

Application of Nanoparticle Iron Oxide in Cigarette for Simultaneous CO and NO Removal in the Mainstream Smoke*

by

Ping Li, Firooz Rasouli, and Mohammad R. Hajaligol

Research Center, Philip Morris USA Inc., Richmond, Virginia 23234, USA.

SUMMARY

Based on the unique temperature and oxygen profiles in a burning cigarette, a novel approach is proposed in this paper to use a single oxidant/catalyst in the cigarette filler for simultaneous removal of carbon monoxide (CO) and nitric oxide (NO) in mainstream smoke. A nanoparticle iron oxide is identified as a very active material for this application due to its multiple functions as a CO catalyst, as a CO oxidant, and in its reduced forms as a NO catalyst. The multiple functions of the nanoparticle iron oxide are characterized in a flow tube reactor and the working mechanisms of these multiple functions for CO and NO removal in a burning cigarette are explained. The effect of smoke condensate on the catalyst are examined and discussed. The advantage of *in situ* generation of the catalyst during the cigarette burning process is illustrated. The test results of nanoparticle iron oxide for CO and NO removal in cigarettes are presented. [Beitr. Tabakforsch. Int. 21 (2004) 1–8]

ZUSAMMENFASSUNG

Auf der Basis der in einer brennenden Zigarette herrschenden Temperatur- und Sauerstoffprofile wird eine neue Vorgehensweise vorgeschlagen, bei der mit einem einzigen Oxidans/Katalysator im Füllmaterial für Zigaretten gleichzeitig sowohl Kohlenmonoxid (CO) als auch Stickoxid (NO) aus dem Hauptstromrauch von Zigaretten entfernt werden. Es wurde herausgefunden, dass ein Nanopartikel-Eisenoxid aufgrund seiner verschiedenen Funktionen als CO-Katalysator, CO-Oxidans und in reduzierten Formen vorliegend als NO-Katalysator für diesen Zweck sehr wirkungsvoll eingesetzt werden kann. Die verschiedenen Funktionen des Nanopartikel-Eisenoxids wurden in einem Durchflussreaktor bestimmt und die Mechanismen dieser mehrfachen Funktionen zum Entfernen von CO und NO aus einer brennenden Zigarette erklärt. Die Wirkung von Rauchkondensat auf den

Katalysator wird untersucht und diskutiert. Der Vorteil einer *in situ* Generierung des Katalysators während des Brennvorgangs der Zigarette wird beschrieben. Die Versuchsergebnisse der Eliminierung von CO und NO aus Zigarettenrauch durch Nanopartikel-Eisenoxid werden präsentiert. [Beitr. Tabakforsch. Int. 21 (2004) 1–8]

RESUME

Basé sur des profils uniques de température et d'oxygène dans une cigarette en combustion, une nouvelle approche, utilisant un seul oxydant/catalyseur dans la charge des cigarettes pour l'élimination simultanée du monoxyde de carbone (CO) et du monoxyde d'azote (NO) de la fumée principale de cigarettes, est proposée. Une nanoparticule d'oxyde de fer a été identifiée comme étant un matériau très actif dans ce contexte, en raison de ses fonctions multiples comme catalyseur de CO, oxydant de CO et, sous forme réduite, comme catalyseur de NO. Les fonctions multiples de cette nanoparticule d'oxyde de fer ont été caractérisées dans un « flow tube reactor » (tube à flux) et les mécanismes de ces fonctions multiples d'élimination de CO et NO d'une cigarette en combustion sont expliqués. L'effet du condensat de la fumée sur le catalyseur est examiné et discuté. L'avantage d'une génération *in situ* du catalyseur au cours de la combustion de la cigarette est élucidé. Les résultats des essais d'élimination du CO et du NO des cigarettes par des nanoparticules d'oxyde de fer sont présentés. [Beitr. Tabakforsch. Int. 21 (2004) 1–8]

INTRODUCTION

Carbon monoxide (CO) and nitric oxide (NO) are products of tobacco pyrolysis and combustion. The sources of CO from a burning cigarette, according to the pioneering studies of R.R. BAKER (1,2,3), are roughly around 30%

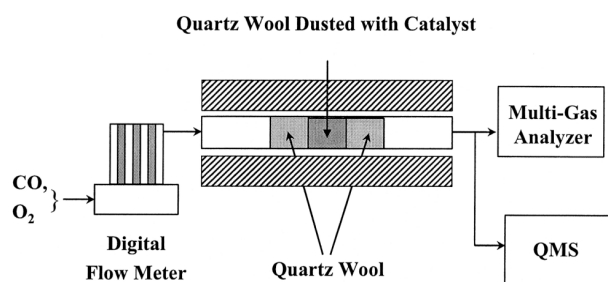


Figure 1. The schematic of the flow tube reactor setup

from thermal decomposition, 36% from combustion, and at least 23% from reduction of carbon dioxide (CO_2) by carbonized tobacco. Comparatively, the sources of NO and its formation are not as clear. It probably comes from the combustion and decomposition of the nitrogen containing compounds. A recent study by IM *et al.* (4) suggests new pathways for NO formation.

Over the years, many empirical approaches have been proposed and tried to remove CO and NO, especially CO, in the mainstream smoke. For CO, these approaches include dilution, filtration, direct oxidation and catalytic oxidation. The obvious problem for dilution is the indiscriminate removal of other smoke constituents. For filtration, there is still no adsorbent available that can selectively adsorb a substantial amount of CO at ambient temperature. The direct oxidation and catalytic oxidation approaches have also received a significant amount of research work. However, due to the high level of complexity in a burning cigarette and the coating and deactivating of the catalyst by the smoke condensate downstream of the burning zone in the cigarette rod, no CO catalyst has reached commercial application in cigarettes yet.

