shock Arrival
Figure 7

The graph shows the reaction of $C_7H_8 + O_2 (\phi = 5)$ with 98% Ar at 1903 K and 0.82 atm, and with CeO$_2$ at 1993 K and 0.90 atm. The [c]/[c]$_{total}$ ratio is plotted against time (µs) from 0 to 3000 µs.
Figure 8

Soot Yield at t = 2 ms

Baseline Data (no Ceria)

Mixtures w/Ceria

C\textsubscript{2}H\textsubscript{8} + O\textsubscript{2} (\(\phi = 5\))

98% Ar

0.85 atm

\([c]/[c]_{\text{ref}}\) at t = 2 ms

Temperature (K)

1500 1600 1700 1800 1900 2000 2100 2200
Preparing aqueous solution 110

Dissolving Surfactant 120

Combining with Nonpolar Solvent 130

Stirring Mixture 140

Treating with Hydrogen Peroxide 150

Allowing Nucleation and Nanoparticle growth 160

Mixing with Combustible Material 170

Figure 9
Figure 10

Mixing Nanoparticles within Hydrocarbon Fuel 210

Igniting Fuel 220
NANOPARTICLES FOR SOOT REDUCTION


FIELD OF THE INVENTION

This invention relates to petroleum and other fuel additives, in particular to methods for making and using a composition of matter comprising nano-sized rare earth metal oxides for use as an additive to reduce soot and the formation of pollutants during fuel combustion.

BACKGROUND AND PRIOR ART

Partial or incomplete combustion of hydrocarbon fuels results in atmospheric pollutants, such as soot, as well as carbon monoxide, and other gases considered toxic and mutagenic, such as the nitrogen oxides. The carbon-containing fuels form soot during the combustion process and are released as emissions, which are harmful to the environment and the health and safety of living beings.

A variety of approaches have focused on reducing the emission of such condensed particles, hereinafter designated as “soot,” whether carbon-based or other type of condensed material. One approach has been to develop a comprehensive emission control system involving the combustion and fuel injection process, the fuel composition, and the overall control strategy for the combined operation of the engine that inhibits the formation of unacceptable emission products. Another approach has been to develop devices, such as catalytic converters, particulate traps, filters and systems that treat exhaust products after their formation. Thus, the challenge is viewed as preventing the formation of soot or collecting and destroying soot after it has formed.

With regard to the use of additives or materials, including rare earth metal oxides and particularly ceria (cerium oxide), in emission control systems, U.S. Pat. No. 6,093,223 to Lemaitre et al. discloses burning a combustible material or fuel after the addition of a concentrated solution of cerium compounds in ranges of from 50 to 150 parts per million (ppm) to reduce the formation of soot, or alternatively, producing aggregates of ceric oxide by burning a hydrocarbon fuel in the presence of a seed amount of ceric oxide crystallites.

U.S. Pat. No. 6,680,279 B2 to Cai et al. discloses a method of dispersing nanosized catalyst particles on the surface of larger catalyst carrier particles, which include cerium oxide mixed with alumina to increase oxygen storage capacity, for automotive exhaust gas treatment or for a fuel cell reformer. U.S. Pat. No. 6,660,683 B1 to Yudin et al. describes a particulate composition comprising acidic metal oxide, alkaline earth metal, an oxygen storage component, such as cerium oxide, and a noble metal component for the reduction of nitrous oxides in refinery processes. U.S. Pat. No. 6,588,204 B2 to Hirota et al. describes a particulate filter in an exhaust system wherein a noble metal catalyst and an active oxygen-releasing agent (such as ceria) are used to oxidize and remove the particulates trapped in the filter. There is also a method for treating the atmosphere to remove pollutants as disclosed in U.S. Pat. No. 6,616,903 B2 to Poles et al. Poles et al. equips billboards, solar panels or similar outdoor devices with catalysts on ceria support to convert pollutants to non objectionable materials or adsorption compositions to collect pollutants for later destruction.

However, the above-mentioned references use ceria crystallites, aggregates, particles and nanoparticles of a different size and oxygen storage capability than the ceria nanoparticles of the present invention. The ceria nanoparticles disclosed herein have been engineered for use in a liquid, gaseous or solid fuel and prevent the formation of soot or other objectionable pollutants during combustion.

