

(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2005/0121044 A1

Banerjee et al. (43) Pub. Date:

> (22) Filed: Dec. 9, 2003

(54) CATALYSTS COMPRISING ULTRAFINE **PARTICLES**

(76) Inventors: Chandra Kumar Banerjee, Clemmons, NC (US); Stephen Benson Sears, Siler City, NC (US); Stephen Keith Cole, Winston-Salem, NC (US); Sheila Lynnette Cash, Greensboro, NC (US)

> Correspondence Address: Charles W. Calkins, Esq. Kilpatrick Stockton LLP 1001 West Fourth Street Winston-Salem, NC 27101-2400 (US)

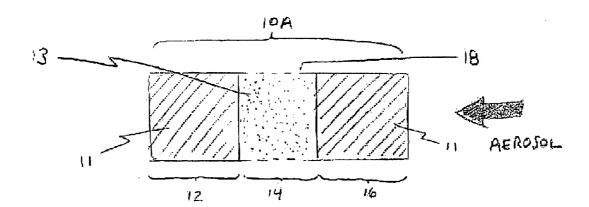
10/730,962 (21) Appl. No.:

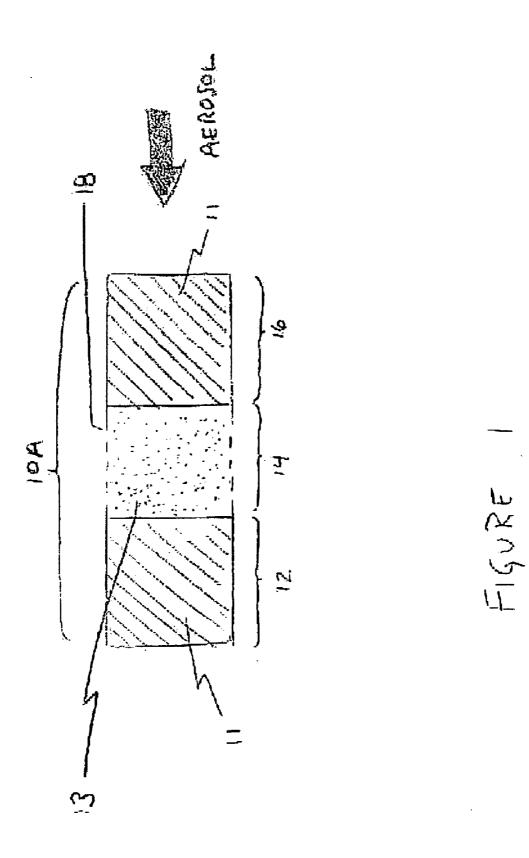
Jun. 9, 2005

Publication Classification

(57)**ABSTRACT**

The present invention provides catalyst compositions, articles of manufacture incorporating the catalyst compositions and methods for producing catalyst compositions. The catalyst compositions comprise a substrate and ultrafine particles. Disclosed articles of manufacture include filter apparatus, such as those utilized in gas masks or smoking articles. Also disclosed are smoking articles comprising the catalyst compositions of the present invention.





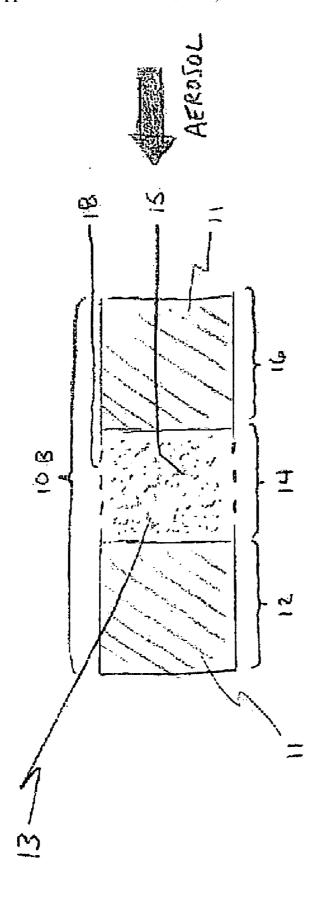
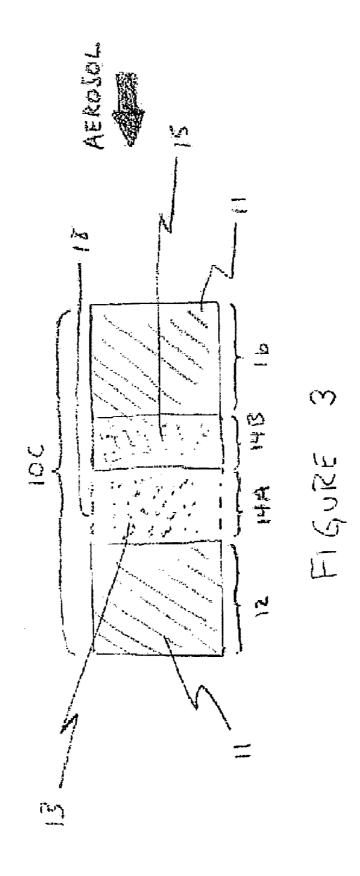


FIGURE 2



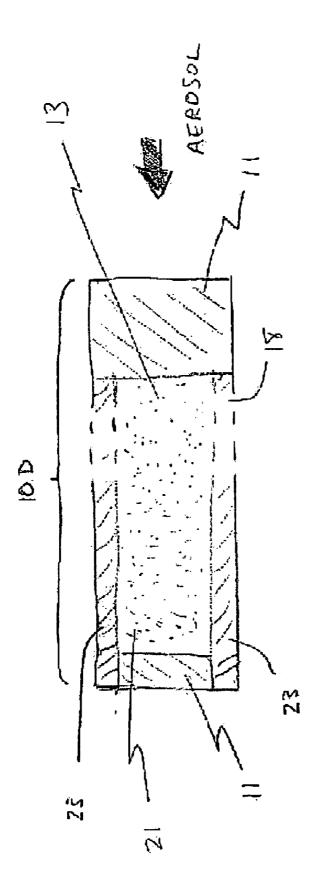
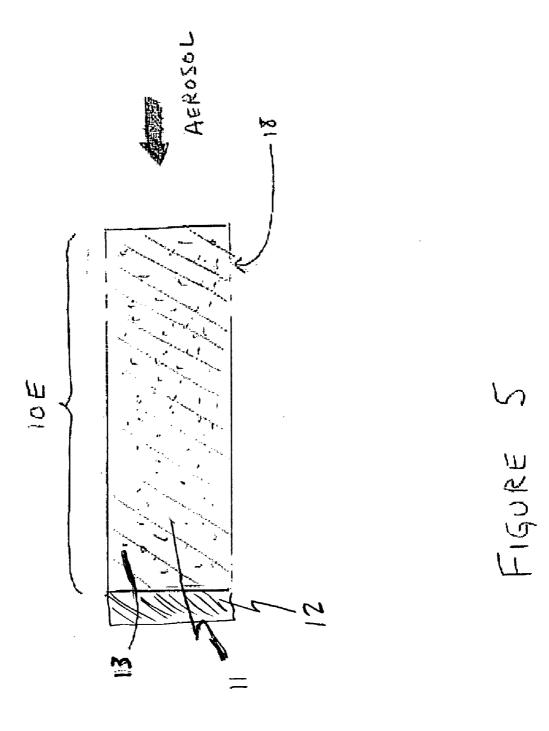


FIGURE 4



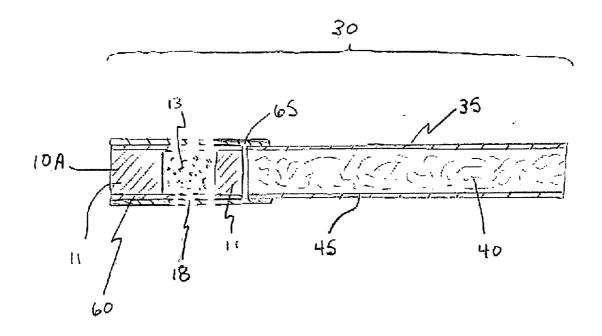
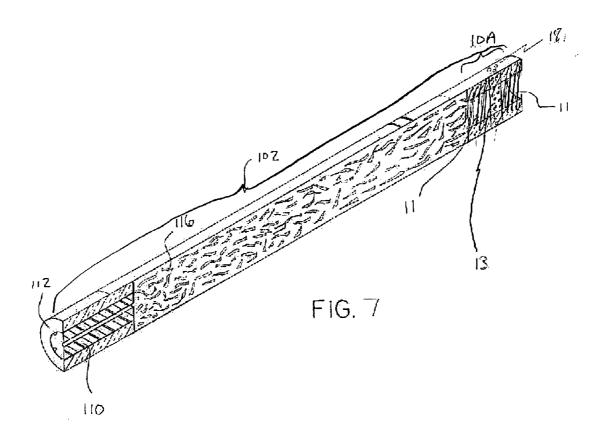


FIGURE 6



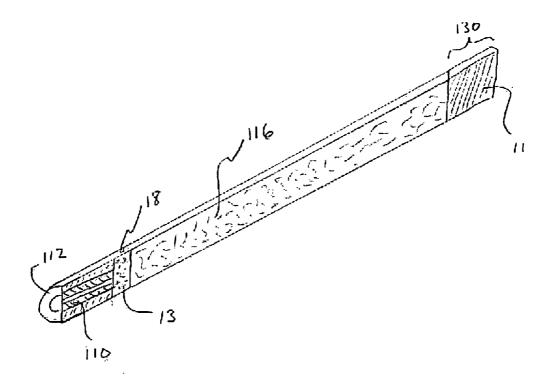
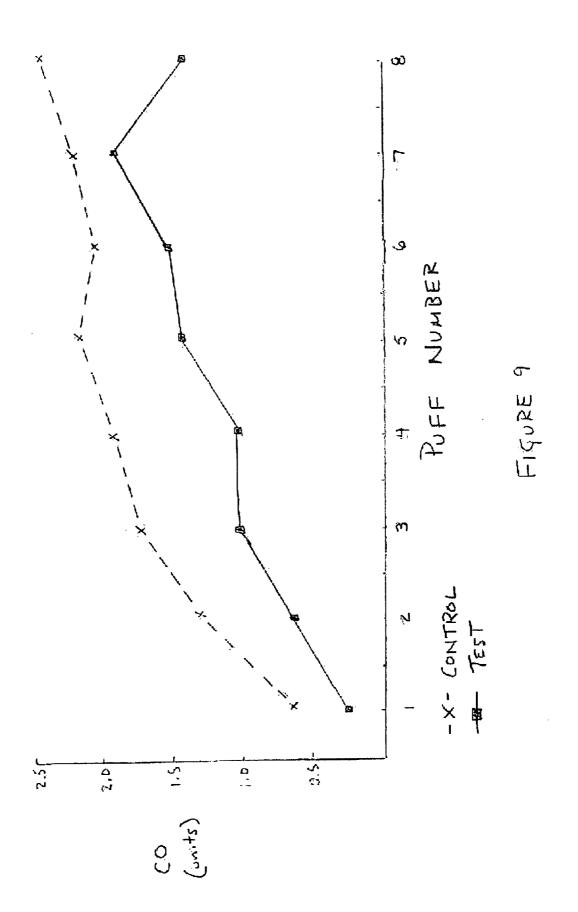


FIGURE B



CATALYSTS COMPRISING ULTRAFINE PARTICLES

FIELD OF THE INVENTION

[0001] The present invention relates generally to catalyst compositions, and more particularly to catalyst compositions comprising ultrafine particles. Embodiments of the present invention are useful in catalyzing reactions in aerosol/gaseous media. In an embodiment, the catalyst compositions may be utilized in a smoking article to reduce the amount of gas phase components, for example carbon monoxide, in the cigarette smoke.