In this paper, a novel working mechanism is proposed to utilize the unique axial temperature and oxygen profiles in a burning cigarette and use a single oxidant/catalyst distributed in the cigarette filler for simultaneous removal of both CO and NO in the mainstream smoke. A nanoparticle iron oxide called NANOCAT® Superfine iron oxide (referred to as NANOCAT® Fe_2O_3 hereafter), manufactured by MACH I, Inc., King of Prussia, PA, is identified as a promising material for this application. This nanoparticle, with an average particle size of 3 nm, consists of the crystalline phase of FeOOH , $\gamma\text{-Fe}_2\text{O}_3$, and some amorphous phases. The multiple functions of NANOCAT® Fe_2O_3 as a CO catalyst, as a CO oxidant and in its reduced forms as a NO catalyst are characterized by the flow tube method. The influence of the smoke condensate on the performance of the catalyst is evaluated and the advantage of generating catalyst *in situ* during the burning process is illustrated. The test results of NANOCAT® Fe_2O_3 for CO and NO removal in cigarettes are also presented.

EXPERIMENTAL SETUP

Two types of experiments were carried out. A flow tube reactor system was used to characterize the catalytic and oxidative properties of NANOCAT® Fe_2O_3 . The effectiveness of NANOCAT® Fe_2O_3 in removing CO and NO in the

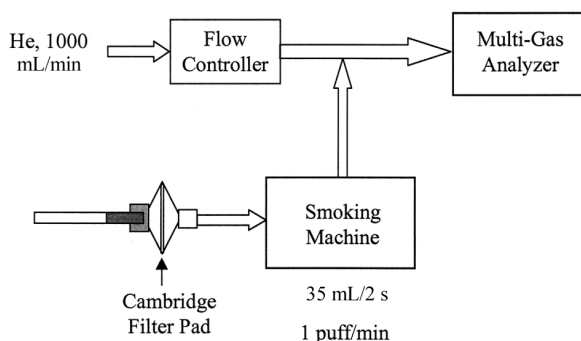


Figure 2. The schematic of the puff-by-puff smoke analyzer

mainstream smoke of a burning cigarette was tested by a puff-by-puff analyzer system. The two experimental setups are described here separately.

Flow tube reactor system

Experiments were carried out by using a quartz flow tube reactor (length 50 cm, i.d. 0.9 cm). A schematic diagram is shown in Figure 1. A piece of quartz wool dusted with a known amount of NANOCAT® Fe_2O_3 was placed in the middle of the flow tube, sandwiched by the two other pieces of quartz wool. The quartz flow tube was then placed inside a Thermcraft furnace (Thermcraft, Inc., Winston-Salem, NC) controlled by a temperature programmer. The sample temperature was monitored by an Omega K-type thermocouple (OMEGA Engineering, Inc., Stamford, CT) inserted into the dusted quartz wool. Another thermocouple was placed in the middle of the furnace, outside the flow tube, to monitor and record the furnace temperature. The temperature data were recorded by a Labview-based program (National Instruments Corporation, Austin, TX). Since the catalytic oxidation of CO is very exothermic, the catalyst bed's temperature could be significantly higher than the heating furnace's temperature, depending on CO concentration and the flow rate.

The inlet gases were controlled by a Hastings Instruments digital flow meter, model HFC 202 (Hastings Instruments, Norfolk, England). The gases were mixed before entering the flow tube. The effluent gas was analyzed either by a Rosemount Analytical's NGA2000-MLT multi-gas analyzer (ROSEMOUNT Analytical, Process Analytic Division, Orrville, OH) or a Balzer Thermal Star quadrupole mass spectrometer (Pfeiffer Vacuum GmbH, Asslar, Germany) through a sampling capillary. The multi-gas analyzer used three non-dispersive near infrared detectors for the measurements of CO, CO_2 and NO, respectively, and one paramagnetic detector for the measurement of oxygen (O_2). When the mass spectrometer was used as the monitor, a 15% contribution from the fragmentation of CO_2 ($m/e = 44$) to CO ($m/e = 28$) had been accounted for.

Puff-by-puff smoking test system

The control and experimental cigarettes were smoked by a single port, puff-by-puff smoking machine. The outlet of the smoking machine was coupled to a multi-gas analyzer as shown in Figure 2. The smoking machine smoked the cigarettes according to Federal Trade Commission (FTC)

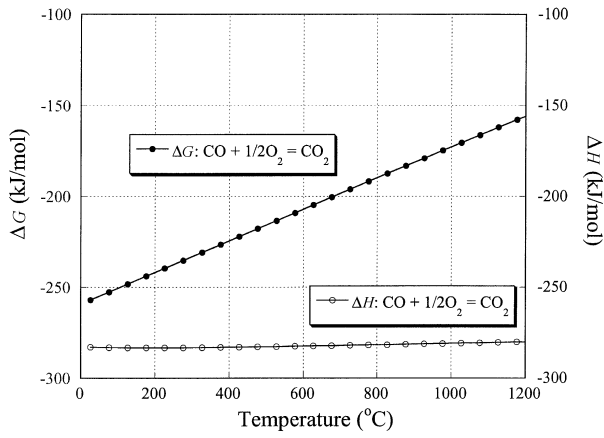


Figure 3. The temperature dependence of ΔH (enthalpy) and ΔG (Gibbs free energy) for the $\text{CO} + 1/2\text{O}_2 = \text{CO}_2$ reaction

conditions (35 mL/2 s, one puff per minute). Each 35 mL puff of smoke was injected into the 1000 mL/min helium stream, which carried the injected smoke to the multi-gas analyzer. The flow rate of the helium stream was controlled by a Hastings digital flow meter. The NGA2000-MLT multi-gas analyzer can measure the concentrations (by volume percentage) of CO and NO in a continuous flow, even with the presence of other organic compounds. The measurement was taken every second to ensure a close monitoring of the concentration changes. The measured concentration data, along with time were logged on a computer for analysis. The integration of the concentration vs. time gives the quantities of CO and NO production during the puff-by-puff smoking process. According to the ideal gas law, the gas volume per mmol at 25 °C can be calculated as follows:

$$\begin{aligned} \frac{V}{n} &= \frac{RT}{P} = \frac{0.08206 \left(\frac{\text{L} \cdot \text{atm}}{\text{K} \cdot \text{mol}} \right) \cdot 298.15 (\text{K})}{1 (\text{atm})} \\ &= 24.45 \left(\frac{\text{mL}}{\text{mmol}} \right) \end{aligned} \quad [1]$$

