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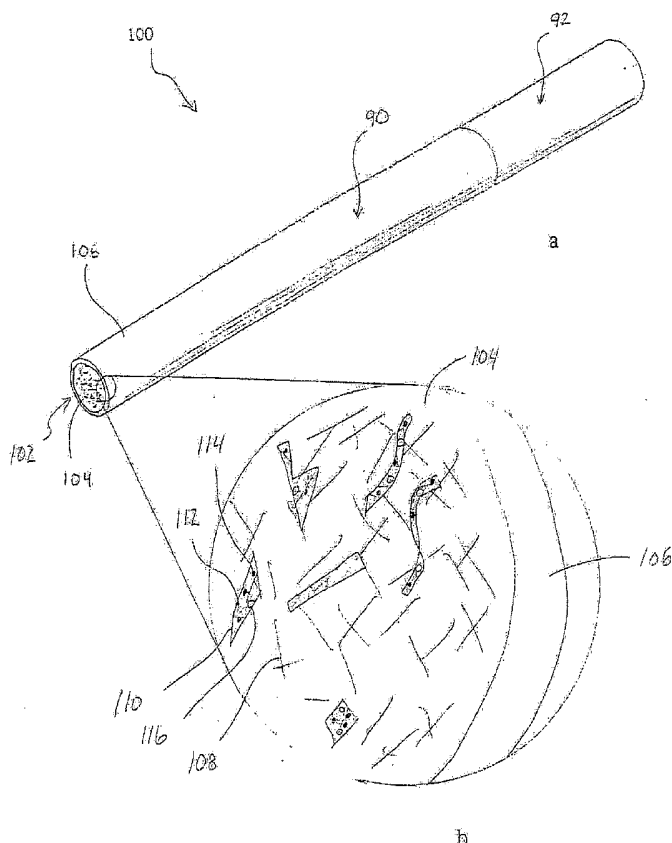
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[Continued on next page]

(54) Title: SHREDDED PAPER WITH CATALYTIC FILLER IN TOBACCO CUT FILLER AND METHODS OF MAKING
SAME



(57) Abstract: A filter composition of a tobacco
rod for a smoking article includes a tobacco cut
filler and a catalytic paper containing a nanopar-
ticle carbon monoxide catalyst. The nanoparticle
carbon monoxide catalyst is incorporated into a
web-filler material utilized in production of the
catalytic paper. The nanoparticle carbon monox-
ide catalyst includes a nanoparticle iron oxide cat-
alytic particle. Also provided is a smoking article
including the tobacco rod having a paper wrapper
encasing a tobacco column containing a catalytic
paper.



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SHREDDED PAPER WITH CATALYTIC FILLER IN TOBACCO CUT FILLER AND METHODS OF MAKING SAME

BACKGROUND

[0001] This application claims priority under 35 USC §119 to U.S. Provisional Application No. 60/477,924 entitled SHREDDED PAPER WITH CATALYTIC FILLER IN TOBACCO CUT FILLER AND METHODS OF MAKING SAME and filed on June 13, 2003, the entire content of which is hereby incorporated by reference.

[0002] In the description that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art.

[0003] Smoking articles, such as cigarettes or cigars, produce both mainstream smoke during a puff and sidestream smoke during static burning. One constituent of both mainstream smoke and sidestream smoke is carbon monoxide (CO). The reduction of carbon monoxide in smoke is desirable.

[0004] Catalysts, sorbents, and/or oxidants for smoking articles are disclosed in the following: U.S. Patent No. 6,371,127 issued to Snider et al., U.S. Patent No. 6,286,516 issued to Bowen et al., U.S. Patent No. 6,138,684 issued to Yamazaki et al., U.S. Patent No. 5,671,758 issued to Rongved, U.S. Patent No. 5,386,838 issued to Quincy, III et al., U.S. Patent No. 5,211,684 issued to Shannon et al., U.S. Patent No. 4,744,374 issued to Deffeves et al., U. S. Patent No. 4,453,553 issued to Cohn, U.S. Patent No. 4,450,847 issued to Owens, U.S. Patent No. 4,182,348 issued to Seehofer et al., U.S. Patent No. 4,108,151 issued to Martin et al., U.S. Patent No. 3,807,416, and U.S. Patent No. 3,720,214. Published applications WO 02/24005, WO 87/06104, WO 00/40104 and U.S. Patent Application Publication Nos. 2002/0002979 A1, 2003/0037792 A1 and 2002/0062834 A1 also refer to catalysts, sorbents, and/or oxidants.

-2-

[0005] Iron and/or iron oxide has been described for use in tobacco products (see e.g., U.S. Patent No. 4,197,861; 4,489,739 and 5,728,462). Iron oxide has been described as a coloring agent (e.g. U.S. Patent Nos. 4,119,104; 4,195,645; 5,284,166) and as a burn regulator (e.g. U.S. Patent Nos. 3,931,824; 4,109,663 and 4,195,645) and has been used to improve taste, color and/or appearance (e.g. U.S. Patent Nos. 6,095,152; 5,598,868; 5,129,408; 5,105,836 and 5,101,839).

[0006] Despite the developments to date, there remains a need for improved and more efficient methods and compositions for reducing the amount of carbon monoxide in the mainstream smoke of a smoking article during smoking.

SUMMARY

[0007] A preferred embodiment of a smoking article comprises a cigarette tobacco rod including a wrapper surrounding a tobacco column, the tobacco column containing a cut filler and a catalytic paper including a web, a web-filler material, and a nanoparticle carbon monoxide catalyst, the web-filler material supporting said nanoparticle catalyst. Preferably, the nanoparticle carbon monoxide catalyst comprises a nanoparticle iron oxide catalyst supported by calcium carbonate.

[0008] A preferred method of making a smoking article comprises (i) optionally supporting a nanoparticle carbon monoxide catalyst on a web-filler material to form a catalyst modified web-filler, (ii) making catalytic paper including the catalyst modified web-filler, (iii) forming a tobacco column, the tobacco column including the catalytic paper and a cut filler, (iv) placing a wrapper around the tobacco column to form the smoking article.

[0009] A preferred smokeable material for a cigarette tobacco rod comprises shredded tobacco and a catalytic paper, the catalytic paper including a web, a web-filler material, and a catalyst modified web-filler, the catalyst modified web-filler including a nanoparticle carbon monoxide catalyst supported on the web-filler material.

[0010] A preferred method of making a smokeable material for a tobacco rod comprises adding catalytic paper to shredded tobacco, the catalytic paper including a

-3-

web, a web-filler material and a nanoparticle carbon monoxide catalyst supported on the web-filler material.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0011] The following detailed description makes reference to the accompanying drawings in which like numerals designate like elements and in which:

[0012] FIG. 1(a) shows an exemplary smoking article with a composition of tobacco including cut filler and a catalytic paper containing a nanoparticle carbon monoxide catalyst. FIG. 1(b) shows an expanded view of the composition of tobacco.

[0013] FIG. 2 shows a schematic of a papermaking machine wherein the chalk box may contain a catalyst modified web-filler.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0014] Catalytic paper in cut filler compositions and smoking articles and methods for making smoking articles which involve the use of shredded paper with nanoparticle additives in cut filler compositions are 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 reduce the amount of carbon monoxide in mainstream smoke.

[0015] The term "mainstream" smoke refers to the mixture of gases passing down the tobacco rod and issuing through the filter end, i.e. the amount of smoke issuing or drawn from the mouth end of a cigarette during smoking of the cigarette. The mainstream smoke contains smoke that is drawn in through both the lighted region, as well as through the cigarette paper wrapper.

[0016] Carbon monoxide (CO) oxidation catalysts, such as nanoparticle iron oxide catalysts of the preferred embodiments, can be incorporated into the tobacco cut filler formed into tobacco rods for smoking articles, such as cigarettes.

Subsequently, the smoking article is consumed during smoking. While not wishing to be bound by theory, it is believed that during smoking, the incorporated

-4-

nanoparticle catalyst catalyzes a constituent gas component in the gas stream, e.g., the carbon monoxide catalyst catalyzes CO to reduce the level of CO in the mainstream and sidestream cigarette smoke by reaction with oxygen (O₂) in the gas stream of the smoking article to form carbon dioxide (CO₂) following equation 1:



It is also believed that subsequent to the catalytic reaction, the catalyst may also act as an oxidant, e.g., can oxidize CO in the absence of oxygen in the gas stream to reduce the level of CO in the mainstream and/or sidestream smoke.

