

CIGARETTE WRAPPER WITH CATALYTIC FILLER AND METHODS OF MAKING SAME

BACKGROUND

5 [0001] This application claims priority under 35 USC §119 to U.S. Provisional Application No. 60/477,922 entitled CIGARETTE WRAPPER WITH CATALYTIC 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
10 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
15 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.
20 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
25 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.

30 [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
5 more efficient methods and compositions for reducing the amount of carbon monoxide in the mainstream smoke of a smoking article during smoking.

SUMMARY

[0006a] In a first aspect, there is provided a catalyst modified web-filler for
10 utilization in production of a wrapper for a smoking article, the catalyst modified web-filler comprising: a web-filler material; and a nanoparticle carbon monoxide catalyst supported on the web-filler material.

[0006b] In a second aspect, there is provided a wrapper for a smoking article, the wrapper comprising: a web; and a catalyst modified web-filler according to the first
15 aspect.

[0006c] In a third aspect, there is provided a smoking article comprising a tobacco rod having a wrapper according to the second aspect.

[0007] A preferred embodiment of a smoking article comprises a cigarette tobacco rod having a wrapper, the wrapper including a web, a web-filler material, and a
20 nanoparticle carbon monoxide catalyst, the web-filler material supporting the 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 incorporating a nanoparticle carbon monoxide catalyst with a web-filler material
25 utilized in production of a wrapper to form a catalyst modified web-filler, (ii) optionally making the wrapper, the wrapper including the catalyst modified web-filler, (iii) providing a cut filler comprising tobacco to a cigarette making machine, and (iv) placing the wrapper including the web-filler material supporting a nanoparticle carbon monoxide catalyst around the cut filler to form a tobacco rod
30 portion of the smoking article. The method optionally includes calcining the

catalyst modified web-filler prior to step (ii) and/or (v) placing a second wrapper around the tobacco rod portion.

[0009] A preferred embodiment of a wrapper for a smoking article comprises a paper web and a catalyst modified web-filler supported on the paper web, the catalyst modified web-filler including a nanoparticle carbon monoxide catalyst supported by a web-filler material.

[0009a] In a fourth aspect, there is provided a method of making a catalyst modified web-filler according to the first aspect, the method comprising: (i) forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material; (ii) optionally spreading the aqueous slurry on a support surface; and (iii) drying the aqueous slurry to evaporate water and to form the catalyst modified web-filler.

[0009b] In a fifth aspect, there is provided a method of making a catalyst modified web-filler according to the first aspect, the method comprising: (i) precipitating the nanoparticle carbon monoxide catalyst from a liquid phase onto the web-filler material; (ii) removing at least a portion of the liquid phase; and (iii) drying the web-filler material with the precipitated nanoparticle carbon monoxide to evaporate a remainder of the liquid phase and to form the catalyst modified web-filler.

[0009c] In a sixth aspect, there is provided a method of making a catalyst modified web-filler according to the first aspect, the method comprising: depositing the nanoparticle carbon monoxide catalyst from a vapor phase onto the web-filler material, wherein the nanoparticle carbon monoxide catalyst comprises FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof and 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 .

[0009d] In a seventh aspect, there is provided a method of manufacturing a wrapper according to the second aspect, the method comprising: (i) supplying the catalyst modified web-filler and a cellulosic material to a head box of a forming section of a papermaking machine; (ii) depositing an aqueous slurry including the catalyst modified web-filler and the cellulosic material onto the forming section of the papermaking machine to form a base web with the catalyst modified web-filler distributed therein; and (iii) removing water from the base web so as to form a sheet of intermediate web.

[0010] Another preferred method of manufacturing cigarette paper comprises (i) supplying a catalyst modified web-filler and a cellulosic material to a head box in a forming section of a papermaking machine, the catalyst modified web-filler including a web-filler material supporting a nanoparticle carbon monoxide catalyst,

(ii) depositing an aqueous slurry including the catalyst modified web-filler and the cellulosic material onto the forming section of the papermaking machine to form a base web with the catalyst modified web-filler distributed therein, and (iii) removing water from the base web so as to form an intermediate web. The method optionally includes calcining the catalyst modified web-filler prior to step (iii).

[0010a] In an eighth aspect, there is provided a method of manufacturing a wrapper according to the second aspect, the method comprising: (i) supplying a cellulosic material to a head box of a forming section of a papermaking machine; (ii) depositing an aqueous slurry from the head box onto the forming section of the papermaking machine so as to form a base web of the cellulosic material; (iii) distributing the catalyst modified web-filler on the base web; and (iv) removing water from the base web so as to form a sheet of intermediate web.

[0011] A further preferred method of manufacturing cigarette paper including a catalyst modified web-filler comprises (i) supplying a cellulosic material to a first head box of a forming section of a papermaking machine, (ii) depositing an aqueous slurry from the first head box onto the forming section of the papermaking machine so as to form a base web of the cellulosic material, (iii) distributing a catalyst modified web-filler on the base web, the catalyst modified web-filler comprising a web-filler material supporting a nanoparticle carbon monoxide catalyst, and (iv) removing water from the base web so as to form an intermediate web. The method optionally includes calcining the catalyst modified web-filler prior to step (iii) and/or distributing the catalyst modified web-filler within a fibrous network of the base web, wherein the layer forms a band, a stripe, or a lattice pattern on the intermediate web.

[0011a] In a ninth aspect, there is provided a method of manufacturing a wrapper according to the second aspect, the method comprising: (i) supplying a furnish including a cellulosic material to a head box of a forming section of a papermaking machine, (ii) transporting a support web through the papermaking machine; (iii) depositing the catalyst modified web-filler onto the support web; (iv) depositing an aqueous slurry from the head box onto the support web so as to form a pulp web of

the cellulosic material with the support web embedded therein; (v) removing water from the pulp web so as to form a sheet; and (vi) taking up the sheet.

[0011b] In a tenth aspect, there is provided a method of manufacturing a wrapper according to the second aspect, wherein the wrapper is a bilayer wrapper, the method comprising: (i) depositing a first layer of the bilayer wrapper from a first head box onto a wire of a papermaking machine, the first head box holding a first furnish composition; (ii) depositing a second layer of the bilayer wrapper from a second head box onto a portion of the first layer, the second head box holding a second furnish composition, the second furnish composition, including the catalyst modified web-filler; (iii) removing water from the first layer and the second layer so as to form a single sheet; and (iv) taking up the sheet.

[0012] A preferred method of manufacturing a bilayer cigarette paper comprises (i) depositing a first layer of the bilayer cigarette paper from a first head box onto a wire of a papermaking machine, the first head box holding a first furnish composition (ii) depositing a second layer of the bilayer cigarette paper from a second head box onto a portion of the first layer, the second head box holding a second furnish composition, the second furnish composition including a catalyst modified web-filler comprising a web-filler material supporting a nanoparticle carbon monoxide catalyst, and (iii) removing water from the first layer and the second layer so as to form a single sheet of intermediate web. The method optionally includes calcining the catalyst modified web-filler.