Governmental concern for the harmful effects of soot on the environment, including the health and safety of all life forms, leads to worldwide regulations enacted to reduce both particulate matter (soot) and nitrogen oxides. In the United States alone, there are regulatory measures mandating a 98.3% reduction in 1990 allowable levels for particulate emissions from on-road vehicles by the year 2007. Smog and particulate matter account for 15,000 premature deaths and 400,000 asthma attacks annually in the US.

There is a need to identify the best technology to address emissions reduction, engine efficiency and fuel consumption issues. None of the prior art methods, processes, and devices is deemed satisfactory. Prior methods have difficulty when combining the emissions-reducing additive with the fuel due to incompatibility and settling issues.

SUMMARY OF THE INVENTION

A primary objective of the present invention is to provide compositions with an oxygen storage capability that can be combined with hydrocarbon fuels and reduce soot formation/emissions during the combustion of carbon-containing fuel or other combustible materials.

A secondary objective of the present invention is to provide nano-sized particles with an oxygen storage capability and methods for obtaining more miles per gallon of fuel consumed by vehicles, such as automobiles, defense vehicles, airplanes, ships and the like.

A third objective of the present invention is to provide nano-sized particles of a rare earth metal oxide using a microemulsion technique, thereby producing large surface area to volume ratio.

A fourth objective of the present invention is to provide nano-sized particles of a rare earth metal oxide using a microemulsion technique, thereby producing an extensive array of oxygen vacancies on the surface of each particle.

A fifth objective of the present invention is to provide methods for evenly dispersing the nano-sized particles in liquid carbon-containing combustible materials by producing agglomerate-free nanoparticles that are uniformly suspended in fuel-compatible mixtures.

A sixth objective of the present invention is to provide methods for enhancing the oxygen storage capability of rare earth metal oxides, including but not limited to, ceria, but by doping ceria with other lanthanides such as, lanthanum, neodymium and preferably, mixtures thereof.

A seventh objective of the present invention is to provide compositions and methods for improving engine efficiency for vehicles fueled by carbon-containing combustible materials, such as gasoline, diesel, and jet fuels.

An eighth objective of the present invention is to provide compositions and methods for improving or obtaining complete oxidation of carbon, thereby reducing soot and other oxidation by-products.

A ninth objective of the present invention is to provide a uniformly dispersed additive that oxidizes the polyaromatic hydrocarbons, precursors to soot formation, before they can form solid carbon particles (i.e., soot). The particles will act
metal oxides with large surface area to volume ratios, and monomer stage, when it would otherwise form without the additive.

A tenth objective of the present invention is to provide a ceria-based additive for liquid hydrocarbon fuels; the ceria particles are less than approximately 5 nm in diameter and remain uniformly dispersed within the fuel, with no agglomeration or settling. The carrier liquid for the particles is also compatible with hydrocarbon fuels.

An eleventh objective of the present invention is to provide a ceria nanoparticle additive that can be introduced into a gaseous fuel or oxidizer using an appropriate carrier fluid for the particles and fluid mechanics techniques, such as spray injection or vaporization.

A twelfth objective of the present invention is to provide a ceria nanoparticle additive that can be introduced into a heterogeneous solid propellant using an appropriate mixing technique commonly utilized to make said heterogeneous solid propellant.

A fourteenth objective of the present invention is to apply the additive to a solid fuel, such as coal, refuse, or wood by spraying onto the surface or mixing by agitation before curing and venting off the carrier liquid using an appropriate distillation method.

A fifteenth objective of the present invention is to apply the additive to non-hydrocarbon propellants. Examples include silicon-containing fuels, oxidizers, and monopropellants that also may form condensed particles, also called soot, but are not carbon based.

The present invention provides novel nano-sized rare earth metal oxides with large surface area to volume ratios, and sufficient oxygen vacancies on the surface of each particle, so that when mixed with carbon-containing or other soot-forming combustible fuels, there is a significant reduction in soot by-products during the combustion process, an increase in engine efficiency, and less fuel consumption per mile traveled. Less soot production also leads to a reduction of harmful emissions in the environment.

Further objects and advantages of this invention will be apparent from the following detailed description of the presently preferred embodiments, which are illustrated schematically in the accompanying drawings.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1A shows an initial step of adding aqueous cerium nitrate to a non-polar solution with a surfactant to form reverse micelle for the synthesis of ceria nanoparticles.