[0017] FIG. 1(a) shows an exemplary smoking article with a cigarette tobacco rod that includes a nanoparticle carbon monoxide catalyst. The preferred smoking article 100 has a tobacco rod portion 90 and filtering tip 92. Optionally, embodiments of the smoking article 100 can be practiced without a filtering tip 92. Preferably, the tobacco rod portion 90 comprises a cigarette tobacco column 102 of a composition of tobacco 104 surrounded by a wrapper 106. As shown in the magnified view of FIG. 1(b), the composition of tobacco 104 contains a cut filler 108 and a catalytic paper 110 including a web of fibrous cellulosic material 112 in which is dispersed particles of web-filler material 114, such as calcium carbonate (CaCO₃). In practice, the web-filler material 114 serves as an agent for determining the permeability of the catalytic paper 110 (measured typically in units of CORESTA, which is defined as the amount of air, measured in cubic centimeters, that passes through one square centimeter of material in one minute at a pressure drop of 1.0 kilopascals) and also serves as a support for nanoparticles of carbon monoxide catalyst, preferably nanoparticles of iron oxide. If desired, the catalytic paper 110 can optionally include a catalyst-free web-filler material 116. The web-filler material is a filler material utilized in production for the wrapper 104. Optionally, the filtering tip can comprise one or more plugs of cellulose tow and optionally could include an adsorbent such as carbon.

[0018] By "nanoparticles" is meant that the particles have an average particle diameter of less than a micron. The nanoparticle catalyst preferably has an average particle diameter of less than about 500 nm, further preferably less than about 300 to 400 nm, more preferably from 1 to 50 nm, even more preferably 1 to 10 nm, and most preferably less than about 5 nm. A bulk density of the nanoparticle catalyst is preferably less than 0.25 g/cc, preferably about 0.05 g/cc. The Brunauer, Emmett, and Teller (BET) surface area of preferred nanoparticle catalyst is about 20 m²/g to 400 m²/g, more preferably about 200 m²/g to about 300 m²/g. An example of a high temperature nanoparticle carbon monoxide catalyst includes nanoparticle iron oxide catalyst. A preferred nanoparticle iron oxide catalyst is NANOCAT[®] Superfine Iron Oxide, available from Mach I, Inc., of King of Prussia, PA. The nanoparticle iron oxide catalyst can comprise FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or mixtures thereof.

[0019] The nanoparticle carbon monoxide catalyst is incorporated into the composition of tobacco by directly mixing the nanoparticle carbon monoxide catalyst with the tobacco cut filler and/or by incorporating the nanoparticle carbon monoxide catalyst into a web-filler material of a catalytic paper, reducing the size of the catalytic paper (by, for example, shredding), and mixing the reduced catalytic paper with the tobacco cut filler in the composition of the tobacco. The nanoparticle carbon monoxide catalyst is incorporated into a web-filler material by fixing the nanoparticle carbon monoxide catalyst to web-filler material utilized as web-filler material in the production of cigarette wrapping paper. The web-filler material can include an oxide, a carbonate, or a hydroxide of a Group II, Group III or Group IV metal, or the web-filler material can be selected from the group consisting of CaCO₃, TiO₂, silicates such as SiO₂, Al₂O₃, MgCO₃, MgO and Mg(OH)₂. In a preferred embodiment, the web-filler material is CaCO₃ or other conventional web-filler material used in cigarette paper manufacture. If desired, the catalytic paper can include web-filler materials which do not include the nanoparticle carbon monoxide catalyst.

[0020] In a preferred embodiment of a smoking article, the nanoparticle iron oxide catalytic particle includes FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or mixtures thereof. The

-6-

nanoparticle iron oxide catalytic particle is supported on a web-filler material selected from the group consisting of CaCO_3 , TiO_2 , silicates such as SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$ to form a catalyst modified web-filler. An average particle size of the catalyst modified web-filler is 0.1 to 10 microns, preferably less than or equal to 1.5 microns.

[0021] In another preferred embodiment, a total amount of nanoparticle carbon monoxide catalyst in the smoking article is an amount effective to convert at least some CO to CO_2 . For cigarettes, a preferred amount of catalyst per cigarette is 1 to 100 mg, 1 to 50 mg or 50 to 100 mg, 2 to 25 mg or 25 to 50 mg, 1 to 15 mg or 15 to 40 mg, or 4 to 10 mg or 10 to 30 mg.

[0022] In one approach, the nanoparticle carbon monoxide catalyst, such as nanoparticle iron oxide catalytic particles, is supported by web-filler material, such as CaCO_3 , by forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material. The CaCO_3 used in this process can be the same as the filler material used in the papermaking process, such as ALBACAR® 5970 commercially available from Specialty Minerals of Bethlehem, Pennsylvania. The slurry is spread, by, for example, spreading the slurry with a doctors blade, and then dried to evaporate the water leaving behind a solid. One method to dry the slurry includes exposure in air while heated by a heat source, such as a radiation lamp at 75EC, although other methods such as vacuum filtering followed by drying can also be used.

[0023] The catalyst and filler can be provided in any desired amount, e.g., 10 to 90% catalyst and 90 to 10% web-filler. The solid is either a powdery substance or a self-supporting solid mass, depending on the nanoparticle carbon monoxide catalyst loading of the slurry. For example, for a slurry containing about 50 to 60 wt.% catalyst loading or less of nanoparticle iron oxide catalytic particle on calcium carbonate, the slurry dries to a powdery substance; for a slurry containing a catalyst loading of greater than about 60 to 70 wt.% catalyst loading of the nanoparticle iron oxide catalytic particle on calcium carbonate, the slurry dries to a self-supporting solid mass. Prior to incorporating the catalyst modified web-filler in catalytic paper,

the average particle size of the catalyst modified web-filler can be reduced to an average particle size of 0.1 to 10 microns, preferably about 1 micron or less. For example, the catalyst modified web-filler can be ball milled to form a powder by milling, for example, with 1 cm agate milling balls for 2 to 4 hours at 100 to 300 rpm. Ball milling may not be necessary where the slurry dries to a powdery substance. Subsequently, the catalyst modified web-filler, e.g., the nanoparticle carbon monoxide catalyst/web-filler material, can be incorporated into the paper through the papermaking processes. For example, the catalyst modified web-filler can be used as filler material in the papermaking processes.

[0024] In another approach, particles of web-filler material, such as CaCO_3 , support the nanoparticle carbon monoxide catalyst, such as nanoparticle iron oxide, by forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material, drying the slurry to form the catalyst modified web-filler, and subsequently calcining the catalyst modified web-filler. The slurry is formed substantially as described above with respect to the first approach. After drying the slurry to form a self-supporting solid mass and ball milling to form a powder (if necessary to reduce the size of the filler), the catalyst modified web-filler is calcined by heating the catalyst modified web-filler to a suitable calcining temperature of no more than 500EC, preferably from 200EC to 400EC, for a suitable period of time such as from 1 to 3 hours, preferably 2 hours. The catalyst modified web-filler, e.g., the nanoparticle carbon monoxide catalyst/web-filler material, can be used as filler material in conventional papermaking processes. For example, the catalyst modified web-filler material can be used as web-filler in the papermaking processes.

[0025] An exemplary process of making catalyst modified web filler comprising a 50/50 NANOCAT[®] iron oxide nanoparticle catalyst/ CaCO_3 mixture utilizing milling can be carried out as follows:

1. Mix 150 lb distilled water and 25 lb CaCO_3 into 55 gallon stainless steel kettle.
2. Add slowly with continued mixing 25 lb NANOCAT[®] iron oxide nanoparticle catalyst.
3. Mix at maximum allowable rate for 2 hours after adding remaining 50 lb

-8-

water.