The integral of concentration over time is converted to milligrams of the specific gas produced by the following equation:

Gas Produced (mg)

$$= \frac{\text{Integral} \left(\frac{\mu\text{L}}{\text{L}} \cdot \text{s} \right) \times \text{Flow rate} \left(\frac{\text{mL}}{\text{s}} \right) \times \text{MW} \left(\frac{\text{mg}}{\text{mmol}} \right)}{10^6 \left(\frac{\text{mL}}{\text{L}} \right) \times 24.45 \left(\frac{\text{mL}}{\text{mmol}} \right)} \quad [2]$$

The flow rate is 1035 mL/min (1000 mL/min from the carrier gas helium and 35 mL/min from the smoke).

The cigarette was lit by a Borgwaldt Technik electric cigarette lighter (Borgwaldt Technik GmbH, Hamburg, Germany). Once the cigarette was lit, the mainstream smoke passed through a Cambridge filter pad first. The aerosol and some of the heavier, condensable products were trapped by the Cambridge filter pad. The other gases in the mainstream smoke, including CO, NO and lighter organic compounds, passed through the Cambridge filter pad and entered the multi-gas analyzer.

Materials

The NANOCAT® Fe_2O_3 was purchased from MACH I, Inc. The average particle size is 3 nm and the BET surface area is 250 m^2/g , according to the manufacturer. The sample was used without further treatment. Another nanoparticle, the Fe_3O_4 nanoparticle, which has an average particle size of 60 nm, was also acquired from the same manufacturer. It was also used without any further treatment. The gases used in the flow tube reactor tests were 4% CO, 21% O_2 , mixture of 3.44% CO with 20.6% of O_2 , and 995 $\mu\text{L}/\text{L}$ of NO, all balanced with Helium (He). They were purchased from BOC Gases (BOC Gases, Murray Hill, NJ) with certified analysis. The concentrations of CO and NO were selected roughly based on the concentrations of CO and NO in the filter end of a cigarette during puffing.

RESULTS AND DISCUSSION

Thermodynamic considerations

The oxidation of CO by O_2 is highly exothermic with the enthalpy of the reaction (ΔH) more than 280 kJ/mol in a wide temperature range, as shown in Figure 3, where the data were taken from reference (5). The negative Gibbs free energy (ΔG) values in the entire temperature range in Figure 3 also indicate that the reaction is a spontaneous reaction if the kinetic reaction barrier can be lowered by the proper catalysts. By incorporating a catalyst into a cigarette to remove CO, the heat generated by the CO oxidation has to be considered. The CO catalyst can be put in the cigarette filler rod or cigarette filter, with respective advantages and disadvantages. In the cigarette filler rod there is high temperature available in the combustion zone and pyrolysis zone. Therefore, it does not require the CO catalyst to be activated at ambient temperature. However, in the high temperature zones, O_2 is significantly depleted (6,7,8). In addition to that, in a burning cigarette with the CO catalyst evenly distributed along the filler rod, only a fraction of the CO catalyst is activated at a time, depending on the length of the high temperature zone. On the other hand, there is not a high temperature zone available in the cigarette filter, at least not for the first few puffs, thus a CO catalyst that can be activated at ambient temperature is required. This requirement would significantly limit the choices of available catalysts. Putting the CO catalyst in the filter does have the advantage of making more efficient utilization of the catalyst since all of the catalyst, not just a fraction of it as is the case when the catalyst is put in the filler rod, will be activated at one time. However, a simple calculation in the next paragraph will show that the buildup of heat by the catalytic oxidation of CO by O_2 will be an almost insurmountable problem. Suppose CO is converted 100% in the filter, the heat (h) generated by the oxidation of the 4% of CO contained in one FTC puff (35 mL) at the room temperature is

$$\begin{aligned} h &= n \cdot \Delta H = \frac{35 (\text{mL}) \times 0.04}{24.45 \left(\frac{\text{mL}}{\text{mmol}} \right)} \cdot 283 \left(\frac{\text{J}}{\text{mmol}} \right) \\ &= 16.2 (\text{J}) \end{aligned} \quad [3]$$

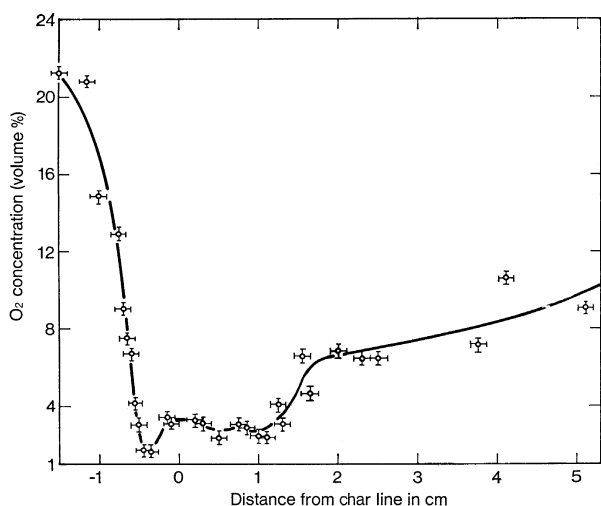


Figure 4. The one-dimensional oxygen concentration profile along the cigarette rod during a puff (graph reproduced from reference (6), Beitr. Tabakforsch. 8 (1975) 219–224, Figure 2, p. 220)

