# Platinum Group Metals in the Potential Limitation of Tobacco Related Diseases

## A REVIEW OF PATENT AND PRIMARY LITERATURE

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*In recent years there has been increased interest in the tobacco industry driven primarily by high-profile disclosures made during health-related litigation in the United States of America. Over the years, tobacco companies and others have filed many patents aimed at reducing the concentrations of known harmful chemicals in tobacco smoke. The literature contains a number of articles and patents which mention the potential for platinum group metals to decrease these harmful effects. This review attempts to summarise the published work in which the platinum group metals have been discussed with respect to cigarette use.*

The World Bank has estimated that 1.15 billion people in the world smoke an average of 14 cigarettes per day (1) and that, from current smoking patterns, 10 million people per annum will die of smoking-related diseases by the third decade of the millennium (2, 3). By 2020 tobacco smoking will contribute to one in three adult deaths, up from one in six in 1990 (4). The Director General of the World Health Organisation (WHO) has said, "Five hundred million people alive today are likely to be killed by tobacco" (5). Indeed, the WHO has made tobacco one of its two priority projects (6), the other one being AIDS.

## The Tobacco Problem

"Tobacco smoke contains over 4000 chemicals and some of these are responsible for cancer, heart disease and respiratory illnesses in smokers" (6). Of these, the following major components have been identified as most likely to cause disease (6, 7):

### Tar

Tar is a complex mixture of toxic chemicals inhaled when a smoker draws on a lighted cigarette. Among the carcinogens present are two major classes of tumour initiators: polycyclic aromatic hydrocarbons (PAHs) and tobacco-specific nitrosamines (TSNAs), see Figure 1.

### Carbon Monoxide (CO)

CO has a number of toxic effects on the body, the most important of which is the impairment of oxygen transportation in the blood. CO may also be linked with the development of coronary heart disease.

### Nitrogen Oxides

Cigarette smoke contains nitrogen oxides in relatively high levels. Some of these are known to cause lung damage in experimental animals similar to that noted in smokers, and may be responsible for initiating lung damage leading to emphysema.

### Hydrogen Cyanide and Other Cilia Toxins

These have a direct, deleterious effect on the cilia which line the airways and are part of the natural lung clearance mechanisms in humans. Interference with this cleaning system can result in an accumulation of toxic agents in the lung, thereby increasing the likelihood of developing disease.

The Department of Health and Human Services, U.S.A., through the National Toxicology Program, lists fifteen PAHs, all of which "form as a result of incomplete burning of organic matter". All are "reasonably anticipated to be carcinogens" and all fifteen have been detected in cigarette smoke and/or smoke condensates (8).

## Changes in Cigarettes

Since the 1950s the trend in manufacturing cigarettes has been towards using filter tips, and since the 1970s cigarettes have been produced with lower tar and nicotine contents. However, the lower tar cigarettes do not burn as efficiently and there has

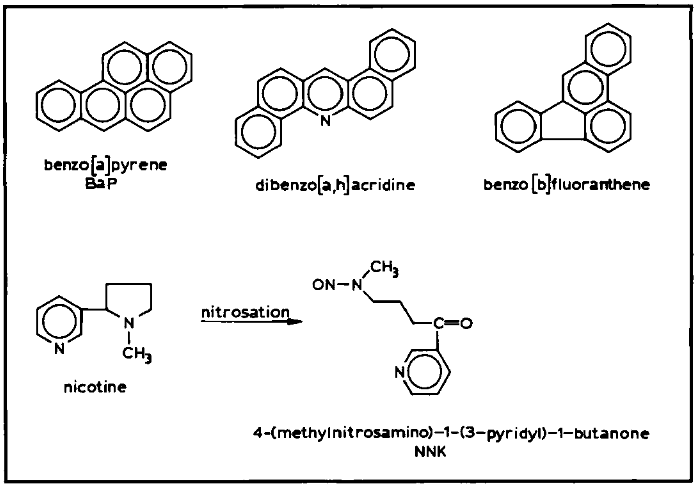


*Fig. 1 Some of the carcinogenic tumour initiators that have been detected in the tar formed from tobacco smoke. The lower reaction shows the formation of a tobacco-specific nitrosamine (TSNA) which is produced from the natural nicotine content of the tobacco*

been a compensating trend of adding increasing amounts of alkali or alkaline earth nitrates to enhance the combustion. There is also evidence that smoking styles and habits have changed as a consequence of the lower nicotine contents.