4. Vacuum filter the slurry into filter cakes using Buchner funnel (25 cm) and flask (2000 ml).
5. Cut the filter cake into small –1 inch pieces and place them in frying pans (pan: 14" – 10"-2").
6. Freeze dry the filter cake.
7. Place pans in vacuum bell and vacuum dry at 110EC for 24 hours.
8. Mill the powders using (Rotary Mill), Ceramic Ball and cylinder for 6 hours.
9. Calcine in air for 2 hours. at 300EC.

[0026] An exemplary process of making catalyst modified web filler comprising a 50/50 NANOCAT[®] iron oxide nanoparticle catalyst/ CaCO_3 mixture utilizing spray drying can be carried out as follows:

1. Prepare a catalyst mixture in water slurry by adding 1 part NANOCAT[®] iron oxide nanoparticle catalyst and 1 part of CaCO_3 with 12 parts of water by weight. Stir the mixture to get a homogenous slurry (at least 30 minutes).
2. Feed the slurry to a spray drying machine.
3. Adjust air temperature to obtain dry powder (e.g., 175EC air temperature).
4. Depending on the temperature used for drying calcination is optional. If carried out, calcination can be performed in air for 2 hours at 300EC.

[0027] Once produced, the catalytic paper is shredded and mixed with the tobacco cut filler to form a composition of tobacco for subsequent manufacture into a cigarette tobacco rod in a cigarette making machine. Any suitable tobacco mixture may be used for the cut filler. Examples of suitable types of tobacco materials include flue-cured, Burley, Maryland or Oriental tobaccos, the rare or specialty tobaccos, and blends thereof. The tobacco material can be provided in the form of tobacco lamina, processed tobacco materials such as volume expanded or puffed tobacco, processed tobacco stems such as cut-rolled or cut-puffed stems, reconstituted tobacco materials, or blends thereof. The tobacco can also include tobacco substitutes.

[0028] In cigarette manufacture, the tobacco is normally employed in the form of cut filler, i.e., in the form of shreds or strands cut into widths ranging from about 1/10 inch to about 1/20 inch or even 1/40 inch. The lengths of the strands range from between about 0.25 inches to about 3.0 inches. The cigarettes may further comprise one or more flavorants or other additives (e.g., burn additives, combustion modifying agents, coloring agents, binders, etc.) known in the art.

[0029] In the catalytic paper, the nanoparticle carbon monoxide catalyst can be fixed to the filler material to form a catalyst modified web-filler material by any suitable technique. For example, the nanoparticle carbon monoxide catalyst can be combined with the web-filler material by co-precipitating the nanoparticle iron oxide catalytic particle from a liquid phase onto the web-filler material or co-depositing the nanoparticle iron oxide catalytic particle from a vapor phase onto the web-filler material.

[0030] According to a preferred embodiment, the catalyst modified web-filler, e.g., the nanoparticle carbon monoxide catalyst/web-filler material, is incorporated in the catalytic paper through conventional papermaking processes. For example, the catalyst modified web-filler can be used as all or part of the web-filler material in the papermaking processes or can be distributed directly onto the paper, such as by spraying or coating onto wet or dry base web to form the catalytic paper. A catalytic paper can be any wrapper for smoking articles, including wrappers containing flax, hemp, kenaf, esparto grass, rice straw, cellulose and so forth. Optional filler materials, flavor additives, and burning additives can be included. Further, the catalytic paper can have more than one layer in cross-section, such as in a bilayer paper as disclosed in commonly-owned U.S. Patent No. 5,143,098, issued to Rogers, the entire content of which is herein incorporated by reference.

[0031] The papermaking process can be carried out using conventional paper making equipment. An exemplary method of manufacturing catalytic paper including catalyst modified web-filler comprising nanoparticle carbon monoxide catalyst supported by a web-filler material comprises supplying the catalyst modified web-filler and a cellulosic material to a papermaking machine. For

-10-

example, an aqueous slurry (or "furnish") including the catalyst modified web-filler and the cellulosic material can be supplied to a head box of a forming section of a Fourdrinier papermaking machine. The catalyst modified web-filler includes a nanoparticle carbon monoxide catalyst, e.g., nanoparticle iron oxide catalyst, supported by a web-filler material, e.g., CaCO_3 . For example, the catalyst modified web-filler can include nanoparticle iron oxide catalyst/ CaCO_3 particles or any other suitable nanoparticle carbon monoxide catalyst and web-filler material, such as an oxide, a carbonate, or a hydroxide of a Group II, Group III or Group IV metal, CaCO_3 , TiO_2 , silicates such as SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$. The aqueous slurry can be supplied to the head box by a plurality of conduits which communicate with a source, such as a storage tank.

[0032] The exemplary method can optionally include calcining the catalyst modified web-filler in a step prior to supplying the furnish to the papermaking machine.

[0033] The catalyst modified web-filler can be supplied to the papermaking process in any suitable form, such as in the form of an aqueous slurry or in the form of a dry powder to be slurried during the papermaking process prior to addition to the head box. For example, the catalyst modified web-filler can be produced on site as a slurry. The aqueous slurry containing the catalyst modified web-filler can be used immediately or stored for future use. In a preferred embodiment, the head box is supplied with an aqueous slurry of furnish containing the catalyst modified web-filler and cellulosic material used to form a web. Optionally, an aqueous slurry of furnish containing catalyst modified web-filler and an aqueous slurry furnish of cellulosic material without catalyst modified web-filler or with a different concentration of catalyst modified web-filler can be supplied to separate head boxes or multiple head boxes.

[0034] An exemplary method deposits the aqueous slurry from the head box onto a forming section so as to form a base web of the cellulosic material and the catalyst modified web-filler. For example, in a typical Fourdrinier machine, the forming section is a Fourdrinier wire which is arranged as an endless forming wire

-11-

immediately below the head box. A slice defined in a lower portion of the head box adjacent to the endless wire permits the aqueous slurry of catalyst modified web-filler and cellulosic material from the head box to flow through the slice onto the top surface of the endless wire to form a wet base web. Optionally, the aqueous slurry can be deposited onto a support web that is retained within the paper. For example, a support web can be transported through the forming section of a papermaking machine and can be a foundation on which the aqueous slurry is deposited. The aqueous slurry dries and the paper sheet (e.g., finished web) is formed with the support web embedded therein. The support web can be a conventional web, such as a flax support web, or can include a web with an incorporated catalytic component, such as a nanoparticle carbon monoxide catalyst. If the support web includes a catalytic component, the incorporated catalytic component can be supported on a web-filler material or can be directly supported on the support web without a web-filler material.

[0035] After depositing the aqueous slurry onto the forming section, water is removed from the wet base web and, with additional processing such as further drying and pressing, if necessary, forms a sheet of catalytic paper (e.g., finished web). The catalytic paper is subsequently taken up for storage or use, e.g. the catalytic paper is coiled in a sheet or roll.

[0036] Referring to FIG. 2, a cigarette papermaking machine 200 includes a head box 202 operatively located at one end of a Fourdrinier wire 204, and source of feed stock slurry such as a run tank 206 in communication with the head box 202. The head box 202 can be one typically utilized in the papermaking industry for laying down cellulosic pulp upon the Fourdrinier wire 204. In the usual context, the head box 202 is communicated to the run tank 206 through a plurality of conduits. The run tank 206 receives furnish from a furnish supply 218. Preferably, the feed stock from the run tank 206 is a refined cellulosic pulp such as a refined flax or wood pulp as is the common practice in the cigarette papermaking industry. Preferably, a chalk tank 228 (containing the catalyst modified filler described above) is communicated

-12-

with the run tank 206 so as to establish a desired "chalk" level in the slurry supplied to the head box 202.

[0037] The Fourdrinier wire 204 carries the laid slurry pulp (e.g., base web) from the head box 202 along a path in the general direction of arrow A in FIG. 2, whereupon water is allowed to drain from the pulp through the wire 204 by the influence of gravity and at some locations with the assistance of vacuum boxes 210, 210', 210" at various locations along the Fourdrinier wire 204 as is the established practice in the art of cigarette papermaking. At some point along the Fourdrinier wire 204, sufficient water is removed from the base web to establish what is commonly referred to as a dry line where the texture of the slurry transforms from one of a glossy, watery appearance to a surface appearance more approximating that of the finished base web (but in a wetted condition, e.g., an intermediate web). At and about the dry line, the moisture content of the pulp material is approximately 85 to 90%, which may vary depending upon operating conditions and the like.