BACKGROUND OF THE INVENTION

[0002] The terminology "catalyst" is generally used to define a substance, usually used in small amounts relative to the reactants, that increases the rate of a reaction without being consumed in the process. Catalysts are widely utilized in process chemistry and have been used to catalyze reactions occurring in a gaseous stream or aerosol. Catalyst compositions have been used in smoking articles to catalyze reactions in the aerosol/gaseous stream flowing through the smoking article.

[0003] Cigarettes are popular smoking articles that use tobacco in various forms. Descriptions of cigarettes and the various components thereof are set forth in *Tobacco Production, Chemistry and Technology*, Davis et al. (Eds.) (1999).

[0004] Cigarettes generally include a substantially cylindrical rod-shaped structure and include a charge, roll or column of smokeable material such as shredded tobacco (e.g., in cut filler form) surrounded by a paper wrapper thereby forming a so-called "tobacco rod." Normally, a cigarette has a cylindrical filter element aligned in an end-to-end relationship with the tobacco rod. Typically, a filter element includes cellulose acetate tow circumscribed by plug wrap, and is attached to the tobacco rod using a circumscribing tipping material. It also has become desirable to perforate the tipping material and plug wrap, in order to provide dilution of drawn mainstream smoke with ambient air.

[0005] Cigarettes and cigarette-like tobacco articles are employed by the smoker by lighting one end thereof and burning the tobacco rod, or igniting the heat source and aerosolizing components in the aerosol-generating rod. The smoker then receives mainstream smoke into his/her mouth by drawing on the opposite end (i.e., the filter end) of the cigarette.

[0006] Numerous cigarettes and cigarette-type smoking articles that employ carbonaceous components have been proposed. Examples of such smoking articles are set forth in U.S. patent application Ser. No. 10/382,244, entitled "Smoking Articles Comprising Ultrafine Particles" and filed on Mar. 5, 2003, which is hereby incorporated by reference. Cigarettes having carbonaceous combustible material components have been marketed by R. J. Reynolds Tobacco Company under the tradenames Premier and Eclipse. It has also been suggested to incorporate catalytic materials into the carbonaceous combustible material components of certain types of smoking articles. See, for example, U.S. Pat. No. 5,040,551 to Schlatter et al.; U.S. Pat. No. 5,211,684 to

Shannon et al.; U.S. Pat. No. 5,240,014 to Deevi et al.; and U.S. Pat. No. 5,258,340 to Augustine et al. The disclosure of each of these patents is incorporated herein by reference.

[0007] Catalysts have been utilized in cigarettes to alter the chemistry of the cigarette smoke. The use of catalysts in cigarettes is described in U.S. Pat. Nos. 4,182,348 to Seehofer et al.; and U.S. Pat. No. 6,286,516 to Bowen et al. (treatment of sidestream smoke). The disclosure of each of these patents is incorporated herein by reference.

[0008] There have also been other attempts to modify the chemistry of cigarette smoke. U.S. patent Publication 2003/0188758 to Hajaligol et al., the disclosure of which is hereby incorporated herein by reference, discloses the use of an oxyhydroxide compound in a cigarette.

[0009] Certain cigarettes have filter elements which incorporate materials such as carbon. Exemplary cigarettes and filters are described in U.S. Pat. No. 2,881,770 to Tovey; U.S. Pat. No. 3,353,543 to Sproull et al.; U.S. Pat. No. 3,101,723 to Seligman et al.; and U.S. Pat. No. 4,481,958 to Ranier et al. and European Patent Application Nos. 532,329 and 608,047. Certain commercially available filters have particles or granules of carbon (e.g., an activated carbon material or an activated charcoal material) dispersed within cellulose acetate tow; other commercially available filters have carbon threads dispersed therein; while still other commercially available filters have so-called "cavity filter" or "triple filter" designs. Exemplary commercially available filters are available as SCS IV Dual Solid Charcoal Filter from American Filtrona Corp.; Triple Solid Charcoal Filter from FIL International, Ltd.; Triple Cavity Filter from Baumgartner Papiers Holding SA; and ACT from FIL International, Ltd. See also, Clarke et al., World Tobacco, p. 55 (November 1992). Detailed discussion of the properties and composition of cigarettes and filters is found in U.S. Pat. No. 5,360,023 to Blakley et al.; U.S. Pat. No. 5,404,890 to Gentry et al.; U.S. Pat. No. 5,568,819 to Gentry et al.; and U.S. Pat. No. 6,537,186 to Veluz, which are hereby incorporated by reference.

[0010] Various annular configurations of filters having carbon-bearing annular filter regions are disclosed in the prior art. For example, European Patent Application No. 579,410 shows a number of cigarette embodiments having an annular carbon-bearing region surrounding either porous filtration material or an empty tubular cavity formed by a vapor-phase-porous membrane. Similarly, U.S. Pat. No. 3,894,545 to Crellin et al. shows various configurations of annular carbon-bearing regions surrounding a vapor-phase-porous membrane or a rod of carbon-bearing material surrounded by a vapor phase porous membrane.

[0011] Cigarette filter elements which incorporate carbon have the ability to change the character of mainstream smoke which passes therethrough. For example, such filter elements have the propensity to reduce the levels of certain gas phase components present in the mainstream smoke, resulting in a change in the organoleptic properties of that smoke. However, such filter elements often incorporate relatively high levels of carbon (e.g., in particulate form), and/or are longitudinally segmented in format and configuration. As such, filter elements incorporating carbon require numerous and labor intensive processing steps; and cigarettes incorporating such filter elements often can be characterized as having slightly metallic, drying and powdery flavor characteristics.

[0012] U.S. patent Publication No. 2002/0014453, to Lilly et al., the disclosure of which is hereby incorporated herein by reference, proposes the removal of unsaturated hydrocarbons from mainstream smoke using nano-clusters, which selectively remove gaseous components such as 1,3 butadiene, isoprene, and toluene from the mainstream smoke. While the nano-clusters described in this publication purportedly remove certain classes of gaseous components, such nano-clusters may not be effective catalysts for other components, for example the conversion of carbon monoxide to carbon dioxide in a cigarette filter.

[0013] U.S. patent Publication No. 2003/0131859 to Li et al., the disclosure of which is hereby incorporated herein by reference, proposes the use of nanoparticle additives capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide and/or catalyst for the conversion of hydrocarbons, aldehydes, or phenolic compounds to carbon dioxide and water. The nanoparticle additives described in this publication act as catalysts/oxidants at temperatures of 150 C or higher and are described as being effective in the combustion and pyrolysis regions of the cigarette.

[0014] U.S. patent Publication No. 2003/0075193 to Li et al., the disclosure of which is hereby incorporated herein by reference, proposes the use of nanoparticle additives capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide and/or as a catalyst for the conversion of carbon monoxide to carbon dioxide. The nanoparticle additives described in this publication act as catalysts/oxidants at temperatures of 150 C or higher and are described as being effective in the combustion and pyrolysis regions of the cigarette. The nanoparticle additives are incorporated into the cut filler used in the tobacco rod.

[0015] Despite the developments to date, there remains a need for improved and more efficient methods and compositions for altering the gas phase components in the mainstream smoke of a smoking article. It would be desirable for such methods and compositions to catalyze or oxidize carbon monoxide to carbon dioxide in mainstream eigarette smoke at temperatures which do not require excess heat to drive the conversion process.

SUMMARY OF THE INVENTION

[0016] The present invention provides catalyst compositions; articles of manufacture, including, but not limited to: smoking articles, catalyst apparatus, and filter apparatus comprising catalyst compositions; and methods for producing catalyst compositions. The catalyst compositions are useful in a variety of applications, particularly in applications involving catalysis of reactions in a gaseous or aerosol medium. Embodiments of the catalyst compositions of the present invention are advantageous for use in smoking articles; and may be particularly advantageous for use in the filter elements of smoking articles. Embodiments of the catalyst compositions of the present invention are also advantageous for use in other filter apparatus.

[0017] In an aspect, the present invention provides a catalyst composition comprising a substrate and ultrafine particles. The choice of substrate and/or ultrafine particles, including the sizes and physical structures of each, may be

made based on the chemical reaction to be catalyzed and the environment in which the reaction will take place.

[0018] In another aspect, the present invention provides articles of manufacture comprising catalyst compositions. An embodiment of the present invention is a smoking article comprising catalyst compositions. In certain embodiments, a filter element of the smoking article comprise catalyst compositions. In other embodiments, other component parts of the smoking article comprise catalyst compositions. Another embodiment of an article of manufacture of the present invention is a filter apparatus comprising catalyst compositions. A further embodiment of an article of manufacture of the present invention is a catalyst apparatus comprising catalyst compositions.

[0019] In a further aspect, the present invention provides methods for producing catalyst compositions. The methods of the present invention may be utilized to produce catalyst compositions of the present invention, and/or may be utilized to produce other useful catalyst compositions.

[0020] Further details relating to the present invention, and its advantages, are set forth in the following sections.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 provides a perspective view of an embodiment of a filter element of the present invention.

[0022] FIG. 2 provides a perspective view of another embodiment of a filter element of the present invention.

[0023] FIG. 3 provides a perspective view of an additional embodiment of a filter element of the present invention.

[0024] FIG. 4 provides a perspective view of a further embodiment of a filter element of the present invention.

[0025] FIG. 5 provides a perspective view of a still further embodiment of a filter element of the present invention.

[0026] FIG. 6 provides a perspective view of an embodiment of a smoking article of the present invention.