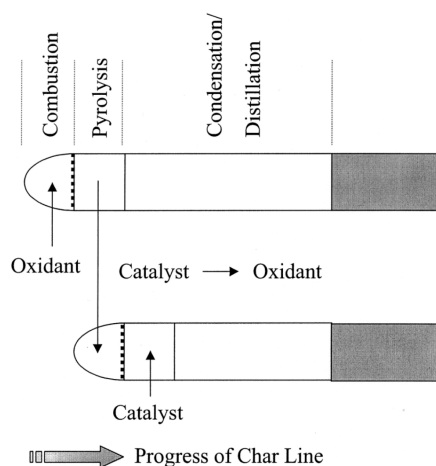


Figure 5. The schematic diagram of the proposed working mechanism of the single catalyst/oxidant applied to the cigarette filler

where n is the number of moles of CO contained in 35 mL FTC puff, ΔH is the heat of reaction for CO oxidation, which is 283 kJ/mol at 25 °C (5). The enthalpy generated in the CO oxidation will heat up both the filter and 35 mL of the air in this one puff. The cigarette's filter is cellulose acetate with a heat capacity of 1.5 J/g · °C and a typical filter weighs 110 mg. The air's heat capacity is 1.03 J/g · °C (9) and 35 mL of air weighs 42 mg. Assuming both air and the filter are heated up to the same temperature, the net temperature increase ΔT will be

$$\Delta T = \frac{16.2(\text{J})}{0.11(\text{g}) \cdot 1.5 \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right) + 0.042(\text{g}) \cdot 1.03 \left(\frac{\text{J}}{\text{g} \cdot ^\circ\text{C}} \right)} \quad [4]$$

$$= 78^\circ\text{C}.$$

Therefore, the catalytic oxidation of CO could potentially increase the temperature of the filter as much as 78 °C in just one puff. Therefore, during the smoking of a cigarette with an average of 8 to 10 puffs, there would be a significant increase of the filter's temperature.

The direct oxidation of CO with other oxidative reagents, such as metal oxides, is much less exothermic. For example, the enthalpy (ΔH) of direct oxidation of CO by Fe_2O_3 is 44 kJ/mol (5). However, direct oxidation usually can not proceed until the temperature reaches a few hundred degrees Celsius. Therefore, if the oxidative reagents are to be positioned in the filter, they have to be heated by some means and that again would result in the temperature of the filter being too high.

This thermodynamic analysis points out that the cigarette filter might not be a suitable place to conduct either catalytic oxidation or direct oxidation of CO in the mainstream smoke. The next section will show that cut filler in the cigarette column might be a better place to accomplish CO removal.

NANOCAT® Fe_2O_3 as a single catalyst/oxidant in cigarette filler for simultaneous CO and NO removal: a novel working mechanism

A burning cigarette can roughly be divided into three zones along the axial direction with different temperature ranges: that is, the combustion zone (950–700 °C), the pyrolysis/distillation zone (600–200 °C), and the condensation/filtration zone (200 °C to ambient) (10). A one dimensional oxygen concentration profile along the cigarette rod during a puff, measured by LANZILLOTTI and WAYTE (6), is shown in Figure 4. It can be seen from Figure 4 that in the combustion zone, oxygen is severely depleted. BAKER also reported that the oxygen concentration in the combustion zone is less than 0.1% (8). However, a CO oxidant can oxidize CO directly in the absence of oxygen in the right temperature range. In the pyrolysis zone, the oxygen concentration is recovered somewhat to about 3% due to dilution from the air flow. This 3% of oxygen is a valuable source to be utilized to oxidize CO to CO_2 through catalytic reaction. The temperature of 600–200 °C in the pyrolysis/distillation zone is high enough for a suitable CO catalyst to be activated. The oxygen concentration continues to recover in the condensation/filtration zone but the temperature in this zone quickly approaches ambient and probably is not high enough to activate any commercially available, non-precious metal based CO catalyst.

As will be shown by the following discussion, the unique temperature and oxygen profiles in a burning cigarette indicate that it is not enough to just put a good CO catalyst in the filler because of oxygen deficiency in the combustion zone. It is better if the CO catalyst is also a CO oxidant such as some metal oxides. For a CO catalyst/oxidant to be effective, it also needs to be in a highly dispersed form with high surface area so that a small amount of it can be distributed evenly over the entire cut filler in the cigarette. NANOCAT® Fe_2O_3 , with its multiple functions for CO and NO removal (will be described in details later) and its small particle size and high surface area, fits this unique application quite well. Based on the unique temperature and oxygen profiles in a burning cigarette described above, we propose a novel working mechanism to remove CO in the mainstream smoke as illustrated in Figure 5. A single CO catalyst/oxidant material is distributed evenly in the cigarette's filler. During a cigarette's smoking process, as the char line moves towards the filter end, this single catalyst/oxidant