[0013] A preferred method of manufacturing cigarette paper comprises (i) supplying a furnish including a cellulosic material to a first head box of a forming section of a papermaking machine, (ii) transporting a support web through the papermaking machine, (iii) depositing a catalyst modified web-filler onto the

support web, the catalyst modified web-filler including a web-filler material supporting a nanoparticle carbon monoxide catalyst, (iv) depositing an aqueous slurry from the first head box onto the support web so as to form a base web of the cellulosic material with the support web embedded therein, (v) removing water from
5 the base web so as to form a sheet, and (vi) taking up the sheet.

[0014] A preferred catalyst modified web-filler utilized in production of a wrapper for a smoking article comprises a web-filler material and a nanoparticle carbon monoxide catalyst supported on the web-filler material.

[0015] A preferred method of making a catalyst modified web-filler including a
10 nanoparticle carbon monoxide catalyst supported on a web-filler material comprises (i) forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material, (ii) optionally spreading the aqueous slurry on a support surface, and (iii) drying the aqueous slurry to evaporate water and to form a catalyst modified web-filler.

15 [0016] A further preferred method of making a catalyst modified web-filler including a nanoparticle carbon monoxide catalyst supported on a web-filler material comprises (i) precipitating the nanoparticle carbon monoxide catalyst from a liquid phase onto the web-filler material, (ii) removing at least a portion of the liquid phase, and (iii) drying the web-filler to evaporate a remainder of the liquid
20 phase and to form the catalyst modified web-filler.

[0017] Another preferred method of making a catalyst modified web-filler including a nanoparticle carbon monoxide catalyst supported on a web-filler material comprises depositing the nanoparticle carbon monoxide catalyst from a vapor phase onto the web-filler material, wherein the nanoparticle carbon monoxide
25 catalyst comprises FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof and 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 .

[0017a] In an eleventh aspect, there is provided a method of making a smoking article according to the third aspect comprising: (i) incorporating the nanoparticle carbon monoxide catalyst with the web-filler material to form the catalyst modified web-filler utilized in production of the wrapper; (ii) making the wrapper; (iii) providing a cut filler comprising tobacco to a cigarette making machine; and (iv) placing the wrapper around the cut filler to form a tobacco rod portion of the smoking article.

[0018] A preferred embodiment of a cigarette comprises a tobacco rod having a wrapper, the wrapper comprising a web of fibrous cellulosic material and a loading of web-filler material, at least some of the web-filler material comprising a mineral particle and a nanoparticle supported by the mineral particle.

[0019] A preferred embodiment of a furnish for use in a papermaking process comprises an aqueous slurry including a catalyst modified web-filler and a cellulosic material.

[0020] A preferred embodiment of a cigarette wrapper comprises a web having a
5 web-filler material, at least some of the web-filler material comprising FeOOH.

BRIEF DESCRIPTION OF THE DRAWING FIGURES

[0021] FIG. 1(a) shows an exemplary smoking article with a nanoparticle carbon
monoxide catalyst supported on the web-filler material of the wrapper. FIG. 1(b)
10 shows a magnified view of the wrapper.

[0022] FIG. 2(a) shows an exemplary smoking article with a nanoparticle carbon
monoxide catalyst supported on the web-filler material of a first wrapper with a
second outermost wrapper. FIG. 2(b) shows a magnified view of the first wrapper
with a second outermost wrapper.

15 [0023] FIG. 3(a) shows an exemplary smoking article with a wrapper including a
nanoparticle carbon monoxide catalyst. An inner web region of the wrapper
contains catalyst-supporting web-filler material. FIG. 3(b) shows a magnified view
of the wrapper.

[0024] FIG. 4 shows a schematic of a papermaking machine wherein the chalk box
20 may contain a catalyst modified web-filler.

[0025] FIG. 5 illustrates one type of construction of a cigarette, which can be used
with an electrical smoking device.

[0026] FIG. 6 is a perspective view of a cigarette having catalyst modified paper
surrounding a fuel element.

25 [0027] FIG. 7 shows a cross section of the cigarette shown in FIG. 6.

[0028] FIG. 8 shows a cross section of a cigarette having catalyst modified
wrapper centrally located in the form of a tube.

[0029] FIG. 9 shows conversion of CO to CO₂ for nanoparticle iron oxide catalyst
and nanoparticle iron oxide catalyst/CaCO₃ mixture.

[0030] FIG. 10 shows the effect of calcination conditions on 30% loading of nanoparticle iron oxide catalyst on web-filler material on the conversion of CO to CO₂ as a function of temperature.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0031] Catalytic paper, compositions of catalyst modified web-filler, cigarettes, methods for making smoking articles which involve the use of nanoparticle additives incorporated into the wrapper as web-filler material 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.

[0032] 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.

[0033] Carbon monoxide (CO) oxidation catalysts, such as nanoparticle iron oxide catalysts of the preferred embodiments, can be incorporated into the web-filler material of a wrapper of smoking articles, such as cigarettes. Such a wrapper is used to assemble the smoking article and is consumed during smoking. While not wishing to be bound by theory, it is believed that during smoking, the incorporated 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.

[0034] Referring to FIG. 1(a), a preferred embodiment of a 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 column of tobacco 102 that is enwrapped with a cigarette (tobacco) wrapper 104. As shown in expanded view in FIG. 1(b), the wrapper 104 includes a web of fibrous cellulosic material 106 in which is dispersed
5 particles of web-filler material 108, such as calcium carbonate (CaCO_3). In practice, the web-filler material 108 serves as an agent for determining the permeability of the wrapper 104 (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
10 serves as a support for nanoparticles of carbon monoxide catalyst, preferably nanoparticles of iron oxide. If desired, the wrapper 104 can optionally include a catalyst-free web-filler material 110. The web-filler material is a filler material utilized in production for the wrapper 104.

[0035] FIGS. 2(a) and 2(b) show an embodiment of a smoking article with a
15 nanoparticle carbon monoxide catalyst supported on the web-filler material of a first wrapper with a second outermost wrapper. In the FIG. 2(a) embodiment, the smoking article 100 includes a cigarette tobacco column 102 surrounded by a first inner wrapper 112. As shown in expanded view in FIG. 2(b), the first wrapper 112 includes a web 114 and a nanoparticle carbon monoxide catalyst supported on a
20 web-filler material 116. If desired, the first wrapper 112 can optionally include a catalyst-free web-filler material 118. The web-filler material is a filler material utilized in production of the first wrapper 112. A ratio, in weight percent, of a nanoparticle carbon monoxide catalyst to a web-filler material in the first inner wrapper is preferably from 0.1 to 3.0, more preferably the ratio is 0.1 to 1.0, and
25 most preferably the ratio is 0.33 to 1.0. The smoking article 100 has a second wrapper 120 surrounding the first wrapper 112. The total amount of nanoparticle carbon monoxide catalyst in the second outer wrapper 120 is preferably less than 1 mg for a given single cigarette 100, more preferably the second wrapper 120 does not include the nanoparticle carbon monoxide catalyst so as to provide an
30 appearance to the cigarette 100 that is not affected by any coloration from the nanoparticle catalyst. In exemplary embodiments, a total amount of nanoparticle

carbon monoxide catalyst in the first wrapper is 10 to 100 mg and in the second wrapper is less than 1 mg, preferably 0 mg and/or a ratio, in weight percent, of a nanoparticle carbon monoxide catalyst in the second wrapper 120 to the nanoparticle carbon monoxide catalyst in the first wrapper 112 is less than 0.25.