[0038] Downstream of the dry line, the intermediate web 212 separates from the Fourdrinier wire 204 at a couch roll 214. From there, the Fourdrinier wire 204 continues on the return loop of its endless path. Beyond the couch roll 214, the intermediate web 212 continues on through the remainder of the papermaking system which further dries and presses the intermediate web 212 and surface conditions it to a desired final moisture content and texture to form a paper 220 (e.g., finished web). Such drying apparatus are well known in the art of papermaking and may include drying section 216 including drying felts, vacuum devices, rolls, and/or presses, applied thermal energy, and the like.

[0039] The cigarette making machine 200 can optionally include more than one head box and/or more than one Fourdrinier wire with either separate or common furnish supply. Referring to FIG. 2, the optional second head box 202', suitably integrated with a run tank and furnish supply, can lay slurry pulp onto the slurry pulp laid from the first head box 202 and carried along Fourdrinier wire 204. The second and/or additional head box can be supplied with catalyst modified web filler to a desired "chalk" level or can be free of catalyst modified web-filler, as desired based

on the number of layers of slurry pulp to be deposited and/or the use of the wrapper formed from the papermaking process.

[0040] Referring to FIG. 2, the optional second Fourdrinier wire 204', suitably integrated with a head box 202' laying slurry pulp on the Fourdrinier wire 204' and draining and drying equipment, can form a second intermediate web 212'. The second intermediate web 212' can be separated from the second Fourdrinier wire 204' at a second couch roll 214' and laid on the first intermediate web 212 from the Fourdrinier wire 204 to be processed into double layer paper. Multiple optional Fourdrinier wires can be employed to form multiple layer paper having any desired number of layers, such as three, four and so forth, up to ten to twelve layers.

[0041] Other papermaking processes can be used to make a catalytic paper, e.g., a paper with a nanoparticle carbon monoxide catalyst. For example, a laminated, a bilayer or multilayer catalytic paper can be made. Examples of bilayer and multilayer paper is disclosed in commonly-owned U.S. Patent No. 5,143,098, issued to Rogers, the entire content of which is herein incorporated by reference. In an embodiment of a bilayer or multilayer catalytic paper including a nanoparticle carbon monoxide catalyst, at least one of a first layer and a second layer can include the nanoparticle carbon monoxide catalyst as described in embodiments herein. The bilayer catalytic paper can then be reduced in size, mixed with tobacco cut filler, and the composition formed into a tobacco rod in a cigarette making machine.

Additional examples of paper configurations and types of paper that can be formed as catalytic paper and used in a composition of tobacco include bilayer paper in which either the first paper layer or the second paper layer can be a banded paper, a paper having a plurality of regions of variable basis weight in the cross direction, and/or a catalytic paper formed with catalyst modified web-filler.

[0042] The bilayer or multilayer single sheet catalytic paper may be made using ordinary paper furnish such as pulped wood, flax fibers, or any standard cellulosic fiber. Preferably flax fibers are used. Different fillers, including different catalytic fillers such as the catalyst modified web-filler described herein, or different fibers may be used for each layer and may be contained in different head boxes, as

disclosed in U.S. Patent No. 5,143,098, issued to Rogers, the entire content of which is herein incorporated by reference. For example, a first head box can hold the materials for a catalytic paper that includes the nanoparticle carbon monoxide catalyst and a second head box can hold the materials for a conventional paper (wrapper).

[0043] In another example of making bilayer or multilayer single sheets of catalytic paper, the first head box can hold the materials for a catalytic paper that includes the nanoparticle carbon monoxide catalyst at a first concentration or loading level and a second head box can hold the materials for a catalytic paper that includes the nanoparticle carbon monoxide catalyst at a second concentration or loading level. In preferred embodiments, the first concentration or first loading level is different from the second concentration or second loading level. For example, the catalytic paper can have a radially inner layer and a radially outer layer, the radially inner layer having a first loading of the nanoparticle carbon monoxide catalyst and the radially outer layer having a second loading of the nanoparticle carbon monoxide catalyst. The first loading of the nanoparticle carbon monoxide catalyst can be greater than the second loading of the nanoparticle carbon monoxide catalyst. In one embodiment, the first loading of the nanoparticle carbon monoxide catalyst is up to 100 mg and the second loading of the nanoparticle carbon monoxide catalyst is less than 1 mg. Preferably, the second loading of the nanoparticle carbon monoxide catalyst is zero. In another embodiment a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the radially inner layer is from 0.1 to 3.0, more preferably from 0.1 to 1.0, most preferably from 0.33 to 1.0, and a total loading of the nanoparticle carbon monoxide catalyst in the radially outer layer is less than 1 mg, more preferably the total loading of the nanoparticle carbon monoxide catalyst in the radially outer layer is zero. Additional details on the manufacturing of bilayer and multilayer papers are disclosed in commonly-owned U.S. Patent No. 5,143,098, issued to Rogers, the entire content of which is herein incorporated by reference.

[0044] Additional examples of papermaking processes include the method for making banded paper for banded smoking article wrappers disclosed in U.S. Patent No. 5,342,484, the entire content of which is herein incorporated by reference, the method for producing paper having a plurality of regions of variable basis weight in the cross direction disclosed in U.S. Patent No. 5,474,095, the entire content of which is herein incorporated by reference, and the method of making a catalytic wrapper disclosed in commonly-owned U.S. Provisional Patent Application No. 60/477,922 (Attorney Docket No. 021238-570) entitled "CIGARETTE WRAPPER WITH CATALYTIC FILLER AND METHODS OF MAKING SAME" and filed on June 13, 2003, the entire content of which is herein incorporated by reference.

[0045] Reducing the size of the catalytic paper can be by any suitable technique such as tearing, shearing, shredding and so forth. In a preferred embodiment, the catalytic paper is reduced in size to approximate the shape, size and form of tobacco cut filler. For example, the reduced catalytic paper can have an average thickness from 0.10 mm to 0.13 mm (with a range of the thickness of 0.03 mm to 0.15 mm), an average width of less than 1.0 mm (with a maximum width of 5 mm), and an average length of less than 3.0 mm (with a maximum length of 25 mm).

[0046] The nanoparticle carbon monoxide catalyst can also be directly incorporated into the catalytic paper either during or after the papermaking process. This can occur instead of, or in addition to, incorporating the nanoparticle carbon monoxide catalyst into the web-filler material. For example, during the papermaking process the nanoparticle carbon monoxide catalyst, with or without being incorporated into a web-filler material, can be distributed, e.g., sprinkled, cast, spread, sprayed, drip coated, curtain coated, or otherwise placed in contact with the spread wet base web prior to drying. The wet base web is subsequently dried to form a catalytic paper and the nanoparticle carbon monoxide catalyst is retained within the catalytic paper. In another example, during the papermaking process the nanoparticle carbon monoxide catalyst, with or without being incorporated into a web-filler material, can be distributed, e.g., sprinkled, cast, spread, sprayed, drip coated, curtain coated, or otherwise placed in contact with the finished web. In both

of the examples, a retention aid can be incorporated into the papermaking process to improve the distribution of the nanoparticle carbon monoxide catalyst in the paper component, e.g., the aqueous slurry used in the paper making process can include a retention aid.

[0047] A preferred catalytic paper for inclusion in a composition of tobacco comprises a web including cellulosic fibers and a catalyst modified web-filler incorporated into the web. The catalyst modified web-filler includes a web-filler material supporting a nanoparticle carbon monoxide catalyst. In the exemplary embodiment, the nanoparticle carbon monoxide catalyst is a nanoparticle iron oxide catalytic particle. For example, the nanoparticle iron oxide catalytic particle can include FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof. A suitable nanoparticle iron oxide catalytic particle is NANOCAT[®] Superfine Iron Oxide.

[0048] The nanoparticle carbon monoxide catalyst, e.g., the nanoparticle iron oxide catalytic particle, is present in the catalyst modified web-filler up to about 60 wt.% catalyst loading, more preferably from about 10 wt.% to about 50 wt.% catalyst loading, and most preferably is at about 20 to 30 wt.% catalyst loading, relative to the total web-filler material.