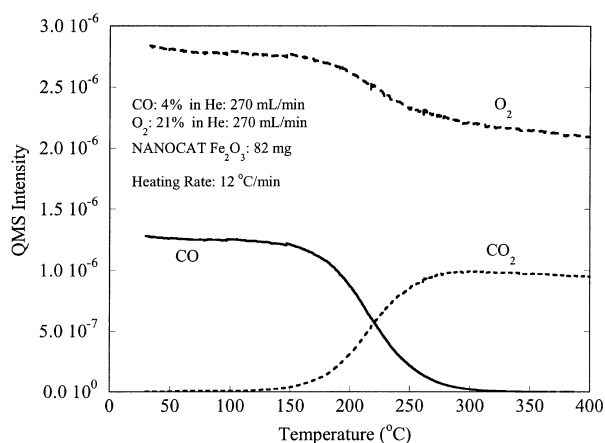


Figure 6. NANOCAT® Fe₂O₃ as a CO catalyst

will go through the pyrolysis zone first, then go through the combustion zone, as shown in Figure 5. When it goes through the pyrolysis zone, it will behave as a CO catalyst, catalyzing the CO to CO₂ oxidation. After it is used as a CO catalyst, it will be used *AGAIN* as a CO oxidant when it goes through the combustion zone. Thus, the same material will be used twice, first as a catalyst, then as an oxidant, during the cigarette's burning process. Potentially, a significant CO removal could be achieved with a minimal amount of the single catalyst/oxidant added in the filler. In a standard smoking condition, the residence time of the gas flow in the combustion and pyrolysis zone is very short. For a 35 mL/2 s standard puff, the linear velocity of the gas flow in the cigarette is 35.7 cm/s (calculated with the cigarette's inner diameter of 0.79 cm). Suppose the length of the combustion zone and the pyrolysis zone is about 0.7 cm each during the smoking (7), then the residence time of the gases in each zone is only 20 ms. Therefore, to effectively remove CO and NO from the mainstream smoke by applying catalyst/oxidant in the cut filler, the potential catalyst/oxidant should have a very small particle size and a large surface area. The very small particle size will ensure that a small quantity of the catalyst/oxidant can be well dispersed on the entire cut filler in the cigarette. The large surface area will ensure that there is sufficient contact between reactant gases and the catalyst/oxidant.

We have identified NANOCAT® Fe₂O₃ as a very promising candidate for this application (11). Iron oxide powder has been tried before to remove CO from cigarette smoke without much success (12). However, it will be shown in the following sections that NANOCAT® Fe₂O₃ is much more effective as a CO catalyst due to its very small particle size of 3 nm and large surface area of 250 m²/g. It also has a unique phase composition that makes its activation temperature 150 °C lower than the activation temperatures of other micron-sized iron oxides. Therefore, a good dispersion of catalyst/oxidant with a sufficiently high surface area could be achieved by applying NANOCAT® Fe₂O₃ in the cigarette cut filler.

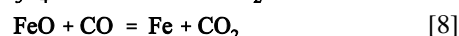
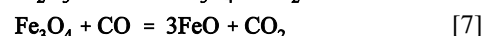
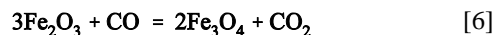
In addition to being effective as a CO catalyst and a CO oxidant, the reduced forms of NANOCAT® Fe₂O₃ (i.e. Fe₃O₄, FeO, and Fe) could also be used to reduce NO in the mainstream smoke to N₂. Fe₃O₄ is known as the active component in iron oxide based catalyst for CO + NO reaction under oxy-

gen deficient conditions (13). The reaction produces N₂ and CO₂. The freshly formed Fe is a catalyst for the disproportionation reaction of CO that produces carbon and CO₂ and thus further removes CO (11). Therefore, the multiple functions of one single material such as NANOCAT® Fe₂O₃, could be used in the cigarette filler for the simultaneous CO and NO removal as summarized below:

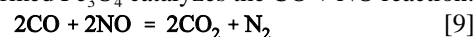
a) In the pyrolysis zone, Fe₂O₃ is used as a catalyst for the CO oxidation by O₂:



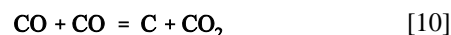
b) As the cigarette burning proceeds, the pyrolysis zone becomes the combustion zone. The Fe₂O₃ used in the pyrolysis zone as the catalyst for CO oxidation is used again here as an oxidant for direct CO oxidation:



c) In the combustion zone, where most of NO is produced, the freshly formed Fe₃O₄ catalyzes the CO + NO reaction:



d) Also in the combustion zone, the newly formed Fe could catalyze the disproportionation of CO and further removes CO:



Characterization of NANOCAT® Fe₂O₃ as CO and NO catalyst by flow tube method

In this section NANOCAT® Fe₂O₃ is characterized briefly as a CO catalyst, a CO oxidant and in its reduced forms as a catalyst for the CO + NO reaction. More detailed information about the reaction kinetics and mechanism of nanoparticle iron oxide as a CO catalyst and its stepwise reduction by CO can be found in reference (11).

a) *NANOCAT® Fe₂O₃ as CO catalyst and oxidant:* Here only the characteristics of NANOCAT® Fe₂O₃ as a CO catalyst and as a CO oxidant are shown. In Figure 6, NANOCAT® Fe₂O₃ is characterized as a CO catalyst. The catalyst was activated at 150 °C and quickly reached full capacity. The activation temperature of 150 °C makes it very suitable for application in the pyrolysis zone of a burning cigarette that has a temperature range of 600 to 200 °C.

After the NANOCAT® Fe₂O₃ sample in Figure 6 was tested as a CO catalyst, the sample was cooled down to the room temperature under the protective environment of helium gas. Then the same sample was tested again as a CO oxidant and the result is shown in Figure 7. In this test, only 4% CO in helium was passed through the sample and the temperature was increased as quickly as possible to 460 °C, which was chosen because it is high enough for reaction [6]–[8] to occur. The decrease of CO and the increase of CO₂ in the effluent flow were almost a mirror image of each other. In this direct oxidation, CO was oxidized by NANOCAT® Fe₂O₃ to CO₂ and the NANOCAT® Fe₂O₃ was reduced to different reduced forms (Fe₃O₄, Fe). In the combustion zone of a burning cigarette, the temperature is high enough (900 to 700 °C) for NANOCAT® Fe₂O₃ to be used again as a CO oxidant to reduce CO in the smoke. Therefore, in the burning process, the NANOCAT® Fe₂O₃