In a comprehensive review, Hoffmann and Hoffmann (9) claim that "in the United States, the sales-weighted average 'tar' and nicotine yields have declined from a high of 38 mg 'tar' and 2.7 mg nicotine" per cigarette "in 1954 to 12 mg and 0.95 mg in 1992, respectively". Whereas "...nitrate levels in cigarette tobacco rose from 0.3–0.5% to 0.6–1.35%, thereby enhancing the combustion of tobacco. More complete combustion decreases the carcinogenic PAH, yet the increased generation of nitrogen oxides enhances the formation of the carcinogenic *N*-nitrosamines, especially the TSNA in the smoke". They conclude that "...during the past two to three decades, there has been a significant, steeper increase in the rate of lung adenocarcinomas than in that of squamous-cell carcinomas of the lung... This observation supports the concept that the smoker of cigarettes with lower smoke yields smokes more intensively, inhales more deeply, and thus exposes the peripheral lung to significant amounts of 'tar', carcinogenic PAH, and TSNA".

In a second review the Hoffmanns and M. V. Djordjevic "...hypothesise that the smoker of cigarettes with lower-nicotine delivery inhales more intensely to satisfy an acquired need for a certain dose of nicotine. Consequently, the peripheral lung is exposed to relatively high amounts of lung carcinogens such as TSNA, specifically NNK", see Figure 1. "Independent of mode or form of application, these *N*-nitrosamines induce primary lung adenoma and adenocarcinoma in mice, rats and hamsters" (10).

Hecht has similarly concluded that: "On the basis of decreases in concentration of BaP", (benzo[*a*]pyrene, a typical PAH), "and increases in levels of NNK in cigarette smoke as well as biologic and pharmokinetic considerations, it is plausible that NNK is partially responsible for the dramatic increase in adenocarcinoma of the lung..." (11). The U.S. Federal Trade Commission has concluded that "The National Cancer Institute and the U.S. Food and Drug Administration stated in comments that new data suggests that the limited health benefits previously believed to be associated with lower tar and nicotine cigarettes, may not exist" (12).

## Studies with Platinum Group Metals

There are very few published papers on platinum group metals in tobacco smoking (13, 14) and the bulk of the literature is in the form of patents, the majority of which originate from the U.S.A. and Japan (15–37). Rowe and Lloyd have published results from studies using several palladium(II)/copper(II) catalysts on alumina to reduce the levels of CO in cigarette smoke (13). They report that over 90 per cent of the CO present could be removed. Muramatsu and colleagues have reported that additions of potassium nitrate to tobacco result in up to a 69 per cent reduction of BaP yield per cigarette, whereas a platinum on alumina catalyst only produces a 28 per cent reduction under similar circumstances (14).

## Palladium

The most extensive application of the platinum group metals considered in the patent literature is the use of palladium in CO oxidation catalysts (15–21). Japan Tobacco hold at least three patents on a variety of formulations, including manganese dioxide/palladium (15), copper/palladium on a mixture of activated carbon and bentonite (16) and copper/palladium/vanadium on a number of supports such as $\gamma$-alumina, active carbon, silica-alumina or a zeolite (17). The latter are said to be promoted by a phosphorus-containing agent and all three patents claim the "removal" of CO from cigarette smoke. In the same category, a palladium or platinum catalyst on an alumina washcoat, which is then coated onto (organic) fibres has been claimed (18) and also a palladium/copper system on a porous support including a second "gas absorbent" containing at least one first row transition element and/or molybdenum or tin (19). Matsushita Electric Industries claim a palladium catalyst on an active carbon, potassium carbonate and alumina substrate mixture which may contain platinum, rhodium or ruthenium as necessary. This is said to "oxidise CO to carbon dioxide, $CO_2$, under normal temperatures under humid conditions" and that "the CO in tobacco smoke can be decreased by 25% without deteriorating the taste or flavour..." (20).

In a different approach, Brown and Williamson Tobacco Company has patented a new form of aerosol "cigarette" (21). Here an organic fuel, such as ethanol, is burned and "when hot gases of combustion including vapor water (*sic*), $CO_2$ and CO are caused to flow" through a catalytic combustion section and then "through a plug a glycerol aerosol is formed". These gases then pass through the "tobacco including top dressing and other materials and flavours to enhance the taste of the gases reaching the smoker's mouth". The catalytic section comprises a honeycomb support coated with alumina, ceria and palladium. Although very different from the usual concept of tobacco smoking, similar glycerol-based aerosol cigarettes, which heat tobacco rather than burning it, have been developed (6).