[0027] FIG. 7 provides a perspective view of another embodiment of a smoking article of the present invention.

[0028] FIG. 8 provides a perspective view of a further embodiment of a smoking article of the present invention.

[0029] FIG. 9 provides a graphical plot illustrating efficiency of a catalyst composition of the present invention in converting carbon monoxide to carbon dioxide.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS

[0030] The present invention provides catalyst compositions comprising ultrafine particles. The present invention also provides articles of manufacture comprising catalyst compositions of the present invention. Included among the articles of manufacture are filter apparatus and catalyst apparatus. Also included are smoking articles. In an embodiment, the present invention provides catalyst compositions that catalyze reactions in and/or among gas phase components in mainstream smoke from a smoking article, for example, the conversion of carbon monoxide to carbon dioxide. Further, the present invention provides methods for producing catalyst compositions comprising ultrafine particles.

[0031] Reference is made below to specific embodiments of the present invention. Each embodiment is provided by way of explanation of the invention, not as a limitation of the invention. In fact, it will be apparent to those skilled in the art that various modifications and variations can be made in the present invention without departing from the scope or spirit of the invention. For instance, features illustrated or described as part of one embodiment may be incorporated into another embodiment to yield a further embodiment. Thus, it is intended that the present invention cover such modifications and variations as come within the scope of the appended claims and their equivalents.

[0032] For the purposes of this specification, unless otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions, and so forth used in the specification are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification are approximations that can vary, depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

[0033] Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviation found in their respective testing measurements. Moreover, all ranges disclosed herein are to be understood to encompass any and all subranges subsumed therein, and every number between the end points. For example, a stated range of "1 to 10" should be considered to include any and all subranges between (and inclusive of) the minimum value of I and the maximum value of 10; that is, all subranges beginning with a minimum value of 1 or more, e.g., 1 to 6.1, and ending with a maximum value of 10 or less, e.g., 5.5 to 10, as well as all ranges beginning and ending within the end points, e.g., 2 to 9, 3 to 8, 3 to 9, 4 to 7, and finally to each number 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 contained within the range. Additionally, any reference referred to as being "incorporated herein" is to be understood as being incorporated in its entirety.

[0034] It is further noted that, as used in this specification, the singular forms "a," an," and "the" include plural referents unless expressly and unequivocally limited to one referent.

[0035] An aspect of the present invention is catalyst compositions comprising a substrate component and ultrafine particles. The ratio, by weight, of ultrafine particles to substrate may be varied based on the reaction to be catalyzed. Typically a catalyst composition of the present invention will comprise 51-99%, by weight substrate and 1-49%, by weight ultrafine particles. In certain embodiments a catalyst composition of the present invention will generally comprise greater than 50%, by weight, substrate, often greater than 80%, by weight, substrate, or greater than 90%, by weight, substrate, or even greater than 95%, by weight substrate with the remainder, or a substantial portion of the remainder comprising ultrafine particles.

[0036] The substrate component of the catalyst composition of the present invention may comprise a metal oxide; a ceramic; a metal; an alloy; a zeolite; a polymer; a carbon-containing material and/or other materials. The substrate may be inert with respect to the reaction being catalyzed, or in certain embodiments, play an active role in the catalysis. A purpose of the substrate in particular embodiments of the present invention is to provide a location to physically immobilize ultrafine particles. The substrate may also assist in catalysis by providing dissociative oxygen for an oxidation reaction.

[0037] The substrate component of the catalyst composition of the present invention may take many forms with porous or non-porous surfaces including, but not limited to, substantially spherical; ovoid, polygonal (eg. cubical), and/or undefined amorphous granules; particles; planar forms/sheets; webs; screens/mesh forms and/or fiber forms. and the like. It is generally advantageous to use physical shapes or forms that increase the contact surface area between the ultrafine particle component of the catalyst composition and a gaseous stream.

[0038] Substrates with large surface areas, BET surface areas of 0.1 to 3000 m²/g are generally preferred. Methods of determining BET surface area are well known and described, for example, in U.S. Pat. No. 4,947,874, to Brooks et. al., the disclosure of which is incorporated herein by reference. As used herein the surface area refers to a nominal surface area as determined by known analytical techniques.

[0039] In embodiments utilizing granular substrates, the substrate may have an average particle diameter of 0.05 mm to 2 mm, preferably 0.2 mm to 1.5 mm, more preferably 0.5mm to 1 mm. It is generally advantageous for a substrate to have sufficient surface area to promote contact between an ultrafine particle located on the substrate and mainstream smoke. As set forth above, in embodiments of the present invention, the nominal surface area of the substrate may range from 0.1 to 3000 m²/g, preferably 50 to 1000 m²/g as determined by ASTM Test Procedure C1274-00.

[0040] The physical form of the substrate may be selected based on the intended use of the catalyst composition. For certain applications, it is advantageous to maximize the surface area of the substrate and distribute ultrafine particles over the largest portion of the surface area possible. In an embodiment, a catalyst composition of the present invention comprises a thin layer coating of substantially uniformly spaced ultrafine particles on the surface of a substrate.

[0041] A number of suitable substrates may be used in embodiments of the present invention. In selecting a substrate, various geometric and thermodynamic considerations may be taken into account, to insure that oxidation and/or catalysis will occur efficiently. For example, substrates useful in embodiments of the present invention may be able to bond with ultrafine particles, such as gold, and may be available in sizes that allow the substrate to be packed fairly tightly in a filter element without resulting in excess performance-detracting pressure drops.

[0042] Metal oxides are particularly well-suited for use as substrates in embodiments of the present invention. Examples of suitable metal oxides for use as substrates in embodiments of the present invention include, without limi-

tation, alumina (Al_2O_3), cerium oxide (CeO_2), iron oxide (Fe_2O_3), itania (TiO2), and a number of other transition metal oxides, including mixtures and alloys thereof. In general, it has been found advantageous for use in filter apparatus for the substrate to comprise at least one of cerium oxide (CeO_2), titanium dioxide (TiO_2), iron oxide (Fe_2O_3), alumina (Al_2O_3), and mixtures thereof.

[0043] In one non-limiting embodiment, the substrate comprises alumina. Alumina may be particularly useful as a substrate in embodiments of the present invention, as alumina will permit oxygen to dissociatively adsorb. In general, any phase of alumina is suitable for use in embodiments of the present invention. For certain embodiments, alpha alumina is preferable to gamma alumina in the present invention. The preparation of alumina for use as a substrate in embodiments of the present invention will be discussed in greater detail below. An example of alumina suitable for use in embodiments of the present invention is activated gamma alumina (8-14 mesh), commercially available from Fisher Scientific International as item #A505-212. For additional information regarding the use of alumina in smoking articles, see U.S. Pat. No. 4,771,795 to White et al.; U.S. Pat. No. 4,917,128 to Clearman et al.; U.S. Pat. No 4,967,774 to White; and U.S. Pat. No. 5,016,654 to Bernasek et al.; which are hereby incorporated by reference.

[0044] As used herein, the terminology ultrafine particle refers to particles having dimensions less than 10,000 nanometers, including nanoparticles and slightly larger particles. The term nanoparticle is generally used to indicate particles with dimensions less than 100 nanometers (one nanometer is one billionth of a meter). Ultrafine particles manifest advantageous and unique properties which can be exploited in embodiments of the present invention for a variety of purposes relating to the catalysis of chemical reactions.

[0045] The size of the ultrafine particle utilized in a catalyst composition of the present invention may vary depending on the reaction being catalyzed. For example, in a certain embodiment of the present invention, the ultrafine particle may comprise a nanoparticle having a particle size of 10 nanometers or less.

[0046] The composition of ultrafine particles suitable for use in the present invention includes, but is not limited to, ultrafine particles capable of catalyzing chemical reactions, including, but not limited to, noble metals, alloys, metal oxides and the like. The ultrafine particles may be doped or coated. Suitable ultrafine particles for use in the present invention include, but are not limited to, those comprising a noble metal; metals such as gold, copper, silver, platinum, palladium, rhodium, nickel, zinc, zirconium, other transition metals; iron; alloys of noble metals; metal oxides; and mixtures thereof.

[0047] For catalyzing the conversion of carbon monoxide to carbon dioxide, noble metals, such as gold, which are capable of catalyzing the conversion at temperatures found in smoking articles or a smoking article filter, are advantageous. Other ultrafine particles having similar properties to gold may also work as catalysts in embodiments of the present invention.

[0048] In embodiments of the present invention utilizing gold ultrafine particles, the gold ultrafine particles may have

an average particle size up to about 100 nanometers. In other embodiments, the gold ultrafine particles may have an average particle size up to about ten nanometers. In still other embodiments, the gold ultrafine particles may have an average particle size up to about five nanometers.

[0049] The catalytic properties of gold depend largely on its particle size. Gold ultrafine particles may be particularly effective at converting carbon monoxide to carbon dioxide when the average particle size is between about two and about four nanometers. Thus, further embodiments of the present invention comprise gold ultrafine particles having an average particle size between about two and about four nanometers.

[0050] The preparation of gold ultrafine particles for use in embodiments of the present invention will be discussed in greater detail below. An example of a suitable starting material for obtaining gold ultrafine particles is hydrogen tetrachloroaurate III, which is commercially available from Alfa Aesar as item #12325.

[0051] While gold ultrafine particles are particularly effective at particle sizes between about two nanometers and four nanometers, such small particle sizes can be difficult to implement in a filter apparatus, such as the filter element of a gas mask or smoking article. When positioned in the filter, such small particles pack so tightly that an unusually high pressure drop results.

[0052] As used herein, the term "pressure drop" refers to the difference between atmospheric pressure and the pressure at the extreme mouthend point of a cigarette, as measured at a given flow rate through the cigarette. Typical pressure drop values for cigarettes of the present invention are greater than about 30 mm of $\rm H_2O$, more frequently greater than about 50 mm of $\rm H_2O$, at 17.5 cc/sec. of air flow

[0053] One other potential issue with the use of gold ultrafine particles in a filter (e.g., gas mask filter or smoking-article filter) is that the active catalyst sites of the gold ultrafine particles may be deactivated by the aerosol passing through the filter. The aerosol may comprise an aerosol composed of a complex mixture of water and many other complex chemicals, some of which can rapidly deactivate the active sites of the catalyst.

[0054] The choice of substrate composition and/or ultrafine particle composition may be made based on the chemical reaction to be catalyzed and the environment in which the reaction will take place. A feature of the present invention is that certain embodiments of the present invention will act as catalysts at temperatures below 300 Celsius (C), in effect temperatures below the operating range of other catalysts. For example, certain embodiments of the present invention will catalyze reactions in a gaseous stream at temperatures between 10 C and 300 C. Other embodiments of the present invention act as catalysts between 80 C and 200 C, or between 130C and 180 C.