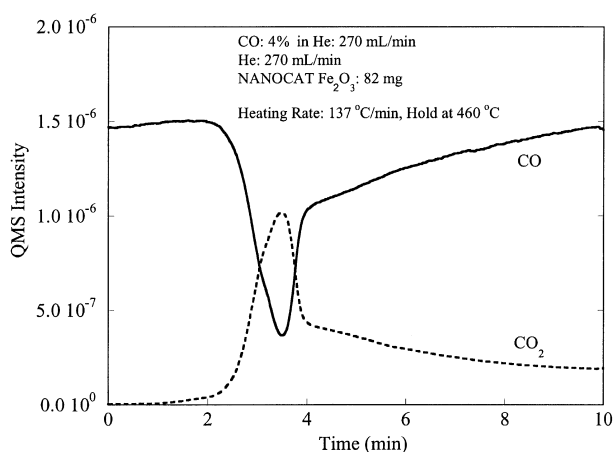


Figure 7. NANOCAT® Fe₂O₃ as a CO oxidant

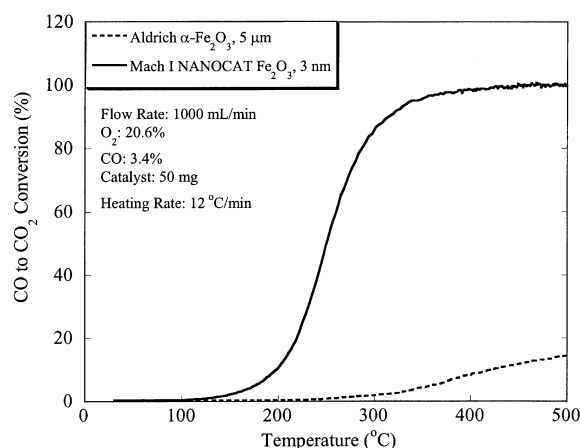


Figure 8. The comparison of the catalytic activity of NANOCAT® Fe₂O₃ and Aldrich α-Fe₂O₃

applied in the filler can be used two times, first as a CO catalyst in the pyrolysis zone, then as a CO oxidant in the combustion zone.

The nano-sized NANOCAT® Fe₂O₃ is much more effective as a CO catalyst than other micron-sized iron oxide powders, as shown in Figure 8. In this experiment, the same amount of NANOCAT® Fe₂O₃ and Aldrich's α-Fe₂O₃ were tested respectively in the flow tube reactor, under identical conditions, for effectiveness as a CO catalyst. There are two significant differences in catalytic performance between these two materials. First, the activation temperature of nanoparticle iron oxide is at least one hundred and fifty degrees lower than that of α-Fe₂O₃ (150 °C vs. 300 °C). Second, the percentage of CO conversion is much higher with nanoparticle iron oxide than with α-Fe₂O₃ (98% vs. 10% at 400 °C). The very small particle size (3 nm) and the larger BET surface area of nanoparticle iron oxide (250 m²/g vs. 3.2 m²/g for α-Fe₂O₃) very likely contribute to the higher CO conversion rate. The low activation temperature of nanoparticle iron oxide probably comes from the FeOOH component existing in this material, as discussed in reference (11). The detailed kinetic and structural studies of the Fe₂O₃ can be seen there.

b) *The reduced form of NANOCAT® Fe₂O₃ as a catalyst of 2CO + 2NO = 2CO₂ + N₂ reaction:* As mentioned in the pre-

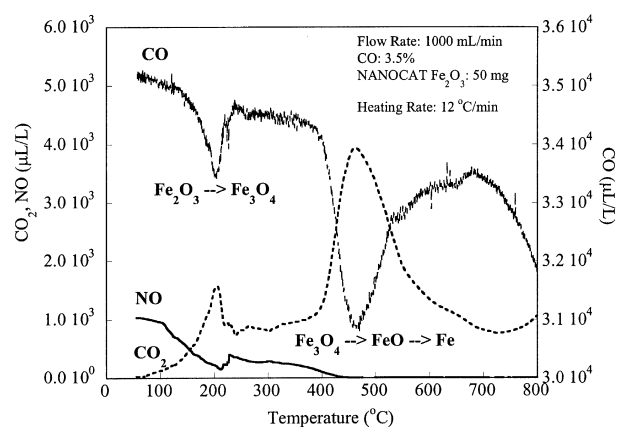


Figure 9. CO + NO reaction catalyzed by Fe₃O₄ generated *in situ* from NANOCAT® Fe₂O₃

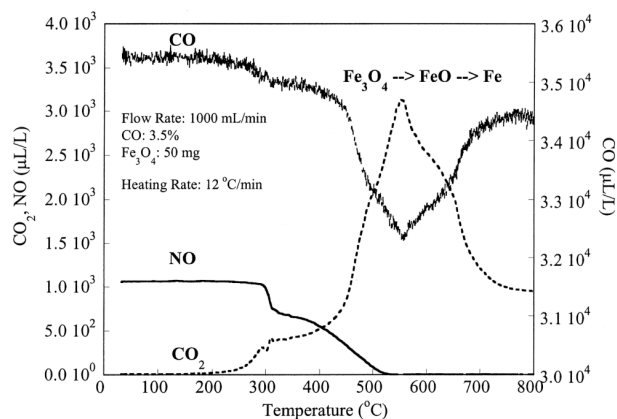


Figure 10. CO + NO reaction catalyzed by the pre-fabricated Fe₃O₄

vious section, Fe₃O₄ is known to be the active catalytic component for the CO + NO reaction (13). In Figure 9, the inlet gas consists of CO, NO but not O₂. As the temperature increases, first CO stepwise reduces NANOCAT® Fe₂O₃ to Fe₃O₄, then to FeO and Fe. As soon as Fe₃O₄ is formed, as indicated by the decrease of CO and the increase of CO₂, NO starts to decrease, at the temperature of only 110 °C. The experiment indicates that the *in situ* generated Fe₃O₄ is a very active catalyst for CO + NO reaction. This conclusion is further confirmed by another experiment, in which the commercial Fe₃O₄ nanoparticles were tested under identical conditions and the result is shown in Figure 10. The CO peak corresponding to the reduction of Fe₂O₃ to Fe₃O₄ disappears since the starting material is already in the Fe₃O₄ form. The decrease of NO is not observed until 300 °C. In the later section, the test result in a cigarette also reveals that the *in situ* generated Fe₃O₄ is more active in removing NO than the pre-fabricated one.