[0049] A preferred catalytic paper can have a basis weight of from about 18 g/m^2 to about 60 g/m^2 and a permeability of from about 5 CORESTA units to about 80 CORESTA units. More preferably, the catalytic paper has a basis weight from about 30 g/m^2 to about 45 g/m^2 and the permeability is about 30 to 35 CORESTA units. However, any suitable basis weight for the catalytic paper can be selected. For example, a higher basis weight, e.g., 35 to 45 g/m^2 , can support a higher loading of catalyst. If a lower catalyst loading is selected, then a lower basis weight wrapper can be used.

[0050] The ratio of nanoparticle carbon monoxide catalyst to web-filler material can be varied by subjecting a slurry of nanoparticle carbon monoxide catalyst/web-filler material, e.g., the slurry of nanoparticle iron oxide catalyst/ CaCO_3 or other catalyst modified web-filler, to calcining at different temperatures for different time periods. Also, the mixing conditions of the slurry can be selected to achieve a

desired distribution of the web-filler material with the nanoparticle carbon monoxide catalyst. For example, the speed, time, blade type, and temperature can all be adjusted to achieve a desired uniformity of the nanoparticle carbon monoxide catalyst to web-filler material ratio. Alternatively, the nanoparticle carbon monoxide catalyst/web-filler material can be co-precipitated to form a particle or a powder, e.g., chemical precipitation methods can be used, such as precipitating CaCO_3 from CaCl_2 by adding a carbonate, such as Na_2CO_3 . Gas phase precipitation methods to deposit nanoparticle carbon monoxide catalyst in-situ onto a web-filler material can also be employed. For example, vapor deposition or spray techniques can be used.

[0051] While not wishing to be bound by theory, it appears that CO catalyst in the form of nanoparticle iron oxide catalyst, such as NANOCAT[®] Superfine Iron Oxide, starts to convert CO to CO_2 at a temperature above 150EC, preferably at a temperature above 400EC. Additionally, the conversion rate of CO to CO_2 by nanoparticle iron oxide catalyst is enhanced by the rapid and efficient transport of CO to the region of the nanoparticle carbon monoxide catalyst and CO_2 away from the region of the catalyst, e.g., air flow within the smoking article. Together, the operating temperature and the air flow within the smoking article can affect the operation of the nanoparticle carbon monoxide catalyst.

[0052] During the puffing process, CO in mainstream smoke flows toward the filter end of a smoking article. As carbon monoxide travels within the smoking article, oxygen diffuses into and carbon monoxide diffuses out of the smoking article through the paper wrapper. During the puffing process, CO is concentrated in the periphery of the cigarette, e.g., near the cigarette paper wrapper, in front of the burn zone. The oxygen concentration is high in the same region as high CO concentration due to diffusion of O_2 from outside the cigarette. Airflow into the tobacco and during the puffing process is largest near the burn zone on the periphery of the smoking article and is approximately commensurate with the gradient of temperature, e.g., larger airflow is associated with higher temperature gradients. Thus, the highest airflow is also the region of highest temperature gradient. For

-18-

example in a typical smoking article, the highest temperature gradient is from >850-900EC at the periphery of the smoking article at the burn zone to approximately 300EC toward the center of the smoking article. The temperature further drops to near ambient near the filter end. Furthermore, the temperature drop at the lit end is very fast and within a couple of mm behind the burn zone in the axial direction the temperature drops from 900EC to 200EC. Further information on airflow patterns, the formation of constituents in cigarettes during smoking and smoke formation and delivery can be found in Richard R. Baker, "Mechanism of Smoke Formation and Delivery", Recent Advances in Tobacco Science, vol. 6, pp. 184-224, (1980) and Richard R. Baker, "Variation of the Gas Formation Regions within a Cigarette Combustion Coal during the Smoking Cycle", Beiträge zur Tabakforschung International, vol. 11, no. 1, pp. 1-17, (1981), the contents of both are incorporated herein by reference.

[0053] The composition of tobacco with catalytic filler can be used as cut filler for conventional cigarettes or non-conventional cigarettes such as cigarettes for electrical smoking systems described in commonly-assigned U.S. Patent Nos. 6,026,820; 5,988,176; 5,915,387; 5,692,526; 5,692,525; 5,666,976; 5,499,636 and 5,388,594 or non-traditional types of cigarettes having a fuel rod such as are described in commonly-assigned U.S. Patent No. 5,345,951.

[0054] The position and quantity of paper with catalyst modified web-filler, e.g., catalytic filler, in the tobacco composition, e.g., the position and quantity of the shredded paper with catalyst modified web-filler, can be selected as a function of the temperature and airflow characteristics exhibited in a burning cigarette in order to adjust, e.g., increase, decrease, minimize or maximize, the conversion rate of CO to CO₂. For example, solid coal in a smoking article reaches the peak temperature of greater than 850-900EC at about the burn zone, e.g., within about 2 mm of the burn zone, and is at 300EC to 400EC within 2 to 3 mm of the burn zone. Thus, a nanoparticle carbon monoxide catalyst can be selected that operates in a given temperature range, and a composition of tobacco can be manufactured in which the catalytic filler can be incorporated in those portions of the tobacco column that are

predicted to coincide with the appropriate temperature for operation of the catalyst. The selective incorporation of catalytic filler can be realized, for example, by using different supply lines to the cigarette making machine, each supply line having a different catalytic filler. The different catalytic filler can differ either in concentration of catalyst modified web-filler, or type of catalyst modified web-filler, or operating temperature of catalyst modified web-filler. The different supply line can be at selected positions in the cigarette making process corresponding to selected locations of the cigarette, e.g., radially or axially positioned.

[0055] For example, a preferred nanoparticle carbon monoxide catalyst for use in a catalytic filler for a tobacco composition of a smoking article is catalytically active at temperature as low as ambient temperature and does not deactivate even at temperatures as high as 900EC. The preferred catalytic filler can be positioned along the entire axial length of the anticipated burn zone, e.g., not only at the filter end of the smoking article, and can be catalytically active from the lit end to the filter end during use. The axial distribution of the catalytic filler provides sufficient contact time between the mainstream smoke and the nanoparticle carbon monoxide catalyst for the CO to be converted to CO₂. Further exemplary distributions of the catalytic filler include a radial distribution within the tobacco column. The radial distribution of catalytic filler can produce a higher concentration of nanoparticle carbon monoxide catalyst along a radially outer portion of the tobacco column, e.g., toward the surface of the cylindrical tobacco column that is encased by the wrapper in the smoking article. Other distributions include a distribution along a length of the tobacco column. A lengthwise distribution can produce a higher distribution of nanoparticle carbon monoxide catalyst toward a butt end of the tobacco rod, e.g., toward the end with a filter in a filtered smoking article. An example of a preferred nanoparticle carbon monoxide catalyst includes NANOCAT[®] Superfine Iron Oxide, which starts to convert CO to CO₂ at a temperature above 150EC.

[0056] In a further example, a mixed catalyst, e.g., a catalyst that is a combination of individual catalyst compositions that each operate at a different temperature range or overlapping temperature ranges, can be used to broaden the temperature range at

which conversion of CO to CO₂ can occur and to increase the operating period of the catalyst as the smoking article burns. For example, a mixed catalyst may operate at both above about 500EC and at 300EC to 400EC and thus converts CO to CO₂ both at the burn zone and behind the burn zone, effectively increasing the conversion time and the area of the smoking article at which conversion occurs.

[0057] Although the catalyst is described herein as having an operating temperature, the term operating temperature refers to the preferred temperature for conversion of CO to CO₂. The catalyst may still operate to convert CO to CO₂ outside the described temperature range, but the conversion rate may be affected.

[0058] In any of these examples, the nanoparticle carbon monoxide catalyst can be distributed continuously or discretely and can be distributed radially or linearly within the tobacco column. Also, the nanoparticle carbon monoxide catalyst can be distributed uniformly within the smoking article.