[0055] In embodiments of the present invention, the substrate advantageously provides a larger structure, which results in a looser packing of the filter element. Accordingly ultrafine particles of a desirable size can be applied to a substrate, which, when incorporated in a filter apparatus, reduces or eliminates high pressure drops. Ultrafine particles

supported on a substrate may also facilitate contact between aerosol components (e.g., CO) and the catalyst.

[0056] Catalyst compositions of the present invention may be produced by a variety of methods, including chemical deposition, precipitation deposition, impregnation, combustion synthesis, vapor deposition, solution chemistry and/or other methods that will be recognized by those of ordinary skill in the art. Representative methods are described herein and also described in "The Preparation of Highly Dispersed Au/Al2O3 by Aqueous Impregnation" by Xu et al., Catalyst Letters Vol. 85, No. 3-4, February 2003, p. 229 et seq., the disclosure of which is incorporated herein by reference.

[0057] In a further aspect, the present invention provides methods for producing catalyst compositions comprising ultrafine particles. The methods of the present invention may be utilized to produce catalyst compositions of the present invention. The methods of the present invention, however may be used to produce other catalyst compositions, e.g. platinum (Pt), palladium (Pd), copper (Cu), rhodium (Rh), gold (Au), silver (Ag), iron (Fe), nickel (Ni), Zinc (Zn) and zirconium (Zr) compositions, and the catalyst compositions of the present invention may be produced by other methods.

[0058] Catalyst compositions of the present invention may be prepared by a method of the present invention and/or other methods. One method of producing a catalyst composition comprising gold ultrafine particles comprises: dissolving hydrogen tetrachloroaurate III (HAuCl₄) in water, acidifying the solution of tetrachloroaurate III in water with hydrochloric acid, coating the substrate with the acidified solution, washing the coated substrate and calcining the washed and coated substrate to form the catalyst composition. Other embodiments may further comprise removing chloride ions and/or drying the coated substrate.

[0059] An embodiment of a method of the present invention comprises:

[0060] applying a solution comprising an ultrafine particle precursor and an acid to a particulate substrate;

[0061] drying the substrate;

[0062] suspending the substrate in water;

[0063] admixing a basic solution to the suspension to form a particle precursor solution;

[0064] separating the thus created substrate and ultrafine particle complex; and

[0065] treating the complex to produce a catalyst composition comprising the substrate and ultrafine particles.

[0066] Optionally, the composition may be heat treated in the presence of hydrogen gas to assist in activation. The ultrafine particle complex may be treated by calcining, drying or similar methods depending on the particular end use of the catalyst composition. The method may be used to deposit an ultrafine catalyst particle on monoliths of various geometries and compositions as well as onto granules of various geometry and composition.

[0067] Suitable ultrafine particle precursors include salts comprising the catalyst composition of interest. Additional ultrafine particle precursors are described in more detail

below and in the patents relating to ultrafine particles referenced herein. Suitable acids include organic and/or inorganic acids such as hydrochloric acid (HCl), sulfuric acid ($\rm H_2SO_4$), hydrofluoric acid (HF), nitric acid (HNO $_3$) and the like.

[0068] The solution comprising an ultrafine particle precursor and acid may be applied to the substrate using conventional production techniques for contacting a physical substrate with a solution. For example, the substrate may be submerged in the solution. It is generally preferred to ensure that the desired catalytically active portion of the substrate is substantially completely coated with the solution. Alternatively, the solution can be added dropwise or sprayed onto the substrate, or deposited thereon by other methods, so as to generate a substantially uniform coverage.

[0069] Drying of the substrate after application of the solution may be accomplished by conventional techniques. Drying may be conducted at a temperature, generally at least above ambient temperature, for a period of time sufficient to drive off a substantial portion of the moisture from the substrate. As shown in the description and examples below, it has been found that drying the substrate at 50 C to 150 C, typically 80 C to 120 C, for 1 to 3 hours, typically 1.5 to 2.5 hours is appropriate for certain substrate/ultrafine particle precursor solutions.

[0070] The particle precursor solution may comprise water (H_2O) or other solvents. The step of suspending the dried substrate in the aqueous solution may be performed by conventional techniques, including admixing the aqueous solution and the dried substrate with slow stirring to form a suspension of the substrate.

[0071] Suitable basic solutions include sodium hydroxide; sodium bicarbonate; sodium carbonate; potassium hydroxide; calcium hydroxide; ammonium hydroxide; and the like. Generally the basic solution will have a pH greater than 8.

[0072] Admixing of the basic solution into the suspension may be performed using conventional techniques including mixing while stirring. After admixing is completed, the particles of the substrate/ultrafine particle complex are separated from the mixture. The separation may be achieved through physical separation means including sieving, filtering, and the like.

[0073] The recovered particles may be calcined using conventional techniques. Generally the particles will be held at a temperature greater than ambient temperature for a period of time sufficient to drive substantially all residual moisture from the particles. In certain embodiments of a method of the present invention, for example, the particles are calcined at a temperature of 100 C to 500 C for 2 to 10 hours, typically at a temperature of 300 C to 400 C for 5 to 7 hours

[0074] Suitable substrates include those listed above and below in the descriptions of the catalyst compositions of the present invention. To produce granular substrates, a granular high-surface-area substrate starting material may be ground and sieved to a preferred particle size, for example between 0.1 millimeters and 2 millimeters, generally 0.3 millimeters to 1.7 millimeters, or for certain embodiments between 0.5 and 1.1 millimeters.

[0075] Particulate catalyst compositions produced by a method of the present invention possess several practical

advantages. In particular, they may be free flowing and substantially free from agglomeration. They may also be substantially free of dust.

[0076] In addition to methods of the present invention described above, gold ultrafine particles may be positioned on alpha alumina using combustion synthesis as set forth in "Combustion synthesis of nanometal particles supported on α -Al₂₀O₃: CO oxidation and NO reduction catalysts", Bera et al., *Journal of Material Chemistry*, Vol. 9, pp. 1801-1805 (1999), which is hereby incorporated by reference.

[0077] In another aspect, the present invention provides articles of manufacture comprising the catalyst compositions of the present invention. The articles of manufacture may comprise catalytic apparatus, for example particles, screens, panels and the like suitable for use in chemical process reactions. In another aspect, the articles of manufacture of the present invention are filter apparatus comprising the catalyst compositions of the present invention. The filter apparatus may further comprise a particulate screening medium, a filler and/or other inert or active ingredients. A particulate screening medium may comprise a fibrous, granular or other material that acts to remove particulate and/or gaseous matter that could poison the catalyst. Examples of filter apparatus include, but are not limited to: gas mask filters; smoke purification filters; and filters utilized in smoking articles.

[0078] In a further aspect, the present invention provides smoking articles. It is desirable that the smoking articles of the present invention deliver good flavor, pleasure and satisfaction.

[0079] In an embodiment, the present invention provides smoking articles comprising a combustible material to provide an aerosol and/or to heat an aerosol-forming material, the smoking articles comprising a catalyst composition of the present invention. For example, aerosol may be formed by burning to produce smoke or by heating aerosol-forming material on a suitable substrate. The location and position of the catalyst composition may be selected such that specific performance properties of the smoking article are modified. For example, in an embodiment of the present invention wherein it is desired to modify the composition of the aerosol, for example mainstream smoke, the catalyst composition(s) are located/positioned within the smoking article such that there is contact between the catalyst composition and the mainstream smoke. An example of such an embodiment includes modification of smoke to reduce levels of carbon monoxide in the smoke.

[0080] In an embodiment of the present invention, the filter component of a smoking article comprises catalyst compositions of the present invention. The catalyst compositions may be present in an amount sufficient to alter the chemistry of an aerosol, e.g. cigarette smoke, drawn through the filter. In an embodiment, the catalyst compositions may act to catalyze reactions occurring within the aerosol, e.g. cigarette smoke. The catalyzed reactions may result from contact between the aerosol and the catalyst composition, the aerosol and the substrate component of the catalyst composition, or both.

[0081] In alternate embodiments of the present invention, catalyst compositions of the present invention may be incorporated into other components of a smoking article, for

example as a part of, and/or surrounding, the aerosolgenerating component and/or tobacco, in addition to, or instead of, incorporation in the filter component.

[0082] In embodiments of the present invention using particulate catalyst compositions in smoking articles, the particle size of the composition may range from 0.1 millimeter (mm) to 1.5 mm. For certain embodiments, the particle size may range from 0.5 mm to 1.0 mm, and more particularly for certain embodiments a particle size of 0.75 mm to 0.85 mm is preferred. Particle size may be determined by ASTM Test Procedure B761-02 and E1617-97 (2002).

[0083] The substrate and ultrafine particle materials of a catalyst composition of the present invention for use in a smoking article may comprise any of the materials set forth above. In general, for the conversion of carbon monoxide to carbon dioxide in an aerosol, the catalyst composition may serve as a substrate for the enhanced oxidation of carbon monoxide to carbon dioxide.

[0084] Embodiments of the present invention include, but are not limited to embodiments utilizing the catalyst compositions of the present invention to modify components of the smoke, for example by lowering levels of carbon monoxide. The catalyst compositions may be incorporated into the smoking article, or component parts of the smoking article, by a variety of methods including those set forth in detail below and/or other methods understood in the art. The catalytic process may occur over a range of temperatures including room temperature or below.

[0085] Smoking articles of the present invention may further include additional materials that enhance the performance of the catalyst composition and/or the smoking article. For example, a filter of a smoking article comprising catalyst compositions of the present invention may further comprise particulate matter to filter components of mainstream smoke that would otherwise impair the catalytic function of the catalyst composition.

[0086] Catalyst compositions for use in smoking-article embodiments of the present invention may comprise a plurality of ultrafine particles positioned on at least one substrate. The location and position of the catalyst compositions may be selected such that specific performance properties of the smoking article are modified. For example, in an embodiment of the present invention wherein it is desired to modify the composition of mainstream smoke, the catalyst compositions comprising ultrafine particles are located/positioned within the filter element such that there is contact between the ultrafine particles and the mainstream smoke. In such an embodiment, the catalyst compositions reduce the levels of carbon monoxide in the smoke. The ultrafine particles can advantageously act as catalysts for the conversion of carbon monoxide to carbon dioxide in mainstream smoke.

[0087] Mainstream smoke refers to the aerosol of gases and particles created when the smoker draws through the tobacco rod. The mainstream smoke includes smoke that has been drawn through the lighted region of the cigarette, the tobacco rod, and the filter (if the smoking article is so equipped).