The effect of smoke condensate on catalyst

Applying catalysts in a cigarette is a unique challenge since many other smoke constituents can potentially deactivate the catalyst or participate in a competitive reaction. During the smoking process, the smoke condensate will condense indiscriminately in the cool zone on both the cut filler and

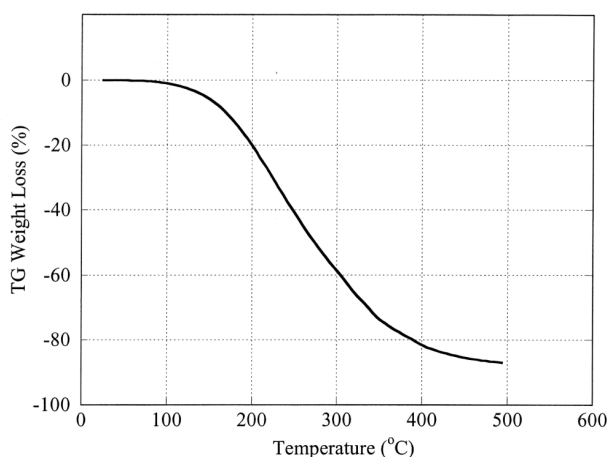


Figure 11. TG trace of the bright tobacco condensate; heating rate: 20 °C/min.

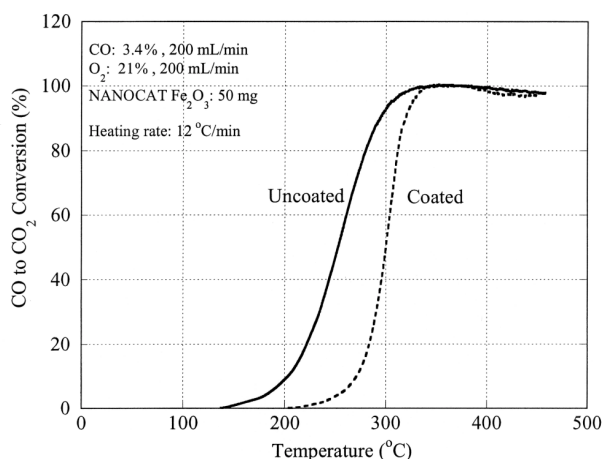


Figure 12. Comparison of the catalytic performance of NANOCAT® Fe₂O₃ with and without the smoke condensate coating

catalyst. Therefore, the influence of the smoke condensate on the catalyst becomes very important. It could even be the controlling factor of the catalytic performance. It is obvious that once the smoke condensate is condensed on the catalyst, the smoke condensate has to be vaporized or decomposed before the catalyst can regain any catalytic activity. Thus, the temperature at which most of the smoke condensate either vaporizes or decomposes will become the actual activation temperature, i.e. the temperature for the catalyst to begin functioning in a cigarette. This temperature could be significantly higher than the intrinsic activation temperature for the same catalyst in other well-controlled chemical environments such as those described in the flow tube experiment earlier.

The majority of the smoke condensate vaporizes when the temperature reaches 300–400 °C, as shown in Figure 11. In this Thermal Gravimetric (TG) experiment, 10 mg of condensate from the pyrolysis of bright tobacco was heated in 150 mL/min of helium flow at the heating rate of 20 °C/min. It is clear that the bright condensate starts to vaporize at 100 °C. At 250 °C, about 40% vaporizes and at 350 °C, about 70% vaporizes.

When the smoke condensate coated on the catalyst starts to vaporize or decompose, some portion of the catalyst surface could become exposed and becomes catalytically active again assuming that the active catalytic sites are not destroyed during the condensation and vaporization of the smoke condensate. The effect of smoke condensate on the catalyst can be tested outside of a cigarette by testing the smoke condensate-coated catalyst. The coating of the smoke condensate is briefly described here: The smoke condensate was generated from the pyrolysis of 1 g of bright tobacco in a flow tube at 300 °C in helium flow. Fifty milligram of NANOCAT® Fe₂O₃ was put in the down stream of the flow tube in the cool zone. The generated condensate in the hot zone was carried over by helium flow to the cool zone and condensed on the nanoparticle iron oxide sample. The NANOCAT Fe₂O₃ sample was then taken out of the flow tube and tested as a CO catalyst. Figure 12 compares the performance of the catalyst coated with smoke condensate and the fresh sample. It is obvious that the coated sample loses catalytic activity at the low temperature. However, as the temperature increases, the coated catalyst starts to regain some catalytic activity at about 250 °C. When the temperature reaches 350 °C, the coated catalyst regains 100% of its catalytic activity and in fact, it performs identically to an un-coated catalyst. This observation is in agreement with the fact that at 350 °C the majority of the smoke condensate has devolatilized. Two useful conclusions can be drawn from this set of experiments. First, the catalytically active sites on NANOCAT® Fe₂O₃ are not destroyed by the condensation and vaporization of the smoke condensate. Second, the vaporization process of the smoke, to certain extent, dictates the actual activation temperature of the catalyst, regardless of the intrinsic activation temperature of the catalyst.

Test results in a cigarette

The multiple functions for the CO removal by NANOCAT® Fe₂O₃ and the test results from the smoke condensate coating experiment indicate that this material should be able to remove CO from the mainstream smoke in the cigarette to a certain extent. The test results in the cigarette confirm that this is the case. In the cigarette test, mixed blends commercial cut filler was used to make both control and experimental cigarettes. The amount of 0.74 g of cut filler was used for each control cigarette. For the experimental cigarette, 3 wt % of NANOCAT® Fe₂O₃ was applied to the same amount of cut filler. Both control and experimental cut fillers were then made into cigarettes by a Supermatic® cigarette maker. Five control cigarettes and five experimental cigarettes were smoked by the puff-by-puff smoking machine described in the experimental section and CO, NO were measured.