[0059] The nanoparticle carbon monoxide catalyst is present in the tobacco composition as catalytic filler in an amount effective to convert at least 40% of carbon monoxide to carbon dioxide at a temperature of at least 400EC to about 900EC. Preferably, the nanoparticle carbon monoxide catalyst converts at least 50% of carbon monoxide to carbon dioxide at a temperature of at least 500EC. More preferably, the nanoparticle carbon monoxide catalyst converts at least 80% of carbon monoxide to carbon dioxide at a temperature of at least 700EC.

[0060] Calcination is achieved by taking catalysts from the slurry method and heating them in the presence of air for an extended duration. For example, calcining at a temperature of no more than 500EC, preferably from 200EC to 400EC, for a period of time of from 1 to 3 hours, e.g., 2 hours. Without being held to any one theory, it is believed that a calcination step can improve the bonding between the catalyst and the paper filler and that during the calcination step the catalyst surface is improved due to evaporation of bound water molecules.

[0061] The surface area of the supported catalyst was investigated using BET surface area measurements. It was observed that the BET surface areas for samples with NANOCAT[®] Superfine Iron Oxide had approximately the same BET surface

-21-

areas before and after calcination, e.g., within 10%, and that the BET surface area of these samples were approximately an order of magnitude greater than the BET surface area of samples without the nanoparticle carbon monoxide catalyst. These results indicate that calcining does not have an adverse effect on the catalyst surface area available for conversion of CO to CO₂.

[0062] In another exemplary embodiment, a low temperature nanoparticle carbon monoxide catalyst can be substituted for the high temperature nanoparticle carbon monoxide catalyst in the catalytic paper. Low temperature and even room temperature catalysts can extend the effective region of the reaction zone for CO to CO₂ conversion to the whole cigarette, provided the temperature rise due to the exothermic reaction remains below the ignition temperature of the tobacco rod and/or its components.

[0063] An example of a suitable low temperature nanoparticle carbon monoxide catalyst includes ceria-based catalysts. Ceria-based catalysts can oxidize CO at near-ambient temperatures. A suitable ceria-based catalyst is disclosed in U.S. Patent Application No. 10/314,449 entitled "CERIA-BASED CATALYSTS FOR CO OXIDATION AT NEAR-AMBIENT TEMPERATURES" and filed on December 9, 2002, the entire contents of which are herein incorporated by reference. Another example of a low temperature nanoparticle carbon monoxide catalyst includes nanoparticle additives capable of acting as an oxidant for the conversion of CO. A suitable nanoparticle additive includes a metal oxide, such as Fe₂O₃, CuO, CeO₂, or Ce₂O₃, a doped metal oxide, such as Y₂O₃ doped with zirconium or Mn₂O₃ doped with palladium, or mixtures thereof as disclosed in U.S. Patent Application No. 10/286,968 entitled "OXIDANT/CATALYST NANOPARTICLES TO REDUCE TOBACCO SMOKE CONSTITUENTS SUCH AS CARBON MONOXIDE" and filed on November 4, 2002, the entire contents of which are herein incorporated by reference.

[0064] Advantageously, supported nanoscale particles exhibit a reduced tendency to agglomerate with each other as well as a reduced tendency to leech out of the catalytic paper during cigarette paper manufacture. The web-filler material for

support of the nanoscale particles can comprise calcium carbonate (CaCO_3), which is used conventionally as a filler material in cigarette paper manufacturing. The catalytic effect of nanoscale catalyst particles (e.g., for the reduction of CO and/or NO_x from mainstream smoke) can be controlled by varying the loading of catalytic particles in the catalytic paper and/or the loading of catalytic paper in the tobacco composition. The catalytic paper can be reduced in size, e.g., shredded in different shapes and sizes, and can be distributed continuously or discontinuously through the tobacco rod along different dimensions of a smoking article. By controlling the shape, size and distribution of the catalytic paper within the tobacco rod, adequate gas flow through the smoking article can be achieved.

[0065] The tobacco column preferably comprises cut filler of a blend of tobaccos typical of the industry, including blends comprising Bright, Burley and Oriental tobaccos and other blend components, including traditional cigarette flavors. In the preferred embodiment, the shredded tobacco (cut filler) of the tobacco column comprises a blend of Bright, Burley and Oriental tobaccos with or without inclusion of reconstituted tobaccos or any after cut flavorings. Optionally, an expanded tobacco component might be included in the blend to adjust rod density, and flavors may be added. Optionally, a single variety of the aforementioned tobaccos may be used instead of a blend.

[0066] Although the present invention has been described in connection with exemplary embodiments thereof, it will be appreciated by those skilled in the art that additions, deletions, modifications, and substitutions not specifically described may be made without departing from the spirit and scope of the invention as defined in the appended claims.

-23-

What Is Claimed Is:

1. A smoking article comprising:
a cigarette tobacco rod including a wrapper surrounding a tobacco column, the tobacco column containing a cut filler and a catalytic paper including a web, a web-filler material, and a nanoparticle carbon monoxide catalyst, the web-filler material supporting said nanoparticle catalyst.
2. The smoking article of claim 1, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalytic particles.
3. The smoking article of claim 2, wherein the nanoparticle iron oxide catalytic particles have an average particle size of less than 50 nm.
4. The smoking article of claim 3, wherein the average particle size is from 1 to 10 nm.
5. The smoking article of claim 4, wherein the average particle size is about 2 to 5 nm.
6. The smoking article of claim 2, wherein the nanoparticle iron oxide catalytic particles have a bulk density of less than 0.25 g/cc.
7. The smoking article of claim 6, wherein the bulk density is greater than or equal to 0.05 g/cc.
8. The smoking article of claim 2, wherein the nanoparticle iron oxide catalytic particles have a BET surface area of about 200 to 300 m²/g.
9. The smoking article of claim 2, wherein the nanoparticle iron oxide catalytic particles include FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or mixtures thereof.

10. The smoking article of claim 1, wherein the web-filler material includes an oxide, a carbonate or hydroxide of a Group II, Group III or Group IV metal.
11. The smoking article of claim 1, wherein the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$.
12. The smoking article of claim 11, wherein the web-filler material is CaCO_3 .
13. The smoking article of claim 1, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalytic particles, the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$, and an average particle size of the web-filler material supporting the nanoparticle catalyst is 0.1 to 10 microns.
14. The smoking article of claim 13, wherein the nanoparticle iron oxide catalytic particles include particles of FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof
15. The smoking article of claim 14, wherein the web-filler material includes CaCO_3 .
16. The smoking article of claim 13, wherein the average particle size of the web-filler material is less than or equal to 1.5 micron.
17. The smoking article of claim 1, wherein a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the composition of tobacco is from 0.1 to 3.0.
18. The smoking article of claim 17, wherein the ratio is 0.1 to 1.0.

19. The smoking article of claim 18, wherein the ratio is 0.33 to 1.0.
20. The smoking article of claim 1, wherein a total amount of nanoparticle carbon monoxide catalyst in the smoking article is from 4 mg to 10 mg.
21. The smoking article of claim 1, wherein the wrapper is a dual wrapper, a bilayer wrapper, a banded wrapper or a catalytic wrapper.
22. The smoking article of claim 1, wherein the catalytic paper is shredded and distributed throughout at least a portion of the tobacco column.
23. The smoking article of claim 22, wherein the shredded catalytic paper is uniformly distributed radially within the tobacco column.
24. The smoking article of claim 22, wherein the shredded catalytic paper is uniformly distributed linearly within the tobacco column.
25. The smoking article of claim 22, wherein the shredded catalytic paper has a thickness from 0.03 mm to 0.15 mm, a width having a maximum of 5 mm, and a length having a maximum of 25 mm.
26. The smoking article of claim 25, wherein an average thickness is from 0.10 mm to 0.13 mm.
27. The smoking article of claim 25, wherein an average width is less than 1.0 mm
28. The smoking article of claim 25, wherein an average length is less than 3.0 mm.

-26-

29. A smoking article comprising:

a cigarette tobacco rod including a wrapper surrounding a tobacco column, the tobacco column containing a cut filler and a catalytic paper including a web, a web-filler material including a calcium carbonate, and iron oxide nanoparticles, the calcium carbonate supporting the iron oxide nanoparticles.