[0088] In an embodiment of the present invention, a catalyst composition of a smoking article may comprise 0.01% to 10%, by weight, preferably 0.1% to 5%, by weight

ultrafine particles. The theoretical loading, which corresponds to the percentage weight of ultrafine particles may be calculated. The percent loading will equal the amount of ultrafine particle salt in grams multiplied by the fraction of ultrafine particle in the ultrafine particle salt, divided by the total amount of ultrafine particle salt plus the amount of substrate, the quotient multiplied by 100.

[0089] The temperature of the mainstream smoke is lower as the smoke passes through the filter element than it is when the smoke passes through the tobacco rod. In the filter element, the temperature ranges from near ambient to about 150 C. By way of comparison, temperatures in the tobacco rod, including temperatures in the so-called combustion and pyrolysis regions, range from 200 C to 900 C. Thus, as the catalyst compositions may be positioned in the filter element in accordance with embodiments of the present invention, the catalyst compositions are effective as catalysts for the conversion of carbon monoxide to carbon dioxide at temperatures below 150 C.

[0090] In one embodiment of the present invention, the ultrafine particles comprise gold. Although gold may not be an active catalyst in its bulk form, gold ultrafine particles exhibit excellent catalytic properties, particularly in the conversion of carbon monoxide to carbon dioxide. Further, gold ultrafine particles can advantageously catalyze the conversion of carbon monoxide to carbon dioxide at room temperature.

[0091] Catalyst compositions for use in filter elements of smoking articles in accordance with embodiments of the present invention may comprise a plurality of ultrafine particles deposited on at least one substrate. A filter element may comprise a plurality of catalyst compositions. In a further embodiment, the plurality of catalyst compositions may be positioned in at least one cavity in the filter element. The plurality of catalyst compositions, in an embodiment, may be positioned in a cavity between two filter plugs.

[0092] In one embodiment of the present invention, catalyst compositions comprise a plurality of gold ultrafine particles positioned on at least one alumina particle. In further embodiments, the gold ultrafine particles comprise gold nanoparticles. In further embodiments, the gold nanoparticles have a particle size up to about ten nanometers. In another embodiment, the gold nanoparticles have a particle size up to about five nanometers. In another embodiment, the gold nanoparticles have a particle size between about two nanometers and about four nanometers.

[0093] The size and geometry of the alumina substrate prior to gold deposition, in embodiments of the present invention, may be selected such that the catalyst composition may be packed into a component part of a smoking article in a manner that maximizes contact between the catalyst composition and the aerosol without exceeding acceptable pressure-drop limits. In one embodiment, the alumina substrate has a particle size of between about 12 and about 35 U.S. mesh (between about 0.5 and about 1.4 millimeters). In another embodiment, the alumina substrate, prior to gold deposition, has a particle size between about eighteen and about thirty U.S. mesh (between about 0.6 millimeters and about 1 millimeter).

[0094] The catalyst compositions in another embodiment of the present invention comprise a plurality of gold ultrafine

particles having particle sizes between about two nanometers and about four nanometers positioned on at least one alumina substrate having a particle size between about 0.6 millimeter and about 1.0 millimeter.

[0095] In an embodiment the untreated gamma alumina substrate for use in a catalyst composition of the present invention has a surface area, as measured by gas adsorption, of approximately 340 m²/g. After addition of gold, the ultrafine alumina-gold composite has a surface area of approximately 270 m²/g.

[0096] As will be appreciated by those of ordinary skill in the art, the relationship between the pore size of the substrate, as reflected in the substrate's surface-area measurement, and the particle size of the ultrafine particle, may be optimized to achieve desired performance properties in a catalyst composition of the present invention.

[0097] Further details relating to embodiments of catalyst compositions of the present invention and articles of the present invention comprising the catalyst compositions will become apparent to those of ordinary skill in the art from the following descriptions of specific embodiments of an article of manufacture of the present invention comprising an embodiment of a catalyst of the present invention.

[0098] Embodiments of the present invention, comprising a plurality of catalyst composition, are illustrated in the appended figures.

[0099] FIGS. 1-5 depict cross-sectional views of embodiments of filter elements, 10A, 10B, 10C, 10D and 10E of the present invention, incorporating catalyst compositions of the present invention. The filter elements may be used as a filter element of a smoking article, wherein the filter element will generally have a substantially circular shape. Designs similar to the filter elements may be used in other applications. For use in the description below FIGS. 1-5 include an arrow indicating the direction of flow of an aerosol through filter element. Like-numbered elements are generally described with reference to the first Figure in which they appear.

[0100] With reference to FIG. 1, filter element 10A includes filter material 11, in filter-element sections 12 and 16. Suitable filter material includes cellulose acetate tow and other materials described in detail below.

[0101] A cavity, 14, is located between sections 12 and 16. In an embodiment of the present invention, catalyst compositions of the present invention, 13, are distributed throughout cavity 14. Cavity 14 further includes air dilution holes 18 that allow air to be drawn into the cavity. The air dilution holes will extend through any outer wrapping material surrounding filter element 10 when the filter element is positioned in a smoking article.

[0102] Catalyst compositions of the present invention may be positioned in the cavity 14 using techniques known to those of skill in the art for positioning particulate matter (e.g., carbon) in a filter element. Examples of such techniques are set forth in U.S. Pat. No. 6,537,186 and in U.S. patent Publication No. 2002/0020420, which are hereby incorporated by reference.

[0103] FIG. 2 illustrates an alternate embodiment of a filter element 10B, of the present invention. In an embodiment of the present invention, cavity 14 includes an admixture of catalyst compositions of the present invention 13, and

particulate carbon 15. The admixture may comprise 1 to 80%, by weight, catalyst compositions of the present invention and 1 to 80% by weight, particulate carbon. The admixture may be positioned in cavity 14 using techniques known to those of skill in the art for positioning particulate matter in a filter element.

[0104] FIG. 3 illustrates another alternative embodiment of a filter element 10C, of the present invention. In the embodiment depicted in FIG. 3, cavity 14 is subdivided into cavities 14A and 14B. Catalyst compositions of the present invention 13, are positioned in cavity 14A, the downstream cavity. Particulate carbon, 15, is positioned upstream of cavity 14A in cavity 14B. The relative positions of the catalyst compositions and the particulate carbon in the cavity may be reversed.

[0105] In FIGS. 1-3, the relative lengths of sections 12 and 16, and cavity 14, or 14A and 14B is not drawn to scale. In general, in embodiments of the present invention similar to filter elements 10A and 10B the percentage length of each section and the cavity, 12/14/16 will be 30 to 45/10 to 40/30 to 45. For a filter element of 27 millimeters length, this translates to section 12 being 8.1 to 12.2 millimeters in length; cavity 14 being 2.7 to 10.8 millimeters in length; and section 16 being 8.1 to 12.2 millimeters in length. For filter element 10C the relative percentage lengths of 12/14A/14B/ 16 will be 30 to 45/5 to 20/5 to 20/30 to 45. For a filter element of 27.2 millimeters length, this translates to 12 being 8.1 to 12.2 millimeters in length; cavity 14A being 1.4 to 5.4 millimeters in length; cavity 14B being 1.4 to 5.4 millimeters in length and section 16 being 8.1 to 12.2 millimeters in length.

[0106] FIG. 4 illustrates another embodiment of a filter element of the present invention. Filter element 10D includes a cavity 21 encircled by a high density filter material 23. Suitable high density filter materials include, but are not limited to, steam bonded cellulose acetate filters available from Filtrona. These steam bonded filters have a filtration efficiency of more than 75%. The ends of the cavity may be bounded by regions of a filter material 11, which may have a lower filtration efficiency than filter material 23 to facilitate the passage of an aerosol/gaseous mixture through filter element 10D. The filter element includes air dilution holes 18 to allow passage of air between cavity 21 and the outside environment.

[0107] The relative dimensions of the cavity may vary depending on the application. In an embodiment, the cavity will have a diameter between 10 and 50 percent of the diameter of the filter element, and a length between 10 and 80 percent of the length of the filter element.

[0108] Cavity 21 includes catalyst compositions of the present invention, 13. Alternatively, cavity 21 may be filled with an admixture of catalyst compositions 13 and particulate carbon.

[0109] As noted in the prior descriptions, the embodiments of the present invention depicted in FIGS. 1-4 include a portion of a filter element comprising catalyst compositions of the present invention. The packing density of the catalyst compositions, or the catalyst compositions and other particulate matter (e.g. particulate carbon), in the filter element will generally range from 0.5 to 2.0 grams per cubic centimeter. Higher or lower packing densities may be desir-

able for particular embodiments in order to maintain an acceptable pressure drop across the filter.

[0110] FIG. 5 illustrates another possible embodiment of a filter element of the present invention. As shown in FIG. 5, filter element 10E includes a filter material, 11, and a cellulose acetate filter segment 12. The filter element 11 comprises a filter material in communication with catalyst compositions of the present invention, 13, that are distributed throughout the filter element. The filter material 11 may be pretreated with the catalyst composition prior to incorporation into the filter element.

[0111] Filter elements 10A-10E depicted in FIGS. 1-5 are depicted and described with reference to a particular inline filtering application, such as found in a smoking article. It should be appreciated that the geometry of the filter elements may be adapted for other applications, for example use in a gas mask filter without departing from the present invention.

[0112] Further details regarding the use of filter elements 10A-10E in a smoking article are provided below with reference to the remaining Figures. The invention is described in more detail with reference to a particular smoking article, namely a cigarette utilizing a catalyst composition comprising ultrafine particles in the filter element. As will be understood by those of ordinary skill in the art, however, the principals/principles of the present invention apply to other tobacco articles and other filter applications

[0113] FIG. 6 illustrates an embodiment of a smoking article of the present invention. As shown in FIG. 6, cigarette 30, includes a generally cylindrical rod 35 of a charge or roll of smokable filler material 40 contained in a circumscribing wrapping material 45. The rod 35 is typically referred to as a "smokable rod" or a "tobacco rod". The ends of the tobacco rod are open to expose the smokable filler material.

[0114] In an embodiment of the present invention, cigarette 30 includes a filter element comprising catalyst compositions such as filter element 10A depicted in FIG. 1. Although filter element 10A is depicted in FIG. 6, any of filter elements 10A, 10B, 10C, 10D, 10E, or any other design incorporating catalyst compositions of the present invention may be utilized in an embodiment of a smoking article of the present invention.