5 [0036] FIG. 3(a) shows an embodiment of a smoking article with a wrapper including a nanoparticle carbon monoxide catalyst. In the FIG. 3(a) embodiment, the smoking article 100 includes a cigarette tobacco column 102 and a wrapper 122. As shown in expanded view in FIG. 3(b), the wrapper 122 includes a web 124 and a nanoparticle carbon monoxide catalyst supported on a web-filler material 126. If
10 desired, the wrapper 122 can optionally include a catalyst-free web-filler material 128. The web-filler material is a filler material utilized in production of the wrapper 122. The wrapper 122 has a radially inner portion 130 and a radially outer portion 132, the radially inner portion 130 having a first loading of the nanoparticle carbon monoxide catalyst and the radially outer portion 132 having a second loading of the
15 nanoparticle carbon monoxide catalyst. In one embodiment, the first loading of the nanoparticle carbon monoxide catalyst is greater than the second loading of the nanoparticle carbon monoxide catalyst. For example, the first loading of the nanoparticle carbon monoxide catalyst in the wrapper for a given single cigarette 100 can be up to 100 mg and the second loading of the nanoparticle carbon
20 monoxide catalyst can be less than 1 mg. Preferably the second loading of the nanoparticle carbon monoxide catalyst is zero. In another embodiment, the ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the radially inner portion 130 is preferably from 0.1 to 3.0, more preferably from 0.1 to 1.0., most preferably from 0.33 to 1.0. The total loading of
25 the nanoparticle carbon monoxide catalyst in the radially outer portion 132 is preferably less than 1 mg, more preferably zero mg.

[0037] 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
30 400 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 NANOCAT7 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.

[0038] The nanoparticle carbon monoxide catalyst is incorporated into the wrapping paper by fixing the nanoparticle carbon monoxide catalyst to 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 example, the web-filler material is CaCO₃ or other conventional filler material used in cigarette paper manufacture. If desired, the wrapper paper can include web-filler material which does not include the nanoparticle carbon monoxide catalyst.

[0039] In a preferred embodiment of a smoking article, the nanoparticle iron oxide catalyst includes FeOOH, α -Fe₂O₃, γ -Fe₂O₃, or mixtures thereof. The catalyst modified web-filler preferably comprises nanoparticle iron oxide catalyst fixed to filler particles selected from the group consisting of CaCO₃, TiO₂, silicates such as SiO₂, Al₂O₃, MgCO₃, MgO and Mg(OH)₂. An average particle size of the catalyst modified paper web-filler is 0.1 to 10 microns, preferably less than or equal to 1.5 microns.

[0040] 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 CO₂. 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 20 mg.

[0041] In one approach, the nanoparticle carbon monoxide catalyst, such as nanoparticle iron oxide catalyst, 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 ALBACAR7 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 radiation lamp at 75EC, although other methods such as vacuum filtering followed by drying can also be used.

[0042] The catalyst and filler can be provided in any desired amounts, e.g., 10 to 90% catalyst and 90 to 10% web-filler material. The dried slurry forms 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 less than about 50 to 60 wt.% catalyst loading of nanoparticle iron oxide on calcium carbonate, the slurry dries to a powdery substance; for a slurry containing greater than about 60 to 70 wt.% catalyst loading of the nanoparticle iron oxide on calcium carbonate, the slurry dries to a self-supporting solid mass. Prior to incorporating the catalyst modified web-filler into the wrapper, e.g., the web-filler material supporting nanoparticle carbon monoxide catalyst such as nanoparticle iron oxide catalyst/ CaCO_3 particles, 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., nanoparticle carbon monoxide catalyst/web-filler material, can be incorporated into the wrapper through a papermaking process. For example, the catalyst modified web-filler can be used as filler material in the papermaking processes. In a preferred

embodiment, the level of web-filler material in the wrapper (both catalyst modified web-filler and/or web-filler material without catalyst), can be from 3 to 50%.

[0043] In another approach, particles of web-filler material, such as CaCO_3 , support the nanoparticle carbon monoxide catalyst, such as nanoparticle iron oxide catalyst, 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 catalyst modified web-filler), the catalyst modified web-filler is calcined by heating the catalyst modified web-filler to a suitable calcining temperature, e.g., up to 500EC, preferably from 200EC to 400EC, for a suitable period of time such as from 1 to 3 hours, preferably 2 hours.

[0044] 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 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.

[0045] An exemplary process of making catalyst modified web filler comprising a 50/50 NANOCAT® iron oxide nanoparticle catalyst/CaCO₃ mixture utilizing spray drying can be carried out as follows:

1. Prepare a catalyst mixture in water slurry by adding 1 part NANOCAT® iron
5 oxide nanoparticle catalyst and 1 part of
CaCO₃ 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).
- 10 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.

[0046] The nanoparticle carbon monoxide catalyst can be fixed to the web-filler material by any suitable technique. For example, the nanoparticle carbon monoxide catalyst can be combined with the web-filler material by precipitating the
15 nanoparticle iron oxide catalyst from a liquid phase onto the web-filler material or
depositing the nanoparticle iron oxide catalyst from a vapor phase onto the web-
filler material.

[0047] According to a preferred embodiment, the catalyst modified web-filler, e.g., the nanoparticle carbon monoxide catalyst/web-filler material, is incorporated
20 in the wrapper through conventional papermaking processes. For example, the
catalyst modified web-filler can be used as all or part of the filler material in the
papermaking processes or can be distributed directly onto the wrapper, such as by
spraying or coating onto wet or dry base web. In production of a smoking article
such as a cigarette, the wrapper is wrapped around cut filler to form a tobacco rod
25 portion of the smoking article by a cigarette making machine, which has previously
been supplied or is continuously supplied with tobacco cut filler and one or more
ribbons of wrapper.

[0048] 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
30 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:

5 [0049] 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
10 modifying agents, coloring agents, binders, etc.) known in the art.

[0050] A wrapper can be any wrapping surrounding the cut filler, 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. When supplied to the cigarette making machine, the wrapper can be
15 supplied from a single bobbin in a continuous sheet (a monowrap) or from multiple bobbins (a multiwrap, such as a dual wrap from two bobbins). Further, the wrapper 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.

20 [0051] The papermaking process can be carried out using conventional paper making equipment. An exemplary method of manufacturing paper wrapper, e.g., cigarette 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.
25 For 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
30 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.

5 [0052] The exemplary method can optionally include calcining the catalyst modified web-filler in a step prior to supplying the furnish to the papermaking machine.

[0053] 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
10 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-
15 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.

20 [0054] 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 immediately below the head box. A slice defined in a lower portion of the head box
25 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
30 machine and can be a foundation on which the aqueous slurry is deposited. The aqueous slurry dries on the Fourdrinier wire in the forming section to an

intermediate web, which may still retain an aqueous component, and is further processed to form a paper sheet (e.g., finished web) 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.