FIG. 1B shows the formation of nano-sized micelles.

FIG. 1C is an enlarged drawing of one micelle showing aqueous precursor solution surrounded by coordinated surfactant molecules.

FIG. 2 shows the sequence of particle formation in the synthesis of ceria nanoparticles that are less than 10 nanometer (nm) in diameter; preferably in a range from approximately 4 nm to approximately 7 nm in diameter.

FIG. 3 is high resolution transmission electron microscopy (HRTEM) image of non agglomerated ceria particles having spherical morphology with particle size of approximately 5 nanometers (nm) in diameter for non-agglomerated ceria sol prepared and stabilized using hydrogen peroxide.

FIG. 4 shows an arrangement of equipment for combustion experiments with toluene and toluene and ceria mixtures.
polar solvent, the dropwise addition of hydrogen peroxide causes the formation of the oxide nanoparticles capable of significant reductions in soot formation during combustion of fuels. Specific quantities of reactants are given below.

Cerium oxide nanoparticles of a size approximately 2 nm to approximately 10 nm in diameter, are prepared by a process including the steps of dissolving approximately 0.5 grams to approximately 1.0 grams of Ce(NO₃)₁₂·6H₂O in deionized water to make approximately 10 ml of solution to form a first solution, followed by dissolving approximately 3 grams to approximately 4 grams of AOT (surfactant) in approximately 200 ml of solvent to form a second solution, followed by combining the first and the second solutions, followed by stirring the combined solutions for approximately 30 minutes, and dropwise adding approximately 30% hydrogen peroxide (H₂O₂) until the stirred combined solution becomes yellow, and subsequently stirring for approximately 30 minutes to approximately 60 minutes more.

The surfactant molecules are influenced by the water molecules to form micelles and changing the water and surfactant ratio can control the size of the micelles. The aqueous solution of rare earth metal salt is then confined to the nano-sized micelles of surfactant forming nano-reactors. When hydro­gen peroxide is added to the solution, it penetrated the micelle to react with cerium nitrate to form ceria nano particles. The reaction is represented as follows in equation 1:

\[
\text{Ce(NO}_3\text{)}_{12}+\text{H}_2\text{O}_2+\text{H}^+ +\text{(aq)} \rightarrow \text{CeO}_3+3\text{HNO}_3
\]

1.

Hydrogen peroxide also converts Ce³⁺ to Ce⁴⁺ as shown below in equation 2:

\[
\text{Ce}^{3+}+\text{H}_2\text{O}_2+2\text{H}^+ +\text{(aq)} \rightarrow \text{Ce}^{4+}+2\text{H}_2\text{O}
\]

2.

Ce⁴⁺ is the most stable state, however, having a mix of Ce³⁺ and Ce⁴⁺ is good because the nanostructure will have many vacancies, which can initiate catalytic reactions. Most of the Ce ions are present on the surface of the nanoparticles, for example approximately 75% for an approximately 2.6 nanometer (nm) particle. Thus, many sites are available for surface chemical reactions for the Ce ions. Oxygen vacancies are generated by such surface chemical reactions. During the surface chemical reactions, oxygen atoms from the ceria surface are taken away leading to non-stoichiometry CeO₂·x₂.

Thus, aqueous reverse micelles (RMs) are surfactant aggregates in nonpolar solvents that enclose packets of aqueous solution in their interior. The size of the water droplet can be tuned by varying the ratio of water to surfactant. RMs used as reaction media in the production of nanoparticles whose size and shape are controlled by water and surfactant ratio.

Referring now to FIG. 1A, in a suitable mixing vessel 10, approximately 0.5 grams (gm) of surfactant (AOT) 12 was dissolved in 50 milliliters (ml) of toluene 14 and approximately 2.5 ml of approximately 0.1 mole (M) cerium nitrate aqueous solution 16 was added. FIG. 1B shows several micelles of AOT molecules 20 are formed due to the polarity of the aqueous solution. FIG. 1C is an enlarged view of micelle 20 showing an aqueous precursor solution 22 surrounded by surfactant molecules 12 forming a nano-reactor.