[0115] The filter element 10A is positioned adjacent one end of the tobacco rod 35 such that the filter element and tobacco rod are axially aligned in an end-to-end relationship, preferably abutting one another. Filter element 10A has a generally cylindrical shape, and the diameter thereof is essentially equal to the diameter of the tobacco rod. The ends of the filter element are open to permit the passage of air and smoke therethrough. The filter element 10A includes filter material 11 which is overwrapped along the longitudinally extending surface thereof with circumscribing plug wrap material 60. The filter element can have two or more filter segments, and/or flavor additives incorporated therein.

[0116] The filter element 10A may be attached to the tobacco rod 35 by tipping material 65 which circumscribes both the entire length of the filter element and an adjacent region of the tobacco rod. The inner surface of the tipping material 65 may be fixedly secured to the outer surface of the

plug wrap 60 and the outer surface of the wrapping material 45 of the tobacco rod, using a suitable adhesive. A ventilated or air diluted smoking article is provided with an air dilution means, such as a series of perforations 18, each of which extend through the tipping material and plug wrap. The wrapping material 45 has a width which is equal to the circumference of the cigarette plus the lap zone of the glue line which ultimately results during cigarette manufacture.

[0117] Catalyst compositions, 13, are positioned in a cavity within filter element 10A. The wrapping material surrounding the catalyst composition may include dilution holes 18 that extend through the tipping material.

[0118] FIG. 7 illustrates an embodiment of a smoking article comprising a filter element with a plurality of catalyst compositions positioned therein. Such a smoking article can be prepared using the techniques described in U.S. Pat. No. 6,537,186.

[0119] As illustrated in FIG. 7, the cigarette 102 includes a combustible material component 110 circumscribed within a retaining jacket of insulating material 112. Situated longitudinally behind the combustible material component 110 is an aerosol-generating means, 116. The aerosol generating means comprises one or more aerosol forming materials (such as glycerin), a form of tobacco (such as tobacco powder, extract or dust), and flavor components, which are volatilized by heat generated by the burning of the combustible material component. Preferably, the aerosol-generating means comprises a substrate advantageously made from a reconstituted tobacco cast-sheet cut-filler material. Such substrates are described in U.S. patent application Ser. No. 07/800,679, filed 27 Nov., 1991, which is incorporated herein by reference. The combustible material component 110 may include ultrafine particles as described in the commonly assigned, co-pending patent application entitled "Smoking Article Comprising Ultrafine Particles", by Crooks et al., U.S. patent application Ser. No. 10/382,244, the disclosure of which is incorporated herein by reference.

[0120] The cigarette may further comprise a filter element 10A or other suitable mouthpiece positioned adjacent one end of the aerosol generating means 116 such that the filter element and tobacco rod are axially aligned in an end-to-end relationship, preferably abutting one another. Filter element 10A has a generally cylindrical shape, and the diameter thereof is essentially equal to the diameter of the tobacco rod. The ends of the filter element are open to permit the passage of air and smoke therethrough. The filter element 10A may include a filter material, 11 which is overwrapped along the longitudinally extending surface thereof with circumscribing plug wrap material. The filter element includes catalyst compositions of the present invention 13 comprising ultrafine particles. As will be realized from the description below, the actual size of a typical ultrafine particle may be less than 100 nm. The portion of the filter element comprising the catalyst compositions will include air dilution holes, 18 in the wrapper material(s) adjacent to the filter portion comprising the ultrafine particles.

[0121] Referring again to the embodiment of the cigarette shown in FIG. 7, the filter element 10A comprises a cavity positioned between two filter plugs, 11. The two filter plugs may be conventional filter materials, such as cellulose acetate filter material. The cavity is filled with a plurality of catalyst compositions 13 of the present invention. The cavity

may further include other components such as those described above (e.g., particulate carbon).

[0122] The particular embodiment of a smoking article of the present invention described with reference to FIGS. 6 and 7 incorporates catalyst compositions in the filter element of the smoking article. The same embodiment, or alternative embodiments, of the present invention may comprise catalyst compositions of the present invention located in other component parts of the smoking article. For example, catalyst compositions may be incorporated into, or positioned near or within, the aerosol generating material; including incorporation into the smokable material; the wrapping material; the fuel element and/or other components.

[0123] FIG. 8 depicts an embodiment of a smoking article of the present invention wherein catalyst compositions 13 are positioned adjacent fuel element 110 in a smoking article similar to the one described with reference to FIG. 7 and U.S. Pat. No. 6,537,186. As shown in FIG. 8, air dilution holes, 18, are provided in the portion of the smoking article comprising the catalyst compositions. Filter element 130 in FIG. 8 represents a conventional cigarette filter, however a filter element of the present invention may also be utilized.

[0124] As will be realized by those of ordinary skill in the art, the description in the following paragraphs applies generally to embodiments of smoking articles of the present invention, including the smoking articles depicted in FIGS. 6 and 7.

[0125] Smoking articles are typically circumscribed by a wrapping material. The wrapping material has a width which is equal to the circumference of the smoking article plus the lap zone of the glue line which ultimately results during manufacture. Suitable wrapping materials are generally known to those of ordinary skill in the art and described in the patent application referenced above and the following U.S. Patents, each of which is incorporated herein by reference, U.S. Pat. No. 4,452,259 to Norman; U.S. Pat. No. 5,878,754 to Peterson et al.; U.S. Pat. No. 5,103,844 to Hayden et al.; U.S. Pat. No. 5,060,675 to Milford et al.; U.S. Pat. No. 4,998,541 to Perfetti et al.; U.S. Pat. No. 4,805,644 to Hampl, Jr. et al.; U.S. Pat. No. 4,461,311 to Matthews et al.; U.S. Pat. No. 4,450,847 to Owens; U.S. Pat. No. 4,420,002 to Cline; and U.S. Pat. No. 4,231,377 to Cline et al.

[0126] Paper wrapping materials suitable for use in carrying out the present invention are commercially available. Representative cigarette-paper wrapping materials have been available as Ref. Nos. 419, 454, 456, 460 and 473 from Ecusta Corp.; Ref. Nos. Velin 413, Velin 430, VE 825 C20, VE 825 C30, VE 825 C45, VE 826 C24, VE 826 C30 and 856 DL from Miquel; Terig LK18, Tercig LK24, Tercig LK38, Tercig LK46 and Tercig LK60 from Tervakoski; and Velin Beige 34, Velin Beige 46, Velin Beige 60, and Ref. Nos. 454 DL, 454 LV, 553 and 556 from Wattens. Exemplary flax-containing cigarette-paper wrapping materials have been available as Grade Names 105, 114, 116, 119, 170, 178, 514, 523, 536, 520, 550, 557, 584, 595, 603, 609, 615 and 668 from Schweitzer-Mauduit International. Exemplary wood-pulp-containing cigarette-paper wrapping materials have been available as Grade Names 404, 416, 422, 453, 454, 456, 465, 466 and 468 from Schweitzer-Mauduit International.

[0127] In certain embodiments of the present invention a wrapping material for the smoking article may comprise ultrafine particles as described in the commonly assigned, co-pending patent application entitled "Smoking Article Wrapping Materials Comprising Ultrafine Particles", by Crooks et al., U.S. patent application Ser. No. 10/342,618, the disclosure of which is incorporated herein by reference.

[0128] The filter element may be attached to the tobaccorod/aerosol-generating rod by a tipping material which circumscribes both the entire length of the filter element and an adjacent region of the tobacco rod. The inner surface of the tipping material is fixedly secured to the outer surface of the plug wrap and the outer surface of the wrapping material of the tobacco rod, using a suitable adhesive. A ventilated or air-diluted smoking article is provided with an air-dilution means, such as a series of perforations, each of which extends through the tipping material and plug wrap.

[0129] A conventional automated cigarette rod-making machine useful for manufacturing smoking articles of the present invention is of the type commercially available from Molins PLC or Hauni-Werke Korber & Co. KG. For example, cigarette rod-making machines of the type known as Mark 8 (commercially available from Molin PLC) or PROTOS (commercially available from Hauni-Werke Korber & Co. KG) can be employed, and can be suitably modified if desired. A description of a PROTOS cigarettemaking machine is provided in U.S. Pat. No. 4,474,190, at col. 5, line 48 through col. 8, line 3, which is incorporated herein by reference. Types of equipment suitable for the manufacture of cigarettes also are set forth in U.S. Pat. No. 4,844,100 to Holznagel; U.S. Pat. No. 5,156,169 to Holmes et al. and U.S. Pat. No. 5,191,906 to Myracle, Jr. et al.; and PCT WO 02/19848. Designs of various components of cigarette-making machines, and the various materials used to manufacture those components, will be readily apparent to those skilled in the art of cigarette making.

[0130] The smoking article typically has a length which ranges from about 50 mm to about 100 mm, and a circumference of about 16 mm to about 28 mm. The aerosolgenerating means and the resulting smoking articles can be manufactured in any known configuration using known cigarette making techniques and equipment. The wrapping material is formed into a circular shape such that the ends of the sides thereof abut one another. The ends of wrapping material can abut one another, nearly abut one another, or slightly overlap one another. A cigarette rod having such a configuration can be provided by supplying a paper wrapper from a bobbin on a suitably equipped cigarette-making machine, passing the wrapping material through the garniture region of the cigarette-making machine, and forming the tobacco rod.

[0131] The tobacco materials used for the manufacture of smoking articles of the present invention can vary. Descriptions of various types of tobaccos, growing practices, harvesting practices and curing practices are set forth in *Tobacco Production, Chemistry and Technology*, Davis et al. (Eds.) (1999). The tobacco normally is used in cut filler form (e.g., shreds or strands of tobacco filler cut into widths of about ½0 inch to about ½0 inch, preferably about ½0 inch to about ½1 inch to about 3 inches). The amount of tobacco filler normally used within a cigarette ranges from about 0.6 g to about 1 g. The tobacco

filler normally is employed so as to fill the tobacco rod at a packing density of about 100 mg/cm³ to about 300 mg/cm³, and often about 150 mg/cm³ to about 275 mg/cm³. As used herein, "packing density" means the weight of the filler material which occupies a unit volume within the smokable rod.

[0132] Tobaccos can have a processed form, such as processed tobacco stems (e.g., cut-rolled or cut-puffed stems), volume expanded tobacco (e.g., puffed tobacco, propane-expanded tobacco and dry-ice-expanded-tobacco (DIET)), or reconstituted tobacco (e.g., reconstituted tobaccos manufactured using paper-making-type or cast-sheet-type processes).