[0055] After depositing the aqueous slurry onto the forming section, water is removed from the wet base web to form an intermediate web and, with additional processing such as further drying and pressing if necessary, forms a sheet of cigarette paper (e.g., finished web). The cigarette paper is subsequently taken up for storage or use, e.g. the cigarette paper is coiled in a sheet or roll.

[0056] Referring to FIG. 4, 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 web-filler described above) is communicated with the run tank 206 so as to establish a desired "chalk" level in the slurry supplied to the head box 202.

[0057] 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. 4, whereupon water is allowed to drain from the pulp through the wire 204 by the influence of gravity and (optionally) 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.

[0058] Downstream of the dry line, the intermediate web 212 is separated 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 the intermediate web 212 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.

[0059] 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. 4, 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. Optionally and/or in the alternative, some or all of the catalyst modified web-filler may be introduced from the first, upstream head box 202.

[0060] Referring to FIG. 4, 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.

[0061] Other papermaking processes can be used to make a wrapper with a
5 nanoparticle carbon monoxide catalyst. For example, a laminated, bilayer or multilayer wrapper can be made. Examples of bilayer and multilayer wrappers 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. In an embodiment of a bilayer or multilayer wrapper including a nanoparticle carbon monoxide catalyst, at
10 least one of a radially inner layer and/or a radially outer layer can include the nanoparticle carbon monoxide catalyst as described in embodiments herein. Preferably, for cosmetic appearance due to darkening of paper containing catalyst modified web-filler with iron oxide as the nanoparticle catalyst, a radially innermost layer of the multilayer paper adjacent the cut filler in the smoking article is the
15 portion of the multilayer wrapper that includes the web-filler material that supports a nanoparticle carbon monoxide catalyst.

[0062] The bilayer or multilayer single sheet wrapper 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
20 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 wrapper that includes the nanoparticle carbon monoxide catalyst and a second head
25 box can hold the materials for a conventional wrapper.

[0063] In another example of making bilayer or multilayer single sheet wrapper, the first head box can hold the materials for a wrapper 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 wrapper that includes the nanoparticle carbon
30 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 wrapper 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
5 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
10 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
15 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.

[0064] Additional examples of papermaking processes include the method for making banded smoking article wrappers disclosed in commonly-owned U.S. Patent
20 No. 5,342,484, the entire content of which is herein incorporated by reference, and the method for producing paper having a plurality of regions of variable basis weight in the cross direction disclosed in commonly-owned U.S. Patent Nos. 5,474,095 and 5,997,691, the entire contents of which are herein incorporated by reference. Further and in the alternative to incorporating nanoparticle catalyst into
25 the web of the wrapper in a papermaking process, it is contemplated that the paper (wrapper) can be manufactured first and the nanoparticle catalyst placed onto the surface. For example, the nanoparticle can be distributed directly onto the wrapper, such as by spraying or coating onto wet base web, the intermediate web or the finished web. Further, the nanoparticle can be coated and/or printed (text or images)
30 within the papermaking process or in a separate application of nanoparticle catalyst on-line during manufacture of the cigarette. The amount of printing and/or the

amount of catalyst can be varied to adjust the level of CO reduction. The use of retention aids is also contemplated.

[0065] The catalyst-containing paper can be used as a wrapper 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.

[0066] FIG. 5 illustrates one type of construction of a cigarette 300, which can be used with an electrical smoking device. As shown, the cigarette 300 includes a tobacco rod 360 and a filter portion 362 joined by tipping paper 364. The filter portion 362 preferably contains a tubular free-flow filter element 302 and a mouthpiece filter plug 304. The free-flow filter element 302 and mouthpiece filter plug 304 may be joined together as a combined plug 310 with plug wrap 312. The tobacco rod 360 can have various forms incorporating one or more of the following items: an overwrap 371, another tubular free-flow filter element 374, a cylindrical tobacco plug 380 preferably wrapped in a plug wrap 384, a tobacco web 366 comprising a base web 368, and a void space 391. The catalyst modified web-filler is preferably incorporated into the overwrap 371, but in addition or in the alternative, could be incorporated into any one or more of the plug wrap 384 or a component or components of the tobacco web 366, preferably the based web 368 thereof.

[0067] FIG. 6 illustrates a cigarette 410 construction having a fuel element 411 as described in U.S. Patent No. 5,345,951, the disclosure of which is hereby incorporated by reference. The cigarette 410 includes the fuel element 411 and an expansion tube 412 overwrapped by cigarette wrapping paper 414, and a filter element 413 attached by tipping paper 405. With reference to FIG. 7, the fuel element 411 includes a heat source 420 and a flavor bed 421 which releases flavored vapors and gases when contacted by hot gases flowing through one or more longitudinal passages in the heat source. The vapors pass into the expansion chamber 412 and then to mouthpiece element 413. The heat source may contain

pure substantially carbon and optionally catalysts or burn additives. One or more layers of catalyst modified paper 418 surrounding the heat source 420 can be used to reduce CO produced by the heat source 420. Alternatively, or in addition thereto, catalyst modified paper can be provided downstream of the heat source 420, e.g., catalyst modified paper can be dispersed between the heat source and the flavor bed 421 or in the flavor bed 421. Flavor bed 421 can include any material that releases desirable flavors, e.g., tobacco filler or inert substrate on which flavor forming compounds have been deposited.

[0068] The fuel element 411 is housed in a composite sleeve having a radiant energy reflector sleeve 422 (e.g., perforated metallized paper) and optional inner sleeve 423 (e.g., perforated metallized paper). The inner sleeve 422 can be folded in to form a lip 424 at the upstream end thereof to hold the heat source suspended away from the interior wall of the reflector sleeve 422 with an annular space therebetween. Flavor bed 421 is held within inner sleeve 423. The wrapper 414 which holds the fuel element and expansion chamber 412 together preferably has sufficient porosity to allow air to be admitted through the paper 414 and support combustion of the heat source. The fuel element 411 also includes a reflective end cap 415 with one or more openings 416 to allow air into the fuel element 411. Methods to make smoking articles can include dual paper wrappers, e.g., an inner wrapper and an outer wrapper. If desired, the catalyst modified paper can be used at other locations and/or for any of the paper layers of the cigarette shown in FIGS. 6 and 7. Further, while one embodiment of a fuel element cigarette is shown in FIGS. 6 and 7, the catalyst modified paper disclosed herein can be used to surround the fuel element and/or in place of paper layers in other fuel element cigarette arrangements than shown in FIGS. 6 and 7.

[0069] FIG. 8 illustrates a cigarette 500 having a concentric tobacco rod 510 that includes an inner tube or sheath of cigarette wrapper 515 whose web-filler material supports a nanoparticle carbon monoxide catalyst, such as an iron oxide and/or any other oxidation catalyst described herein. As shown, the cigarette 500 comprises a filter 505 and a tobacco rod 510 which are attached to one another with tipping paper 511 in a conventional fashion. The tobacco rod 510 is a "concentric core" or

"coaxial" layout that can be produced on a Hauni Baby rod making machine available from Hauni Maschinenbau AG of Hamburg, Germany. An inner core region 512 is defined by the inner wrapper 515, which is surrounded by tobacco cut filler material 520. An outer cigarette wrapper 525 extends along the outside of the tobacco rod 510. The filter 505 can comprise one or more plugs of cellulose tow and optionally could include an adsorbent such as carbon. In this embodiment, any coloration in the inner wrapper 515 is hidden from view.