The stepwise sequence of cerium oxide nanoparticle formation by single microemulsion process is shown in FIG. 2. Starting with a micelle 20, approximately 7.5 ml of approximately 30% hydrogen peroxide (H₂O₂) 25 is added to begin nucleation 27 and growth 29 in the presence of cerium dioxide nanoparticles. The solution obtained by the microemulsion process is used as is; no separation or other processing is involved.

FIG. 3 is an HRTEM image of ceria nanoparticles, prepared using the technique described above. The HRTEM image shows spherical particle 35 morphology with a uniform particle size distribution. The ceria nano particles are less than approximately 10 nanometers (nm) in diameter, preferably in a range from approximately 2 nm to approximately 7 nm with a mean size of approximately 5 nm.

FIG. 4 is an arrangement of equipment 40 for combustion experiments with toluene 42 and toluene and ceria mixtures premixed in a stainless steel mixing chamber 44 with approximately 98% argon gas (Ar) 46 and oxygen to the desired fuel/oxygen ratio, where φ represents the fuel/oxygen mass ratio relative to the stoichiometric fuel/oxygen ratio. The mixture is then introduced into the shock tube 48 where it is heated to combustion temperatures by a reflected shock wave. Fuel-rich mixtures (φ>1) are demonstrated herein but the experiments can be performed at any φ and any overall concentration.

FIG. 5 is the layout of a shock tube facility 50 used to perform combustion experiments using Helium-Neon laser 55 for the detection of soot 57. The shock-tube test section 59 receives a mixture containing fuel/oxygen/argon. The shock tube is used to quantify the effectiveness of the additive over a wide range of temperatures and mixture compositions. The fuel is toluene with or without ceria additive. The partial pressure of the toluene in the mixing tank is less than the vaporization pressure of toluene at room temperature. The mixture is introduced into the test section 59 as a gas. The operation of the shock tube and the method of introduction of the gas mixture into the tube are standard procedures and well known to those skilled in the art. The introduction of the ceria nano-particle additive does not depend on whether it is introduced with the fuel, oxidizer, or diluent, as it is only the final combustion mixture that matters.

An experimental technique used to monitor the level of soot formation behind reflected shock waves in the shock tube is the well-known laser extinction method, where the ratio of the transmitted (I) to incident (Io) laser light intensity is related to the number density of soot particles, N, via the Beer-Lambert law. The concentration of soot particles [c] is then obtained from the measured number density.

FIG. 6 shows the relative soot concentration as a function of time for a typical shock-tube experiment without ceria addition. The fuel-to-oxidizer equivalence ratio, φ, is defined as the actual fuel-to-oxidizer ratio divided by the stoichiometric fuel-to-oxidizer ratio. The soot concentration is normalized by the total concentration of carbon in the mixture, producing the soot yield. The soot yield at approximately 2 milliseconds is used as the point of comparison between mixtures with and without ceria.

FIG. 7 shows soot yield as a function of time with and without ceria addition. The soot yield is dramatically reduced for the case with ceria addition and is represented as a normalized value, relative to the total concentration of carbon in the mixture. After approximately 2 milliseconds, the ceria additive reduces the normalized soot yield to approximately 0.05, while the combustion of toluene without the ceria additive produced a normalized soot yield of approximately 0.22.

The use of the ceria additive resulted in over approximately 67% reduction in soot yield for the experimental results shown.

FIG. 8 shows soot yield after 2 milliseconds with and without ceria addition. Both Mix #1 and Mix #2 are the same toluene/argon compositions, but are separate mixtures made at different times to demonstrate repeatability. Soot yield is reduced approximately 84% at point 90, approximately 67% at point 92, and approximately 57% at point 94; thus, soot yield is reduced in all three instances by approxi-
FIG. 9 is a flowchart of method steps of providing nanosized particles into a combustible material. The method can include an efficient method of providing nano-sized particles, having excellent oxygen storage capability, that are uniformly incorporated into a combustible material and reduce soot formation during combustion of said material. The method steps can include the steps of preparing an aqueous solution of a rare earth metal salt and dissolving a surfactant in a nonpolar solvent, followed by mixing the aqueous solution of the rare earth metal salt with the nonpolar solvent and surfactant. Next, the mixture is stirred to form micelles, followed by treating the micelles with hydrogen peroxide, and allowing nucleation and growth of nanoparticles of a rare earth metal oxide, and mixing the rare earth metal oxide nano-particle reaction product with the combustible material prior to combustion.