[0133] Typically, tobacco materials for cigarette manufacture are used in a so-called "blended" form. For example, certain popular tobacco blends, commonly referred to as "American blends," comprise mixtures of flue-cured tobacco, burley tobacco and Oriental tobacco, and in many cases, certain processed tobaccos, such as reconstituted tobacco and processed tobacco stems. The precise amount of each type of tobacco within a tobacco blend used for the manufacture of a particular cigarette brand varies from brand to brand. See, for example, Tobacco Encyclopedia, Voges (Ed.) p. 44-45 (1984), Browne, The Design of Cigarettes, 3_{rd} Ed., p.43 (1990) and Tobacco Production, Chemistry and Technology, Davis et al. (Eds.) p. 346 (1999). Other representative tobacco blends also are set forth in U.S. Pat. No. 4,924,888 to Perfetti et al.; U.S. Pat. No. 5,056,537 to Brown et al.; and U.S. Pat. No. 5,220,930 to Gentry; and Bombick et al., Fund. Appl. Toxicol., 39, p. 11-17 (1997). See, also, U.S. patent Publication No. 2003/0131860 to Ascraft et al. the disclosures of which are hereby incorpated by reference.

[0134] If desired, in addition to the aforementioned tobacco materials, the tobacco blend of the present invention, or aerosol-generating materials may further comprise catalyst compositions of the present invention. The catalyst compositions may be distributed substantially uniformly throughout the tobacco or aerosol-generating materials, or may be located as a separate component part in the smoking article. By way of example, catalyst compositions may be incorporated in processed tobacco which is utilized in a smoking article. Details relating to processed tobacco are disclosed in U.S. patent application Ser. No. 10/463,211 filed Jun. 17, 2003, the disclosure of which is hereby incorporated herein by reference.

[0135] The tobacco and/or aerosol generating material can further include other components. Other components include casing materials (e.g., sugars, glycerin, cocoa and licorice) and top dressing materials (e.g., flavoring materials, such as menthol). The selection of particular casing and top dressing components is dependent upon factors such as the sensory characteristics that are desired, and the selection of those components will be readily apparent to those skilled in the art of cigarette design and manufacture. See, Gutcho, Tobacco Flavoring Substances and Methods, Noyes Data Corp. (1972) and Leffingwell et al., Tobacco Flavoring for Smoking Products (1972).

[0136] Smoking articles also can incorporate at least one flavor component within the side-seam adhesive applied to the wrapping material during the manufacture of the tobacco rods. That is, for example, various flavoring agents can be

incorporated in a side-seam adhesive, such as CS-2201A available from National Starch, and applied to the seam line of the wrapping material. Those flavoring agents are employed in order to mask or ameliorate any off-taste or malodor provided to the smoke generated by smoking articles. Exemplary flavors include methyl cyclopentenolone, vanillin, ethyl vanillin, 4-parahydroxyphenyl-2-butanone, gamma-undecalactone, 2-methoxy-4-vinylphenol, 2-methoxy-4-methyl-2(5H)-furanone, methyl salicylate, clary sage oil and sandalwood oil. Typically, such types of flavor components are employed in amounts of about 0.2 percent to about 6.0 percent, based on the total weight of the adhesive and flavor components.

[0137] Typically, the tipping material circumscribes the filter element and an adjacent region of the tobacco rod such that the tipping material extends about 3 mm to about 6 mm along the length of the tobacco rod. Typically, the tipping material is a conventional paper-tipping material. The tipping material can have a porosity which can vary. For example, the tipping material can be essentially air-impermeable, air-permeable, or may be treated (e.g., by mechanical or laser-perforation techniques) so as to have a region of perforations, openings or vents thereby providing a means for air dilution to the cigarette. The total surface area of the perforations and the positioning of the perforations along the periphery of the cigarette can be varied in order to control the performance characteristics of the cigarette.

[0138] Embodiments of the present invention include embodiments wherein catalyst compositions comprising ultrafine particles are incorporated into the filter element of a smoking article. Typically, the filter element has a length which ranges from about 5 mm to about 40 mm, preferably about 10 mm to about 35 mm; and a circumference of about 17 mm to about 27 mm, preferably about 22 mm to about 25 mm. The catalyst compositions of the present invention may be positioned within the filter element in a position that maximizes their catalytic activity while maintaining the desired performance characteristics of the smoking article. In an embodiment, the catalyst compositions of the present invention are located between 10-15 mm from the mouth end of the filter.

[0139] The filter element can have a wide range of filtration efficiencies. The filter element can have one segment of filter material, two or more longitudinally positioned segments, or other configurations. The filter may also include an axially located hole to form a hollow filter element.

[0140] The filter material can be any suitable material such as cellulose acetate, polypropylene, tobacco material, or the like. The filter material may further comprise carbon, for example carbon particles. Examples of suitable filter materials are cellulose acetate tow items having (i) about 3 denier per filament and about 35,000 total denier, and (ii) about 3.5 denier per filament and about 35,000 total denier. Such tow items conveniently provide filter elements exhibiting a removal efficiency of particulate matter from mainstream smoke of greater than about 40 weight percent. The plug wrap typically is a conventional paper plug wrap, and can be either air-permeable or essentially air-impermeable. However, if desired, a nonwrapped cellulose acetate filter element can be employed. Filter elements having two or more segments, and which are provided using known plug-tube-

combining techniques, also can be employed. The various filter elements suitable for use in this invention can be manufactured using known cigarette filter-making techniques and equipment.

[0141] Certain filter elements can provide minimal mainstream-smoke removal efficiencies while maintaining the desirable draw characteristics of the cigarette. Such minimal smoke-removal efficiencies are provided by the so-called "low-efficiency" filters. Low-efficiency filters have a minimal ability to remove mainstream-smoke particulates. Generally, low-efficiency filters provide about 40 weight percent mainstream-smoke particulate-removal efficiency or less. The low-efficiency filter can be used because the relatively low "tar" yield is obtained primarily as a result of a relatively high level of filter ventilation or air dilution. Such cigarette configurations provide a means for reducing the yields of mainstream gaseous components. An example of a suitable material for providing a low-efficiency filter element is a cellulose acetate tow item having about 8 denier per filament and about 40,000 total denier.

[0142] Filter elements can be manufactured with cavities to be filled with particulate matter such as carbonaceous materials. For example, filter elements can be manufactured to have a cavity between two filter plugs, such as those traditionally used in making cellulose acetate filters. An apparatus and process for manufacturing such filter elements is described in U.S. Pat. No. 6,537,186, which is hereby incorporated by reference. As will be set forth below, the catalyst compositions of the present invention can be positioned in the cavity of such a filter element. The cavity may also comprise other suitable active or inactive components, including sepiolite, silica gel, and activated or non-activated carbon.

[0143] Embodiments of catalyst compositions for use in smoking articles of the present invention will now be illustrated in the following specific, non-limiting examples.

EXAMPLE 1

Catalyst Preparation

[0144] A catalyst composition of the present invention is prepared in the following manner.

[0145] Approximately 0.5128 g of hydrogen tetrachloroaurate III (49.5% gold metal, Alfa Aesar) is dissolved in 10 ml of deionized water and the solution is acidified with 0.0671 g of 6N hydrochloric acid. About 20.0233 g of alumina (18-30 US mesh) is evenly coated with this acidified gold solution. The gold-coated alumina particles (which had a yellow tint) were dried at 95 C for sixteen hours. The dried gold-coated alumina is added to 750 ml of deionized water containing 35 ml of 5.0 N ammonium hydroxide. The suspension is vigorously stirred overnight. Next, the goldcoated alumina is allowed to settle and the liquid decanted. About 750 ml of deionized water is added and the mixture stirred for an additional twenty minutes. The gold-coated alumina is allowed to settle for approximately thirty minutes and the supernatant is tested for the presence of chloride ions with an aqueous silver nitrate solution. The gold-coated alumina is washed several times with deionized water. Washing is complete when no chloride ions were present in the supernatant. The gold-coated alumina is dried overnight at 95 C. The dried gold-coated alumina is heated to 375 C

for about 8 hours. The final catalyst particles were free flowing granules, deep purple in color, and had a theoretical gold loading of about 1.2% (weight of ultrafine particles to weight of catalyst composition (W/W)). The catalyst is stored in sealed container.

EXAMPLE 2

Catalyst Preparation

[0146] An alternate embodiment of a catalyst composition of the present invention is prepared as follows:

[0147] Granular high surface area, activated alumina (8-14 U.S. mesh) is obtained as item number A505-212 from Fisher Scientific International. The alumina is ground in a pestle mortar to reduce the particle size of the alumina. A set of sieves were used to collect 18-30 U.S. mesh-fraction ground alumina, which corresponds to particle sizes between about 0.6 millimeters and about one millimeter. The collected alumina is dried at 95 C for two hours.

[0148] Gold is obtained in the form of hydrogen tetrachloroaurate III (49.5% gold metal) as item number 12325 from Alfa Aesar. Approximately 0.5022 grams of hydrogen tetrachloroaurate III is dissolved in ten milliliters of deionized water and the solution is acidified with 0.050 grams of six normal (6N) hydrochloric acid. About 20.35 grams of the dried alumina (from above) is evenly coated with this acidified gold solution. The gold-coated alumina particles, which have a yellow tint, were dried at 95 C for two hours. The dried gold-coated alumina is poured in 700 milliliters of deionized water containing 35 milliliters of five normal (SN) ammonium hydroxide. The suspension is vigorously stirred overnight. The following day, the gold-coated alumina is allowed to settle and the liquid decanted. About 750 milliliters of deionized water is added and the mixture stirred for an additional five minutes. The gold-coated alumina is allowed to settle and the supernatant tested for the presence of chloride ions with an aqueous silver nitrate solution. The gold-coated alumina is washed several times with deionized water. When no more chloride ions were detected in the supernatant using the aqueous silver nitrate solution, washing is considered complete. The gold-treated alumina is dried overnight at 95 C. The dried gold-coated alumina is then heated to 375 C for sixteen hours. The final catalyst particles were free-flowing granules, deep purple in color and had a theoretical gold loading of 1.2% (W/W). When not in use, the catalyst compositions were stored in a sealed container.

EXAMPLE 3

Catalyst Performance Properties

[0149] The efficacy of the catalyst compositions of the present invention produced in Examples 1 and 2 is demonstrated in a gas mixture containing 95% air and 5% carbon monoxide and in mainstream whole smoke generated by smoking ECLIPSE® prototype cigarettes and conventional burn down cigarettes.

[0150] For the following tests, a carbon monoxide/carbon dioxide NDIR (nondispersive infrared analyzer) is attached at one end of a Filamatic Smoking Machine, Model DAB-5, produced by National Instruments Co., of Baltimore, Md.

The CO/CO₂ NDIR analyzer used in the following examples is commercially available from Rosemount Analytical Inc.