[0070] The central core region 512 can be hollow and/or can be partially or wholly filled with tobacco cut filler and is preferably approximately 2-5 mm in diameter, more preferably 2-3 mm in diameter. In one alternative, the inner wrapper 515 can be constructed in a layered arrangement with at least one of the layers formed of catalytic paper wherein a nanoparticle catalyst, such as nanoparticle iron oxide, is supported on a web-filler material, such as CaCO_3 . Optionally, the outer wrapper 525 may be constructed similarly to include a nanocatalyst.

[0071] Optionally, the central tube can be constructed such that heat applied to an end of the tube will cause the end portion of the tube to collapse upon itself and seal off (or close) the end of the tube. The collapsing feature can be achieved by a number of different embodiments of the central tube. In an alternative where the central tube collapses when heat is applied, the central tube 515 can be constructed in a layer arrangement such that an outer or top layer is made from a material having a higher thermal expansion coefficient than an inner or bottom layer. As a result, when the end of the tube is heated, the difference in thermal expansion coefficient between the two layers will result in the end portion of the tube collapsing upon itself and, optionally, sealing off the end. The layers of the central tube 515 can be constructed from different types of paper having the different thermal expansion coefficients. The difference in thermal expansion coefficients of the layers can be a result of the types of paper having different proportions of cellulose and/or different binders. One or more of the different types of paper can be a catalytic paper wherein a nanoparticle catalyst, such as nanoparticle iron oxide, is supported on a web-filler material, such as CaCO_3 . Alternatively, other polymeric, starch or

cellulosic based films can be used for the central tube 515, anyone of which can include the catalyst modified web-filler.

[0072] If desired, the catalytic paper can be used at other locations and/or for any of the paper layers of the cigarette shown in FIG. 8. Further, while one embodiment of a cigarette with a porous heat transfer tube is shown in FIG. 8, the catalytic paper disclosed herein can be used to surround the tobacco rod portion, or can be used as the wrapper, be incorporated into a cellulosic component of the filter portion, and/or in place of paper layers in other porous heat transfer tube cigarette arrangements than shown in FIG. 8.

[0073] Referring now to the embodiment of FIGS. 2(a) and 2(b), the inner wrapper and the outer wrapper are individual wrappers formed in separate papermaking processes and later wrapped around tobacco cut filler to form a cigarette tobacco rod. The inner wrapper, the outer wrapper or both wrappers can include the catalyst modified web-filler, e.g., the nanoparticle carbon monoxide catalyst supported by a web-filler material. In examples where both wrappers include a catalyst modified web-filler, the specific nanoparticle carbon monoxide catalyst and the catalyst loading in each wrapper can be the same or different. In some embodiments, the addition of a catalyst modified web-filler can discolor the wrapper, e.g., the wrapper becomes non-white or brown. For aesthetic reasons, an outer wrapper that is a conventional color, e.g., white, can be placed around the inner wrapper. Both the inner wrapper and the outer wrapper can be selected to give a desired smoking article performance with respect to smoking article properties, such as puff count, tar, burn rate, and ash appearance. Accordingly and as shown and described, for example, with reference to FIGS. 2(a) and 2(b), preferred embodiments of smoking articles and methods of making smoking articles can include a tobacco rod portion of a cigarette with a nanoparticle carbon monoxide catalyst supported on the web-filler material of a first wrapper with a second outermost wrapper, which does not contain the catalyst modified web-filler. Also with reference to FIG. 8, the central tube formed with catalytic paper can satisfy aesthetics by placing the catalytic paper in the interior of the smoking article.

[0074] An exemplary wrapper for a smoking article comprises a paper web including cellulosic fibers and a catalyst modified web-filler incorporated into the paper web. The catalyst modified web-filler includes a web-filler material supporting a nanoparticle carbon monoxide catalyst.

5 [0075] The wrapper can be any suitable conventional wrapper. For example, a preferred wrapper can have a basis weight of from about 18 g/m² to about 60 g/m² and a permeability of from about 5 CORESTA units to about 80 CORESTA units. More preferably, the wrapper has a basis weight from about 30 g/m² to about 45 g/m² and the permeability is about 30 to 35 CORESTA units. However, any suitable
10 basis weight for the wrapper can be selected. For example, a higher basis weight, e.g., 35 to 45 g/m², can support a higher loading of catalyst. If a lower catalyst loading is selected, then a lower basis weight wrapper can be used.

[0076] Other permeabilities of the wrapper (as measured by CORESTA units) can be selected based on the application and location of the wrapper. For example, in
15 multilayer wrappers the permeability of a first layer can be up to 30,000 CORESTA units, although a permeability that is lower or higher can be utilized. Thickness of single-layer wrapper can preferably be from 15 to 100 microns, more preferably from 20 to 50 microns. Additional layers in a multilayer wrapper can be from 0.1 to 10 times the permeability of the first layer and can have a thickness of from 0.1 to 2
20 times the thickness of the first layer. Both the permeability and the thickness of the first layer and the second layer can be selected to achieve a desired total air permeability and total thickness for the smoking article.

[0077] Nanoparticle carbon monoxide catalyst loaded wrappers were produced and compared to wrappers without the nanoparticle carbon monoxide catalyst.
25 Table 1 summarizes selected properties of a control paper (designated X) and a wrapper paper with a catalyst modified web-filler, e.g., nanoparticle carbon monoxide catalyst/support material (designated Y) as a filler material. The nanoparticle carbon monoxide catalyst was nanoparticle iron oxide catalyst in the form of iron oxide and was supported on the CaCO₃ web-filler material at 25 wt.%
30 catalyst loading. The nanoparticle carbon monoxide catalyst/web-filler material was formed as described herein from a slurry without calcining.

Table 1 - Selected Properties of Wrapper with Catalyst Modified Web-filler as Compared to Paper Wrapper Without Catalyst Modified Web-filler

Sample	Web-Filler Material	Catalyst Loading in Catalyst Modified Web-filler (wt.% catalyst loading)	Catalyst Modified Web-filler Loading in Wrapper (% paper filler loading)	Total Catalyst Loading in Sample (wt.%)	Basis Weight (g/m ²)	Permeability (CORESTA Units)
X	CaCO ₃ (ALBACAR7 5970)	—	30	—	45V1	33V5
Y	nanoparticle iron oxide catalyst/CaCO ₃ particles	25	30	7.5	45V1	33V5

- 5 [0078] The nanoparticle carbon monoxide catalyst to web-filler material ratio can be varied by subjecting a slurry of nanoparticle carbon monoxide catalyst/web-filler material, e.g., the slurry of nanoparticle iron oxide catalyst/CaCO₃ 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
- 10 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
5 can be used.

[0079] While not wishing to be bound by theory, it appears that CO catalyst in the form of nanoparticle iron oxide catalyst, such as NANOCAT7 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
10 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.

15 [0080] 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. After a typical 2-second puff of a cigarette, CO is concentrated in the periphery of the cigarette, e.g., near the cigarette wrapper, in
20 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 rod 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
25 region of highest temperature gradient. For 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
30 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.