FIG. 10 is a flowchart for enhanced fuel efficiency with nanosized particles. The efficient system for obtaining vehicular fuel efficiency can include the steps of mixing a solution of nano-sized particles of an oxygen storage component, such as cerium oxide nanoparticles, and a carrier liquid by agitating until the nano-sized particles are in uniform suspension within the hydrocarbon fuel, followed by igniting the fuel with the solution of nano-sized particles.

The following methods and techniques can be used to introduce the oxide nanoparticles of the present invention to combustible materials that currently produce soot and other particulate matter polluting the environment.

For a gaseous fuel, the ceria nanoparticles can be introduced into the combustion chamber via the air stream if an air-intake apparatus is used. A suitable fluid mechanics technique, such as, but not limited to, spray injection or vaporization, can be used for uniform dispersion of the nanoparticle solution in a gaseous fuel.

In a liquid fuel, the ceria nanoparticles can be introduced into a liquid oxidizer using an appropriate carrier fluid for the particles, such as toluene or octane to form a nanoparticle solution, which is mixed by agitation into the fuel.

In addition, for solid propellant and solid fuels, such as coal, rocket fuel, refuse, or wood, the ceria nanoparticles can be added to the solid fuel as a solution, comprising the nanoparticles and a hydrocarbon carrier liquid. The nanoparticle solution can be either sprayed onto the fuel or homogeneously mixed into the fuel during manufacture. The volatile carrier liquid is then removed by vaporization, curing, venting, or similar method, leaving only the nano-particle/solid fuel blend.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:

1. An efficient system and process for obtaining vehicular fuel efficiency, comprising:

   adding an oxygen storage component consisting of a plurality of agglomerate-free, spherical nano-sized particles wherein the particle size is less than approximately 10 nanometers (nm) in diameter to a carrier liquid for the plurality of nano-sized particles to facilitate combustion of fuel;
   adding a hydrocarbon fuel to the carrier liquid containing nano-sized particles;
   mixing the plurality of nano-sized particles with the carrier liquid and the hydrocarbon fuel by agitating until the plurality of nano-sized particles are suspended uniformly in the hydrocarbon fuel; and
   igniting the mixture of hydrocarbon fuel and the uniformly suspended nano-sized particles wherein the mixture is combusted in a vehicular combustion chamber thereby obtaining a reduction in soot and by-products of combustion and an increase in fuel efficiency.

2. The system and process of claim 1 wherein the oxygen storage component consists of cerium oxide nanoparticles.

3. The system and process of claim 2 wherein the cerium oxide nanoparticles are in a size range from approximately 3 nanometers (nm) to approximately 7 nanometers (nm).

4. The system and process of claim 2 wherein the cerium oxide nanoparticles are in a size range between approximately 2 nanometers (nm) to approximately 5 nanometers (nm).

5. The system and process of claim 1 wherein the carrier liquid is a non-polar solvent.

6. The system and process of claim 5 wherein the carrier liquid is selected from the group consisting of toluene and octane.

7. The system and process of claim 1 wherein the combustion chamber is in the engine of a vehicle selected from at least one of an automobile, a defense vehicle, an airplane, and a ship.

8. An efficient system for obtaining vehicular fuel efficiency, comprising:

   adding an oxygen storage component consisting of a plurality of non-agglomerated, spherical nano-sized cerium oxide particles wherein the particle size is less than approximately 5 nanometers (nm) in diameter with oxygen vacancies on the surface of each particle and having a plurality of cerium (Ce) ions present on the surface of the nanoparticles providing sites available for surface chemical reactions of the Ce ions to a carrier liquid;
   adding a hydrocarbon fuel to the carrier liquid containing nano-sized cerium oxide particles;
   mixing the plurality of cerium oxide particles with the carrier liquid and the hydrocarbon fuel by agitating until the plurality of nano-sized particles are suspended uniformly in the hydrocarbon fuel; and
   igniting the mixture of hydrocarbon fuel and the uniformly suspended cerium oxide nanoparticles wherein the mixture is combusted in a vehicular combustion chamber thereby obtaining an approximately 60% to approximately 85% reduction in soot and by-products of combustion and obtaining vehicular fuel efficiency.

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