30. The smoking article of claim 26, wherein the iron oxide nanoparticles have an average particle size of 0.1 to 10 nm and the web-filler material comprises 10 to 60 % by weight of the catalytic paper.

31. A method of making a smoking article, comprising:

- (i) optionally supporting a nanoparticle carbon monoxide catalyst on a web-filler material to form a catalyst modified web-filler;
- (ii) making catalytic paper including the catalyst modified web-filler;
- (iii) forming a tobacco column, the tobacco column including the catalytic paper and a cut filler;
- (iv) placing a wrapper around the tobacco column to form the smoking article.

32. The method of claim 31, wherein a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the tobacco column is from 0.1 to 3.0.

33. The method of claim 32, wherein the ratio is 0.1 to 1.0.

34. The method of claim 33, wherein the ratio is 0.33 to 1.0.

35. The method of claim 31, wherein a total amount of nanoparticle carbon monoxide catalyst in the catalytic paper is from 4 mg to 10 mg.

-27-

36. The method of claim 31, further comprising shredding the catalytic paper to form shredded catalytic paper, step (iii) comprising mixing the shredded catalytic paper with the tobacco cut filler.
37. The method of claim 36, wherein the shredded catalytic paper has a thickness from 0.03 mm to 0.15 mm, a width having a maximum of 5 mm, and a length having a maximum of 25 mm.
38. The method of claim 37, wherein an average thickness is from 0.10 mm to 0.13 mm.
39. The method of claim 37, wherein an average width is less than 1.0 mm
40. The method of claim 37, wherein an average length is less than 3.0 mm.
41. The method of claim 36, wherein the shredded catalytic paper is distributed continuously throughout the cigarette tobacco rod.
42. The method of claim 36, wherein the shredded catalytic paper is distributed discontinuously throughout the cigarette tobacco rod.
43. The method of claim 31, wherein the nanoparticle carbon monoxide catalyst used in step (i) has an average particle size less than 50 nm.
44. The method of claim 43, wherein the average particle size is from 1 to 10 nm.
45. The method of claim 44, wherein the average particle size is about 3 nm.

-28-

46. The method of claim 31, further comprising supporting the nanoparticle carbon monoxide catalyst on the web-filler material by forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material and drying the slurry to form the catalyst modified web-filler.

47. The method of claim 31, comprising calcining the catalyst modified web-filler prior to step (ii).

48. The method of claim 47, wherein the calcining includes heating the catalyst modified web-filler at a calcining temperature of no more than 500EC for a period of up to three hours.

49. The method of claim 48, wherein the calcining temperature is from 200EC to 400EC.

50. The method of claim 31, further comprising supporting the nanoparticle carbon monoxide catalyst on the web-filler material by forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material, drying the slurry to form the catalyst modified web-filler, reducing an average particle size of the catalyst modified web-filler, and subsequently calcining the catalyst modified web-filler prior to step (ii).

51. The method of claim 50, wherein calcining includes heating the catalyst modified web-filler at a calcining temperature of no more than 500EC for a period of one to three hours.

52. The method of claim 51, wherein the calcining temperature is from 200EC to 400EC.

53. The method of claim 31, further comprising supporting the nanoparticle carbon monoxide catalyst on the web-filler material by precipitating the nanoparticle iron oxide catalyst from a liquid phase onto the web-filler material or by depositing the nanoparticle carbon monoxide catalyst from a vapor phase onto the web-filler material.

54. The method of claim 53, wherein the nanoparticle carbon monoxide catalyst comprises iron oxide nanoparticles.

55. The method of claim 54, wherein the iron oxide nanoparticles include FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof.

56. The method of claim 54, wherein the iron oxide nanoparticles include FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof, the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and Mg(OH)_2 , and an average particle size of the catalyst modified web-filler is 0.1 to 10 microns.

57. The method of claim 56, wherein the average particle size of the catalyst modified web-filler is less than or equal to 1.5 microns.

58. The method of claim 31, wherein the web-filler material includes an oxide, a carbonate or a hydroxide of a Group II, Group III or Group IV metal.

59. The method of claim 58, wherein the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and Mg(OH)_2 .

60. The method of claim 59, wherein the web-filler material is CaCO_3 .

61. A smokeable material for a cigarette tobacco rod, comprising:

-30-

shredded tobacco; and

a catalytic paper, the catalytic paper including a web, a web-filler material, and a catalyst modified web-filler, the catalyst modified web-filler including a nanoparticle carbon monoxide catalyst supported on the web-filler material.

62. The smokeable material of claim 61, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalytic particles.

63. The smokeable material of claim 62, wherein the nanoparticle iron oxide catalytic particles have an average particle size of less than 50 nm.

64. The smokeable material of claim 63, wherein the average particle size is from 1 to 10 nm.

65. The smokeable material of claim 64, wherein the average particle size is about 2 to 5 nm.

66. The smokeable material of claim 62, wherein the nanoparticle iron oxide catalytic particles have a bulk density of less than 0.25 g/cc.

67. The smokeable material of claim 66, wherein the bulk density is greater than or equal to 0.05 g/cc.

68. The smokeable material of claim 62, wherein the nanoparticle iron oxide catalytic particles have a BET surface area of about 20 to 300 m²/g.

69. The smokeable material of claim 62, wherein the nanoparticle iron oxide catalytic particles include FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or mixtures thereof.

70. The smokeable material of claim 61, wherein the web-filler material includes an oxide, a carbonate or a hydroxide of a Group II, Group III or Group IV metal.

71. The smokeable material of claim 61, wherein the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$.

72. The smokeable material of claim 71, wherein the web-filler material is CaCO_3 .

73. The smokeable material of claim 61, wherein the nanoparticle carbon monoxide catalyst includes nanoparticles of FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof, the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$, and an average particle size of the catalyst modified web-filler is 0.1 to 10 microns.

74. The smokeable material of claim 73, wherein the average particle size of the catalyst modified web-filler is less than or equal to 1.5 microns.

75. The smokeable material of claim 61, wherein a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the composition is from 0.1 to 3.0.

76. The smokeable material of claim 75, wherein the ratio is 0.1 to 1.0.

77. The smokeable material of claim 76, wherein the ratio is 0.33 to 1.0.

78. The smokeable material of claim 59, wherein the catalytic paper is shredded and distributed throughout at least a portion of the composition.

-32-

79. The smokeable material of claim 78, wherein the shredded catalytic paper has a thickness from 0.03 mm to 0.15 mm, a width having a maximum of 5 mm, and a length having a maximum of 25 mm.

80. The smokeable material of claim 79, wherein an average thickness is from 0.10 mm to 0.13 mm.

81. The smokeable material of claim 79, wherein an average width is less than 1.0 mm

82. The smokeable material of claim 79, wherein an average length is less than 3.0 mm.

83. A method of making a smokeable material for a tobacco rod, the method comprising adding catalytic paper to shredded tobacco, the catalytic paper including a web, a web-filler material and a nanoparticle carbon monoxide catalyst supported on the web-filler material.

84. The method of claim 83, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalytic particles.

85. The method of claim 84, wherein the nanoparticle iron oxide catalytic particles include FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof.

86. The method of claim 84, wherein the nanoparticle iron oxide catalytic particles include FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof and an average particle size of the nanoparticle iron oxide catalytic particles supported on the web-filler material is 0.1 to 10 microns.

-33-

87. The method of claim 86, wherein the average particle size is less than or equal to 1.5 microns.
88. The method of claim 86, wherein the web-filler material includes an oxide, a carbonate, or a hydroxide of a Group II, Group III or Group IV metal.
89. The method of claim 86, wherein the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and Mg(OH)_2 .
90. The method of claim 89, wherein the web-filler material is CaCO_3 .
91. The method of claim 83, further comprising shredding the catalytic paper and adding the shredded catalytic paper to the shredded tobacco.
92. The method of claim 91, wherein the shredded catalytic paper is distributed uniformly throughout the smokeable material.
93. The method of claim 91, wherein the shredded catalytic paper has a thickness from 0.03 mm to 0.15 mm, a width having a maximum of 5 mm, and a length having a maximum of 25 mm.
94. The method of claim 93, wherein an average thickness is from 0.10 mm to 0.13 mm.
95. The method of claim 93, wherein an average width is less than 1.0 mm
96. The method of claim 93, wherein an average length is less than 3.0 mm.