[0081] The position and quantity of nanoparticle carbon monoxide catalyst in the wrapper 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, by depositing aqueous slurry with catalyst modified web-filler selectively during the papermaking process. For example, the 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 wrapper can be manufactured in which the catalyst modified web-filler, e.g., nanoparticle iron oxide catalyst/CaCO₃, can be incorporated in those portions of the wrapper that are predicted to coincide with the appropriate temperature for operation of the catalyst. The selective incorporation of catalyst modified web-filler can be realized, for example, by using different head boxes containing the selected concentration of catalyst modified web-filler and/or locating head boxes with different concentrations of catalyst modified web-filler at selected positions in the papermaking process corresponding to selected locations of the catalytic paper to be produced.

[0082] For example, a preferred nanoparticle carbon monoxide catalyst for use in a wrapper for a smoking article is catalytically active at temperatures as low as ambient temperature and preferably does not deactivate even at temperatures as high as 900E C. The preferred nanoparticle carbon monoxide catalyst 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 nanoparticle carbon monoxide catalyst provides sufficient contact time between the mainstream smoke and the nanoparticle carbon monoxide catalyst for the CO to be converted to CO₂. An
5 example of a preferred nanoparticle carbon monoxide catalyst includes NANOCAT7 Superfine Iron Oxide, which starts to convert CO to CO₂ at a temperature above 150EC.

[0083] 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
10 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
15 conversion time and the area of the wrapper at which conversion occurs.

[0084] 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.

20 [0085] Samples of wrapper with CaCO₃ web-filler and wrapper with catalyst modified web-filler, e.g., nanoparticle iron oxide catalyst/CaCO₃ web-filler material, were produced and tested in smoking article configurations under standard FTC testing conditions. The nanoparticle iron oxide catalyst was NANOCAT7 Superfine Iron Oxide. CaCO₃ supported the nanoparticle iron oxide catalyst and was produced
25 by a slurry method without calcining. Nanoparticle iron oxide catalyst loadings in the catalyst modified web-filler of from 15 wt.% to 50 wt.% were tested and compared to a control sample without nanoparticle iron oxide catalyst.

Characteristics of sheets containing 30% web-filler loading (either CaCO₃ web-filler material or catalyst modified web-filler) at two different basis weights of paper (35
30 g/m² and 45 g/m²) were investigated. The smoking article configuration included a

rod length of 63 mm having a diameter of about 8 mm and a full flavor filter having a length of 21 mm. Each sample had the same conventional tobacco blend. In each category 20 cigarettes were smoked. The average results for mainstream smoke are summarized in Table 2.

5

Table 2 - Average Results for Mainstream Smoke

45 g/m ² Samples	Catalyst Loading in Web- Filler (wt.%)	Tar (mg/Cig.)	Puff Ct. (puff/Cig.)	CO (mg/Cig.)	CO:Tar Ratio	% reduction in CO:Tar compared to Control
I	0	17.7	8.1	18.3	1.03	control
II	15	15.6	8.1	12.3	0.79	24
III	25	15.9	8.2	11.6	0.73	29
IV	50	14.4	8.7	9.9	0.69	34
35 g/m ² Samples	Catalyst Loading in Web- Filler (wt.%)	Tar (mg/Cig.)	Puff Ct. (puff/Cig.)	CO (mg/Cig.)	CO:Tar Ratio	% reduction in CO:Tar compared to Control
i	0	18.1	8.2	16.6	0.92	Control
iii	25	17.0	8.2	11.6	0.68	26
iv	50	14.5	8.7	9.5	0.66	29

[0086] The results in Table 2 indicate that there is an increasing reduction in CO:Tar ratio in the test cigarettes made with wrapper having catalyst modified web-filler as compared to the control cigarette. The percent reduction in CO:Tar ratio increases from 24% to 34% as the catalyst increases from 15 wt.% to 50 wt.% catalyst loading in the catalyst modified web-filler. Coincident to the reduction in CO:Tar, there is little variation (e.g., <1 or <10%) in the puff count. Further, the CO:Tar ratio decreased indicating correlation between the CO catalyst and the reduction in CO. When used in paper, the nanoparticle catalyst was more selective to CO and CO was reduced by a greater proportion than Tar. Advantageously, the impact of the CO catalysis upon tar level is reduced. The amount of catalyst used in the wrapper for each cigarette is about 4 to 8 mg/cigarette, depending on the loading levels.

[0087] Table 3 illustrates comparative test results of conventional cigarette designs hand made without a filter. Sample A was wrapped in a handmade 45 g/m² wrapper without catalyst modified web-filler and Sample I was wrapped in a handmade 45 g/m² wrapper having embedded catalyst modified web-filler, e.g., nanoparticle iron oxide catalyst fixed to CaCO₃ support material. In the Sample I shown, the embedded nanoparticle iron oxide catalyst loading in the catalyst modified web-filler was 30 wt.% catalyst loading of NANOCAT7Superfine Iron Oxide with respect to the catalyst modified web-filler (about 9 wt.% catalyst loading with respect to the wrapper). The smoking article configuration included a rod length of 63 mm having a diameter of about 8 mm and a full flavor filter having a length of 21 mm. Each sample had the same conventional tobacco blend. The two sample cigarettes were then tested under the standard FTC conditions. Table 3 shows the change in properties of the two cigarettes.

Table 3 - Comparative Test Results of Select Properties of Designated Cigarettes

Sample	Puff	Total Particulate	TPM/puff	CO	CO/puff	CO/TPM
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		Matter (TPM) (mg)		(mg)		
Sample A	7.5	50.5	6.7	21.3	2.8	0.42
Sample I	8.3	48.7	5.9	13.5	1.6	0.28
change (%)	+10.3	-3.6	-11.9	-36.6	-42.9	-33.3

[0088] FIG. 9 shows the conversation of CO to CO₂ for a 50 mg sample (A) of NANOCAT7 Superfine Iron Oxide (Trace i) and a sample (B) of 100 mg mixture of 25 wt.% catalyst loading of NANOCAT7 Superfine Iron Oxide and CaCO₃ (Trace ii). In FIG. 9, the conversion of CO to CO₂ was investigated as a function of temperature in a flow tube reactor containing the samples (A) and (B) and an atmosphere with 3.7% O₂ and 22% CO. The flow rate was 1000 ml/minute and the heating rate was 12EC/minute. For both the sample of NANOCAT7 Superfine Iron Oxide and the mixture of NANOCAT7 Superfine Iron Oxide and CaCO₃ the onset of conversion occurs at about 100-125EC, indicating that the activation temperature of NANOCAT7 Superfine Iron Oxide is not substantially affected by the CaCO₃.

[0089] A calcination process was also investigated for heat treating the NANOCAT® Superfine Iron Oxide on CaCO₃. 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 web-filler material and that during the calcination step the catalyst surface is improved due to evaporation of bound water molecules.