Compared to the control cigarette, the CO in the experimental cigarette is reduced from 14.8 (± 0.8) mg to 9.3 (± 0.6) mg, a 37% reduction. The puff count is also reduced slightly from 8.2 (± 0.1) to 7.6 (± 0.3). For the NO test, an additional set of experimental cigarettes was made. An amount of 1.5% of NANOCAT® Fe₂O₃ plus 1.5% of Fe₃O₄ were applied to the cut filler of this set. The purpose is to correlate the test result from the flow tube method to the actual catalytic performance of these two materials in a cigarette. The results from the flow tube test indicate that

NANOCAT® Fe₂O₃ is more active in NO removal than Fe₃O₄ because it could generate fresh Fe₃O₄ *in situ*. The test result in a cigarette shows that with 3% of Fe₂O₃ in the cut filler, NO is reduced from 328 (± 13) µg to 179 (± 19) µg, a 45% reduction. However, with 1.5% of Fe₂O₃ plus 1.5% of Fe₃O₄, NO is only reduced to 234 (± 35) µg, a 29% reduction. The result in the cigarette test is in good agreement with the flow tube test. It indicates that *in situ* produced Fe₃O₄ is a more active catalyst for the CO + NO reaction in a cigarette.

These test results clearly show the promise of NANOCAT® Fe₂O₃ as a single catalyst/oxidant that can simultaneously remove CO and NO in the mainstream smoke in a burning cigarette. NANOCAT® Fe₂O₃ is a non-precious metal based catalyst that it is especially suitable in a non-recyclable application such as a cigarette.

CONCLUSIONS

NANOCAT® Fe₂O₃ is identified as a promising cut filler additive to reduce CO and NO in mainstream cigarette smoke. It can be used as a CO catalyst in the presence of O₂ and used again as a CO oxidant in the absence of O₂. The activation temperature of NANOCAT® Fe₂O₃ as a catalyst and as an oxidant match very well with the temperature and oxygen profiles of the pyrolysis zone and the combustion zone in a burning cigarette. In addition, the reduced form of NANOCAT® Fe₂O₃ removes NO by catalyzing the CO + NO reaction in the combustion zone of the cigarette. The influence of the smoke condensate on the catalyst was evaluated. It was found that its effect on the catalytic performance of NANOCAT® Fe₂O₃ is minimal at high temperatures. It is potentially feasible to reduce a significant amount of CO and NO in the mainstream smoke by including a small amount (3 wt %) of NANOCAT® Fe₂O₃ in the cigarette's filler. The test results of applying NANOCAT® Fe₂O₃ on cigarette filler to reduce CO and NO is very encouraging.

ACKNOWLEDGEMENT

The authors gracefully acknowledge the literature survey on previous research of CO reduction in cigarette smoke by Dr. Robert N. Ferguson and Dr. Peter J. Lipowicz, and the technical and editorial comments by Dr. Robert Fenner. The authors also thank Bruce E. Waymack and Dr. Oja Vahur for providing TG information of smoke condensate and Shahryar Rabiei's assistance in the catalyst coating experiments.

REFERENCES

1. Baker, R.R.: Mechanisms of smoke formation and delivery; Rec. Adv. Tob. Sci. 6 (1980) 184–224.
2. Baker, R.R.: A review of pyrolysis studies to unravel relation steps in burning tobacco; J. Anal. Appl. Pyrolysis 11 (1987) 555–573.
3. Baker, R. R.: The formation of the oxides of carbon by the pyrolysis of tobacco; Beitr. Tabaforsch. 8 (1975) 16–27.
4. Im, H., F. Rasouli, and M.R. Hajaligol: Formation of nitric oxide during tobacco oxidation; J. Agric. Food Chem. 51 (2003) 7366–7372.
5. Knacke, O., O. Kubaschewski, and K. Hesselmann: Thermochemical properties of inorganic substances I & II; 2nd edition, Springer-Verlag, Berlin, 1991.
6. Lanzillotti, H.V. and A.R. Wayte: One-dimensional gas concentration profiles within a burning cigarette during a puff; Beitr. Tabaforsch. 8 (1975) 219–224.
7. Baker, R.R.: Variation of the gas formation regions with a cigarette combustion coal during the smoking cycle; Beitr. Tabaforsch. Int. 11 (1981) 1–17.
8. Baker, R.R.: Combustion and thermal decomposition regions inside a burning cigarette; Combust. Flame 30 (1977) 21–32.
9. Lide, D.R.: CRC Handbook of chemistry and physics, 81st edition, CRC Press, Boca Raton, 2000–2001, pp. 6–2.
10. Baker, R.R.: The effect of ventilation on cigarette combustion mechanisms; Rec. Adv. Tob. Sci. 10 (1984) 88–150.
11. Li, P., D. Miser, S. Rabiei, R. Yadav, and M.R. Hajaligol: The removal of carbon monoxide by iron oxide nanoparticles; Appl. Catalysis B: Environmental 43 (2003) 151–162.
12. Andrews, M.N. and J.H. Reynolds: Tobacco additives for reduction of carbon monoxide, hydrogen cyanide and oxides of nitrogen in cigarette smoke; R.J. Reynolds Tobacco Company, August 5, 1971, Bates No. 501002248, see <http://www.rjrtdocs.com>, accessed June 20, 2002.
13. Randall, H., R. Doepper, and A. Renken: Reduction of nitric oxide by carbon monoxide over an iron oxide catalyst under dynamic conditions; Appl. Catalysis B 17 (1998) 357–369.

Address for correspondence

Mohammad Hajaligol
Philip Morris USA Inc.
Research Center
Richmond, Virginia 23234, USA
E-mail: mohammad.r.hajaligol@pmusa.com