97. A smoking article comprising:

a cigarette tobacco rod including a wrapper surrounding a tobacco column, the tobacco column containing a cut filler and a catalytic paper including a web and a modified web-filler material comprising a carbon monoxide iron oxide catalyst supported on web-filler material, the catalyst modified web-filler being in a calcined state.

98. The smoking article of claim 97, wherein an average particle size of the catalyst modified web-filler is 0.1 to 10 microns.

99. A method of making a smoking article, comprising:

(i) forming a tobacco column, the tobacco column including catalytic paper and a cut filler, the catalytic paper including a web and a modified web-filler material comprising a carbon monoxide iron oxide catalyst supported on web-filler material, the catalyst modified web-filler being in a calcined state;

(ii) placing a wrapper around the tobacco column to form the smoking article.

100. The method of claim 99, wherein an average particle size of the catalyst modified web-filler is 0.1 to 10 microns.

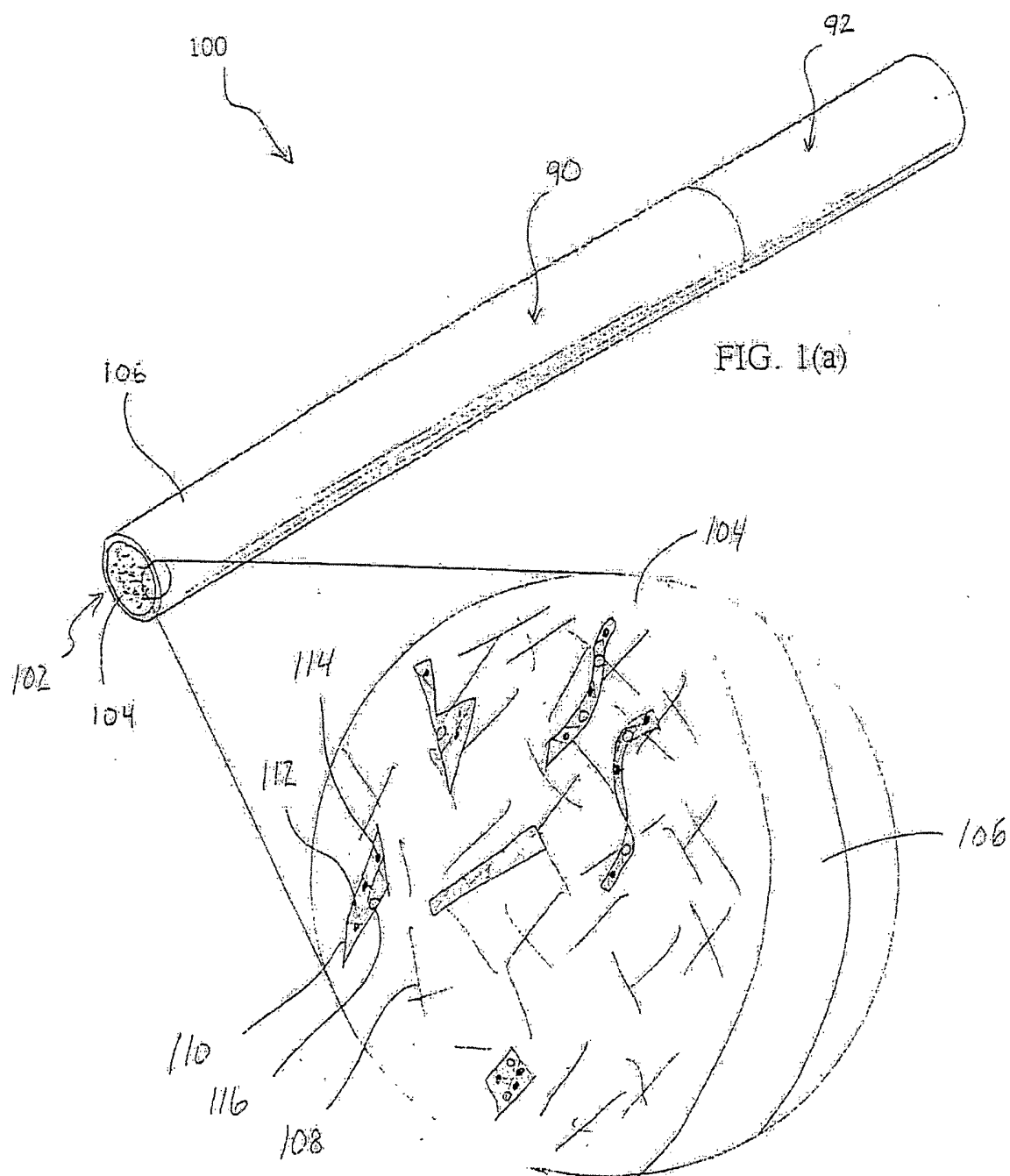


FIG. 1(b)

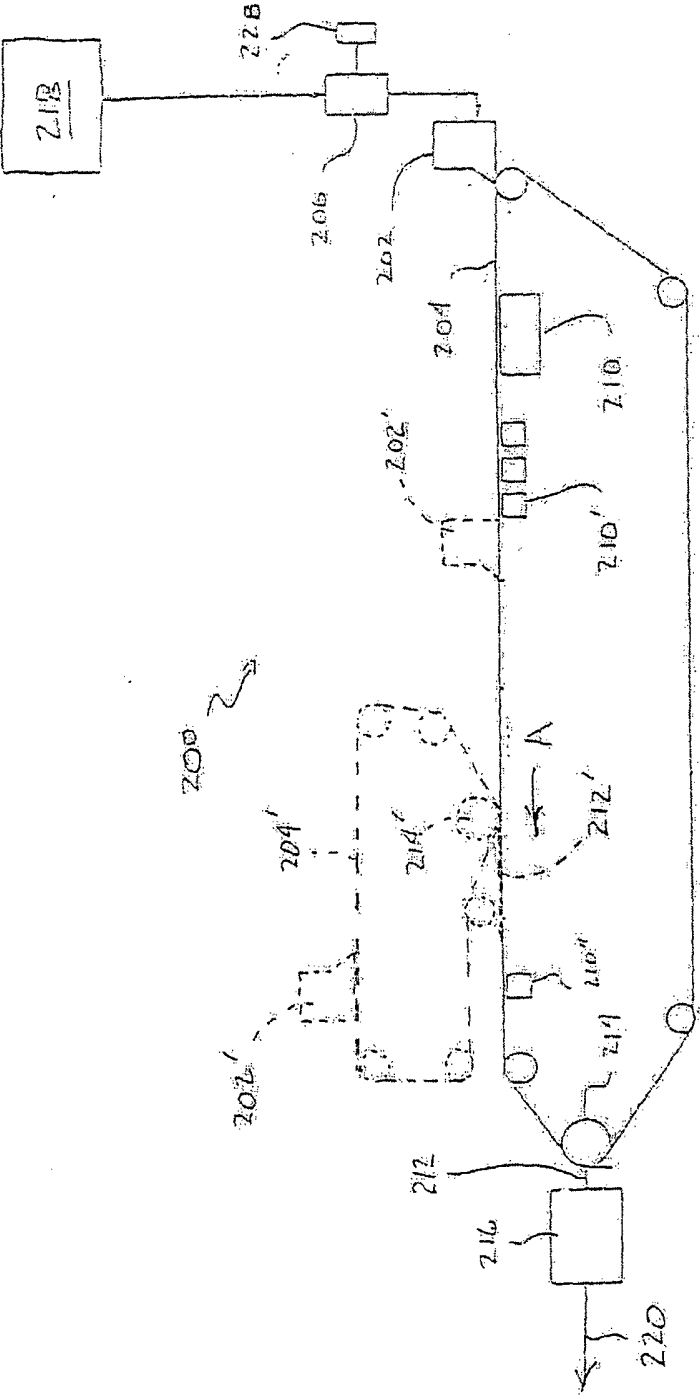


FIG. 2