[0090] FIG. 10 shows the effect of calcination of NANOCAT7 Superfine Iron Oxide and CaCO_3 at a 30 wt.% catalyst loading in the catalyst modified web-filler. The conversion of CO to CO_2 was determined as a function of temperature in a flow tube reactor containing catalyst modified web-filler. The atmosphere included 20.6 % O_2 and 3.4 % CO and the atmosphere flow rate was 1000 ml/minute. The heating rate was 12EC/minute. Five traces are presented in FIG 10. Trace A represents results of the catalyst modified web-filler without calcination, Trace B represents a sample of catalyst modified web-filler calcined at 200EC for 2 hours, Trace C represents a sample of catalyst modified web-filler calcined at 300EC for 2 hours, Trace D represents a sample of catalyst modified web-filler calcined 400EC for 2 hours, and Trace E represents a sample of catalyst modified web-filler calcined at 500EC for 1 hour. As indicated by an increase in conversion to CO_2 , the onset temperature and the conversion percentage is substantially unchanged between the four samples. At temperatures above about 400EC, all calcined samples had higher conversion percentages than the noncalcined sample (Trace A).

[0091] Based on the CO to CO_2 conversion percent, in the exemplary embodiment the nanoparticle carbon monoxide catalyst is present in an amount effective to convert at least 10% 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 25% of carbon monoxide to carbon dioxide at a temperature of at least 500EC. More preferably, the nanoparticle carbon monoxide catalyst converts at least 50% of carbon monoxide to carbon dioxide at a temperature of at least 700EC.

[0092] Following the investigation into the effect of calcination, the surface area of the supported catalyst was investigated using BET surface area measurements. Three samples were tested: Sample 1 was as-prepared 30 wt.% catalyst loaded NANOCAT7 Superfine Iron Oxide and CaCO_3 , Sample 2 was 30 wt.% catalyst loaded NANOCAT7 Superfine Iron Oxide and CaCO_3 calcined at 400EC for 2 hours, and sample 3 was CaCO_3 formed by chemical precipitation (so called precipitated calcium carbonate (PCC)), as opposed to natural ground CaCO_3 , so

called ground calcium carbonate (GCC)) and was used as a control sample. All samples were outgassed at 150EC for 1 hour prior to the BET measurement.

[0093] It was observed that the BET surface areas for the samples with NANOCAT7 Superfine Iron Oxide, e.g., Samples 1 and 2, had approximately the same BET surface 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, e.g., Sample 3. Thus, Samples 1 and 2 indicate that calcining does not have an adverse effect on the catalyst surface area available for conversion of CO to CO₂.

[0094] In another exemplary embodiment, a low temperature nanoparticle carbon monoxide catalyst can be used, either alone or in combination with another catalyst, as a nanoparticle carbon monoxide catalyst. 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 wrapper.

[0095] 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 commonly-owned 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 commonly-owned 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.

[0096] In addition, any of the wrappers, smoking articles or methods described herein can include additional additives conventionally used in wrappers for smoking
5 articles. These additives can include, for example, additives to control the appearance, e.g., color, of the wrapper, additives to control the burn rate of the wrapper, and/or additives to result in a desired ash appearance and/or web-fillers used in cigarette paper.

[0097] The method can be implemented in an easy to use and economical manner
10 as explained herein. The catalyst modified web-filler can be used to: (1) remove carbon monoxide in the mainstream cigarette smoke or sidestream smoke of smoking articles; (2) reduce or eliminate particle entrainment since the catalyst is embedded in the wrapper; (3) remove a target constituent, such as carbon monoxide, highly selectively since the catalyst in the wrapper only catalyzes those gases that
15 are near the wrapper and/or for which the catalyst has an affinity; and/or (4) easily implement in large scale production through the papermaking process.

[0098] 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
20 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
25 used instead of a blend.

[0099] 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
30 the appended claims.

Claims:

1. A catalyst modified web-filler for utilization in production of a wrapper for a smoking article, the catalyst modified web-filler comprising:
 - a web-filler material; and
 - a nanoparticle carbon monoxide catalyst supported on the web-filler material.
2. A catalyst modified web-filler according to claim 1, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalyst.
3. A wrapper for a smoking article, the wrapper comprising:
 - a web; and
 - a catalyst modified web-filler according to claim 1.
4. A wrapper according to claim 3, wherein the web includes cellulosic fibers.
5. A wrapper according to claim 3 or 4, wherein the nanoparticle carbon monoxide catalyst includes a nanoparticle iron oxide catalyst.
6. A wrapper according to claim 5, wherein the nanoparticle carbon monoxide catalyst further includes a nanoparticle catalyst other than iron oxide.
7. A wrapper according to claim 5 or 6, wherein the nanoparticle iron oxide catalyst includes FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof.
8. A wrapper according to any of claims 3 to 7, wherein the web-filler material includes an oxide, a carbonate, or a hydroxide of a Group II, Group III, or Group IV metal.
9. A smoking article comprising a tobacco rod having a wrapper according to claim 3.
10. A smoking article according to claim 9, wherein a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler is from 0.1 to 3.0, preferably from 0.1 to 1.0, more preferably from 0.33 to 1.0.
11. A smoking article according to claim 9 or 10, wherein a total amount of nanoparticle carbon monoxide catalyst in the wrapper is up to 100 mg.

12. A smoking article according to claim 9, 10 or 11, wherein the wrapper is a plug wrap, an overwrap or a tobacco web of the smoking article.
13. A smoking article according to any of claims 9 to 12, wherein the wrapper overwraps a
5 fuel element and/or an expansion tube of the smoking article.
14. A smoking article according to any of claims 9 to 13, wherein the wrapper surrounds a heat source of the smoking article.
15. A smoking article according to any of claims 9 to 14, wherein the wrapper is between a heat source and a flavor bed.
16. A smoking article according to claim 9, 10 or 11, wherein the wrapper is an inner tube surrounded by tobacco cut filler.
17. A smoking article according to claim 16, wherein the inner tube is hollow.
18. A smoking article according to claim 16, wherein the inner tube is at least partially filled with tobacco cut filler.
19. A smoking article according to any of claims 9 to 18, wherein the nanoparticle catalyst comprises a nanoparticle iron oxide catalyst and the web-filler material comprises calcium carbonate.
20. A smoking article according to claim 19, wherein the nanoparticle iron oxide catalyst has an average particle size of 0.1 to 10 nm and the calcium carbonate comprises 10 to 60 % by weight of the wrapper.
21. A smoking article according to claim 9, wherein the smoking article is a cigarette, the wrapper comprises a web of fibrous cellulosic material and at least some of the web-filler material comprises a mineral particle.
22. A smoking article according to claim 21, wherein the mineral particle comprises at least one of calcium carbonate, titanium dioxide, silicon dioxide, alumina, magnesium carbonate, magnesium oxide, and magnesium hydroxide and the nanoparticle catalyst comprises iron oxide.