[0151] Reduction of Amount Carbon Monoxide in Carbon Monoxide-Air Mixture

[0152] A gas mixture consisting of 5% carbon monoxide (CO) and 95% air, by weight, is drawn through a glass tube containing a packed bed of catalyst composition. The tube is twelve centimeters long and 1.25 centimeters in diameter. The catalyst composition used is the catalyst composition prepared in Example 1.

[0153] Approximately five grams of catalyst composition is packed approximately to the dimensions of the tube and is held in place with glass wool. A packed bed of this dimension had a pressure drop of about 70 millimeters of water measured at a flow rate of 17.5 cubic centimeters per second. The gas stream is passed through the packed bed at a flow rate of 50 cubic centimeters per two seconds, in a puff cycle of 30 second intervals (i.e., 50/30/2 smoking conditions).

[0154] The gas exiting the bed is passed through the CO/CO NDIR analyzer. The control (glass tube with no catalyst composition) did not result in the conversion of any carbon monoxide to carbon dioxide. The catalyst composition, however, is effective in oxidizing carbon monoxide to carbon dioxide. In the first puff of fifty milliliters, about 85% of the carbon monoxide is converted to carbon dioxide. Several puffs of the same gas composition were passed through the bed. The bed of catalyst composition maintained the efficiency of conversion even after passing 750 milliliters of gas through it. Average efficiency of conversion is about 74.4% for fifteen puffs of fifty milliliters each. There is no deactivation of the catalyst even after heavy exposure to the test gas mixture.

[0155] Reduction in Carbon Monoxide in Mainstream ECLIPSE®-type Cigarette Smoke

[0156] A glass tube containing the catalyst composition of Example 1 is prepared as described above. An experimental prototype of an ECLIPSE®-type cigarette is used for this example. The prototype is similar to the current market product. Whole smoke from the mouth end of the cigarette is directly passed through the bed of catalyst composition. Fifty milliliters of smoke were passed through the bed for a duration of two seconds every thirty seconds. Smoke exiting the bed is passed through a Cambridge pad to trap the particulate phase of the smoke. The resulting particulate-free gas phase of the smoke is passed through the NDIR analyzer for CO/CO₂ analysis. Subsequently two additional prototype cigarettes were smoked under the same smoking conditions and the smoke passed through the same bed of catalyst compositions. In all, smoke from three cigarettes is passed through the catalyst bed.

[0157] A prototype cigarette is smoked with no catalyst composition in the glass tube to establish the amount of carbon monoxide in the prototype cigarette. The prototype cigarette yielded 33.5 units of carbon monoxide in fifteen puffs of fifty milliliters each. Smoking the first test cigarette smoked through the catalyst bed resulted in a reduction in carbon monoxide from 33.5 units/cigarette in the control to 13.9 units /cigarette, a 58.55% reduction in carbon monoxide. Smoking a second prototype cigarette smoked through the same packed bed resulted in 22.9 units of carbon

monoxide per cigarette, a 31.6% reduction in carbon monoxide. Smoking a third prototype cigarette through the same packed bed resulted in 25.6 units of carbon monoxide per cigarette, a 23.5% reduction in carbon monoxide.

[0158] The deactivation seen in the catalyst composition with the smoking of the second and third prototype cigarettes is not observed when the catalyst composition is subjected to the mixture of air and carbon monoxide only. Thus, the deactivation observed may be due to a specific component, or components, other than carbon monoxide in the smoke.

EXAMPLE 4

Measurement of Catalytic Activity

[0159] This example illustrates the catalytic activity of the ultrafine particle catalyst composition produced in Example 2 above.

[0160] Catalytic activity is expressed herein in terms of "Turn-Over Frequency" or TOF. For this application TOF is measured by placing a known amount of the test catalyst composition in a 12 cm long glass tube of 1.25 cm diameter. The catalyst composition is sandwiched between two fiberglass mats. A gas mixture comprising 5% carbon monoxide and 95% air at room temperature is passed through the bed of catalyst at a rate of 50 cubic centimeters per 2 seconds in a puff cycle of 30 second intervals. This results in an effective flow rate of 1.5 liter/minute. The exit gas is passed through a non-dispersive infrared analyzer where concentrations of CO and CO₂ are recorded. To measure the TOF, fifteen 50 milliliter puffs of the test gas (5% CO, 95% air) are passed through the bed containing the catalyst composition. The concentrations of CO and CO₂ exiting the bed are recorded in the final 50 milliliter puff of the exit gas. TOF is expressed as % CO converted per gram of catalyst per second. Thus

TOF=(CO_{Input}-CO_{Output})×100/(CO_{Input}×Weight of Catalyst×2)

[0161] Table 1 provides the TOF of the catalyst composition produced by the procedures described herein.

TABLE 1

TOF of Gold Catalyst Compositions					
Example No.	Catalyst Composition, g	Input CO, mg	Output CO, mg	TOF	
1 2	5 2	3.4 3.2	0.81 0.5	7.6 21.1	

[0162] The catalyst composition from Example 2 showed about 2.8 times the catalytic activity of the catalyst composition from Example 1.

EXAMPLE 5

Reduction in Carbon Monoxide in Mainstream Smoke of a Conventional Cigarette

[0163] A conventional cigarette equipped with a cavity filter containing activated carbon is used to measure the efficacy of the catalyst preparations in reducing the amount of CO in cigarette smoke for this study. Smoke exiting from

the cigarette is passed through a bed of the catalyst composition produced in Example 2 contained in a glass tube (12 cm in length by 1.25 cm in diameter). The smoke exiting from the catalyst bed is filtered through a Cambridge pad. The filtered smoke is fed to the NDIR analyzer.

[0164] This arrangement subjects the catalyst composition to the whole (i.e., both particulate and gas-phase) smoke. Wet Total Particulate Matter ("WTPM") is determined as gain in weight of the Cambridge pad, and CO is determined by NDIR.

[0165] As a control, 25 cigarettes were smoked under FTC 35/60/2 smoking conditions. Results for the control cigarettes are presented in Table 2. The data represents the average of 25 cigarettes.

TABLE 2

Results for C	Control	
PUFFS/CIG WIPM mg/cig NIC mg/cig H ₂ O mg/cig TAR mg/cig mg CO	7.7 11.7 0.84 1.2 9.7 9.3	
mg CO ₂	28.5	

[0166] Table 2 presents the FTC smoking yields from the Control cigarette. The cigarette produced 11.7 mg WTPM, 9.7 mg of Tar and 9.3 mg CO when smoked under standard FTC conditions.

[0167] For this example, cigarettes were smoked for eight puffs at 50/30/2 smoking conditions. The Control cigarette produced 31 mg WTPM and 11.0 mg CO. The same cigarette when smoked in the presence of the catalyst produced 27 mg WTPM and 7.6 mg CO. These results are presented in FIG. 9. The catalyst bed removed 3.4 mg CO and 4 mg WTPM. Thus CO is reduced by about 31%.

[0168] One potential issue with the use of a catalyst composition in a filter element of a cigarette is that the active sites of the catalyst may be deactivated by cigarette smoke. Several methods to reduce the deactivating effects of smoke on the catalyst composition were tested. Removal efficiency of the catalyst composition "doubled" when 1 gram activated carbon (Pica G277, 20 X 50 US mesh) is mixed with 1 gram of the catalyst composition from Example 1 and the test described herein is repeated. The mixture containing only half the amount of catalyst removed the same amount of CO from the smoke as 2 g of the catalyst composition from Example 1. Removal efficiency of the mixture is significantly reduced when activated carbon is replaced with the same amount of high-surface-area alumina (Fisher Scientific). Thus, the activated carbon is potentially more effective than alumina in removing smoke components which pollute the catalyst.

[0169] While the invention has been described with reference to preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the invention as defined by the claims appended hereto.

What is claimed is:

- 1. A catalyst composition comprising: a substrate and ultrafine particles.
- 2. The catalyst composition of claim 1 wherein the substrate comprises a metal oxide; a ceramic; a metal; an alloy; a zeolite; a polymer; a carbon-containing material or mixtures thereof.
- 3. The catalyst composition of claim 1 wherein the ultrafine particles comprise gold, copper, silver, platinum, palladium, rhodium, nickel, and other transition metals; iron; alloys of noble metals; metal oxides; and mixtures thereof.
 - 4. A smoking article, comprising:
 - a rod of aerosol generating material
 - a filter element coupled to a first end of the rod; and
 - at least one catalyst composition comprising ultrafine particles the at least one catalyst composition being operative to convert carbon monoxide to carbon dioxide at temperatures below 150 C.
- 5. The smoking article of claim 4 wherein the catalyst composition is located within the filter element.
- **6.** The smoking article of claim 5 wherein the filter element comprises carbon.
- 7. The smoking article of claim 6 wherein the filter element further comprises an adsorbent.
- **8**. The smoking article of claim 4 wherein the catalyst composition is located within the rod of aerosol generating material.
- **9**. The smoking article of claim 4 further comprising a heat source.
- **10**. The smoking article of claim 9 wherein the catalyst composition is located adjacent the heat source.
- 11. The smoking article of claim 9 wherein the catalyst composition is located in the filter element.
- 12. The smoking article of claim 4, wherein the catalyst composition comprises a plurality of ultrafine particles positioned on at least one substrate.

- 13. The smoking article of claim 12, wherein the at least one substrate comprises at least one of cerium oxide (CeO₂), titanium dioxide (TiO₂), alumina (Al₂O₃), or mixtures thereof.
- 14. The smoking article of claim 13, wherein the at least one substrate comprises alumina (Al₂O₃).
- **15**. The smoking article of claim 13 wherein the ultrafine particles comprise a noble metal.
- 16. The smoking article of claim 15, wherein the noble metal has an average particle size up to about 100 nanometers.
- 17. The smoking article of claim 16, wherein the noble metal has an average particle size up to about 10 nanometers.
- 18. The smoking article of claim 17, wherein the noble metal has an average particle size between about 2 and about 4 nanometers.
- 19. A method for facilitating the conversion of carbon monoxide to carbon dioxide in a smoking article, comprising incorporating at least one catalyst composition in a filter element of the smoking article, the at least one catalyst composition comprising:
 - at least one substrate; and
 - a plurality of ultrafine particles positioned on the at least one substrate.
- **20**. The method of claim 19, wherein the at least one substrate comprises at least one of cerium oxide (CeO₂), titanium dioxide (TiO₂), alumina (Al₂O₃), or mixtures thereof.
- 21. The method of claim 19, wherein the at least one substrate comprises alumina (Al_2O_3) .
- 22. The method of claim 21, wherein the ultrafine particles comprise gold.
- 23. An article of manufacture comprising a catalyst composition of claim 1.
- 24. A filter element comprising a catalyst composition of claim 1.

* * * * *