23. A smoking article according to claim 22, wherein the nanoparticle catalyst further comprises a nanoparticle other than iron oxide.
24. A smoking article according to claim 22 or 23, wherein the nanoparticle catalyst comprises FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$ or mixtures thereof.
25. A smoking article according to claim 9, wherein the wrapper has a radially inner portion and a radially outer portion, the radially inner portion having a first loading of the nanoparticle carbon monoxide catalyst and the radially outer portion having a second loading of the nanoparticle carbon monoxide catalyst.
26. A smoking article according to claim 25, wherein the first loading of the nanoparticle carbon monoxide catalyst is greater than the second loading of the nanoparticle carbon monoxide catalyst.
27. A smoking article according to claim 26, wherein the first loading of the nanoparticle carbon monoxide catalyst is up to 100 mg.
28. A smoking article according to claim 25, wherein a ratio, in weight percent, of the nanoparticle carbon monoxide catalyst to the web-filler material in the radially inner portion is from 0.1 to 3.0, preferably from 0.1 to 1.0, more preferably from 0.33 to 1.0.
29. A smoking article according to any of claims 25 to 28, wherein the second loading of the nanoparticle carbon monoxide catalyst is less than 1 mg, preferably zero.
30. A smoking article according to claim 9 or 28, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalyst.
31. A smoking article according to claim 9, wherein the wrapper is a first wrapper and the smoking article further comprises a second wrapper.
32. A method of making a catalyst modified web-filler according to claim 1, the method comprising:
- (i) forming an aqueous slurry of the nanoparticle carbon monoxide catalyst and the web-filler material;
 - (ii) optionally spreading the aqueous slurry on a support surface; and
 - (iii) drying the aqueous slurry to evaporate water and to form the catalyst modified web-filler.

33. A method according to claim 32, wherein the nanoparticle carbon monoxide catalyst comprises nanoparticle iron oxide catalyst.

34. A method according to claim 32 or 33, wherein the nanoparticle carbon monoxide catalyst is a nanoparticle iron oxide catalyst and the web-filler material is calcium carbonate.

35. A method of making a catalyst modified web-filler according to claim 1, the method comprising:

- (i) precipitating the nanoparticle carbon monoxide catalyst from a liquid phase onto the web-filler material;
- (ii) removing at least a portion of the liquid phase; and
- (iii) drying the web-filler material with the precipitated nanoparticle carbon monoxide to evaporate a remainder of the liquid phase and to form the catalyst modified web-filler.

36. A method of making a catalyst modified web-filler according to claim 1, the method comprising:

depositing the nanoparticle carbon monoxide catalyst from a vapor phase onto the web-filler material, wherein the nanoparticle carbon monoxide catalyst comprises FeOOH , $\alpha\text{-Fe}_2\text{O}_3$, $\gamma\text{-Fe}_2\text{O}_3$, or mixtures thereof and the web-filler material is selected from the group consisting of CaCO_3 , TiO_2 , SiO_2 , Al_2O_3 , MgCO_3 , MgO and $\text{Mg}(\text{OH})_2$.

37. A method of manufacturing a wrapper according to claim 3, the method comprising:

- (i) supplying the catalyst modified web-filler and a cellulosic material to a head box of a forming section of a papermaking machine;
- (ii) depositing an aqueous slurry including the catalyst modified web-filler and the cellulosic material onto the forming section of the papermaking machine to form a base web with the catalyst modified web-filler distributed therein; and
- (iii) removing water from the base web so as to form a sheet of intermediate web.

38. A method according to claim 37, wherein the nanoparticle carbon monoxide catalyst includes a nanoparticle iron oxide catalyst, the web-filler material includes CaCO_3 , and the method comprises calcining the catalyst modified web-filler prior to supplying the catalyst modified web-filler to the papermaking machine.

39. A method of manufacturing a wrapper according to claim 3, the method comprising:

- (i) supplying a cellulosic material to a head box of a forming section of a papermaking machine;

(ii) depositing an aqueous slurry from the head box onto the forming section of the papermaking machine so as to form a base web of the cellulosic material;

(iii) distributing the catalyst modified web-filler on the base web; and

(iv) removing water from the base web so as to form a sheet of intermediate web.

40. A method according to claim 39, wherein step (iii) includes distributing the catalyst modified web-filler on a portion of the base web.

41. A method according to claim 40, wherein the catalyst modified web-filler forms a band, a stripe, or a lattice pattern.

42. A method of manufacturing a wrapper according to claim 3, the method comprising:

(i) supplying a furnish including a cellulosic material to a head box of a forming section of a papermaking machine,

(ii) transporting a support web through the papermaking machine;

(iii) depositing the catalyst modified web-filler onto the support web;

(iv) depositing an aqueous slurry from the head box onto the support web so as to form a pulp web of the cellulosic material with the support web embedded therein;

(v) removing water from the pulp web so as to form a sheet; and

(vi) taking up the sheet.

43. A method of manufacturing a wrapper according to claim 3, wherein the wrapper is a bilayer wrapper, the method comprising:

(i) depositing a first layer of the bilayer wrapper from a first head box onto a wire of a papermaking machine, the first head box holding a first furnish composition;

(ii) depositing a second layer of the bilayer wrapper from a second head box onto a portion of the first layer, the second head box holding a second furnish composition, the second furnish composition, including the catalyst modified web-filler;

(iii) removing water from the first layer and the second layer so as to form a single sheet; and

(iv) taking up the sheet.

44. A method according to claim 43, wherein the portion of the second layer deposited in step (ii) forms a band, a stripe, or a lattice pattern.

45. A method according to claim 44, wherein the portion is in the finished web.

46. A method according to claim 43, 44 or 45, wherein the second furnish composition includes a retention aid.
47. A method according to any of claims 43 to 46, comprising calcining the catalyst modified web-filler.
48. A method according to any of claims 43 to 47, wherein the first furnish composition is free of catalyst modified web-filler.
49. A method of making a smoking article according to claim 9, comprising:
- (i) incorporating the nanoparticle carbon monoxide catalyst with the web-filler material to form the catalyst modified web-filler utilized in production of the wrapper;
 - (ii) making the wrapper;
 - (iii) providing a cut filler comprising tobacco to a cigarette making machine; and
 - (iv) placing the wrapper around the cut filler to form a tobacco rod portion of the smoking article.
50. A method according to claim 49, wherein the wrapper is a first wrapper and the method further comprises:
- (v) placing a second wrapper around the tobacco rod portion.
51. A method according to claim 50, wherein the second wrapper is radially outward from the first wrapper.
52. A method according to claim 49, 50 or 51, wherein the nanoparticle carbon monoxide catalyst is incorporated with the web-filler material by precipitating a nanoparticle iron oxide catalyst from a liquid phase onto the web-filler material or depositing a nanoparticle iron oxide catalyst from a vapor phase onto the web-filler material.
53. A method according to claim 52, wherein the nanoparticle carbon monoxide catalyst is incorporated with the web-filler material by precipitating the nanoparticle iron oxide catalyst and the web-filler material is also precipitated to form the catalyst modified web-filler.
54. A method according to any of claims 49 to 53, wherein the nanoparticle carbon monoxide catalyst includes a nanoparticle iron oxide catalyst and the web-filler material includes calcium carbonate.

55. A method according to claim 53, wherein the nanoparticle carbon monoxide catalyst further includes a nanoparticle catalyst other than iron oxide.

56. A method according to claim 49, wherein the nanoparticle carbon monoxide catalyst is incorporated with 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 agglomerates of the nanoparticle catalyst modified web-filler, reducing an average particle size of the agglomerates, and subsequently calcining the catalyst modified web-filler prior to step (ii).