## Platinum

The use of platinum as a CO oxidation catalyst for use in breathing masks, for removing CO from $CO_2$ lasers and from tobacco smoke has been patented by Phillips Petroleum (22–25). Their catalyst formulations include platinum/iron oxide on titania in the presence of alkali compounds (preferably potassium) (22) and vanadium oxide/platinum/iron oxide on a support such as alumina (23, 24). They have also patented another form of aerosol cigarette, whereby a fuel is burned, the combustion gases passed through a catalyst and then glycerol to form an aerosol, which is then passed over the tobacco. The catalyst in this case, is copper oxide/manganese dioxide or titania supported platinum/iron oxide or silver-manganese-cobalt oxide or combinations of any two or more thereof (25). Catalytica Inc. have also patented a supported platinum catalyst containing one or more of iron, copper, chromium, cobalt or manganese or their oxides for use with these aerosol-type "cigarettes" (26).

## Rhodium

Only one specifically rhodium cigarette patent has been identified. This is for the use of alums (mixed monovalent/trivalent metal sulfates) to reduce "nicotine and other harmful substances such as tars in tobacco smoke". Rhodium is claimed as one of the trivalent metals (27). Another patent does claim platinum, rhodium, ruthenium and iridium with other transition elements and rare earths supported on tin(IV) oxide for low-temperature CO oxidation, for a number of applications, including cigarette smoke (28).

## Polycyclic Aromatic Hydrocarbons

Catalyst systems for decreasing the yield of polycyclic aromatic hydrocarbons have been patented by Liggett & Myers (29–35). These include the use of zeolite supported platinum, silver or palladium catalysts (29, 30) and additions of unsupported palladium or palladium salts – decomposable to metallic palladium – to the tobacco in the presence of a "non-toxic (*sic*) inorganic nitrate" (31–35). Comment in the press, reporting on litigation against Liggett & Myers, has stated that in testimony, B. J. "Robinson said that in 1985 ...Pres KvR Dey told him about experiments Liggett had performed with palladium in cigarettes that eliminated tumours in mice" (38).

### Reduction of Nitrogen Oxides

Ruthenium has been patented for the "elimination" of nitric oxide or CO from tobacco smoke using perovskite-type compounds, such as $M_1(II)M_2(III)Ru(V)O_6$, in the cigarette filters. In this case $M_1$ is preferably strontium or barium and $M_2$ is yttrium or lanthanum. These are claimed to be effective while not forming "volatile, physiologically harmful $RuO_4$" (36). Another decomposition catalyst for nitrogen oxides has been patented, where the platinum group metals are supported on an oxide substrate of composition: $A_xB_yC_zO_{a-b}$, where A is an alkali metal (*sic*) such as barium, strontium, etc., B is a rare earth metal such as yttrium, neodymium, gadolinium, etc., and C is a copper group element such as copper, silver, etc.; x = 0–3, y = 0–2, z = 0–4; a = 4–8 and b = 0–2. These are claimed to decompose nitrogen oxides without a reducing agent, even when excess oxygen is present (37).

## The Challenge

It seems economically unrealistic to consider any system for ameliorating the effects of tobacco smoke which would contain only a platinum group metals catalyst. Any solution sought would have to be restricted to using thrifted, supported platinum metals or platinum metals in very small quantities to enhance the properties of more readily available base metal systems. In such formulations the challenge would be to optimise the efficiencies of the noble metals. As such systems might have to be disposable, an infrastructure to collect and transport metal into the existing platinum metals recycling industry would be required.

The criteria for technical success of a less-harmful cigarette superficially appear to be easier to define:

- to denature (that is, to decrease the biological activity of) PAHs, TSNAs and other biologically active components of tobacco smoke
- to oxidise CO; and
- to reduce nitrogen oxides in an air-rich gas stream and show that this can reduce health risks while, at the same time, achieving an acceptable degree of consumer satisfaction.

Indeed, there could be other, as yet hidden, problems which detract from the commercialisation of a product which successfully meets these criteria. The ability to maintain sufficient nicotine and flavours, while denaturing the most toxic components may not be at all simple in a variable and uncontrolled gas stream and the possibility that new health risks might become apparent once the well-characterised ones are reduced cannot be discounted. Despite all this, there is a tantalising possibility that an optimum technical solution could be found.

## Conclusions

The safest form of tobacco smoking is not to start and a truly medically safe cigarette will never be developed (6, 9, 11, 39, 40). However, what then is the plight of the existing one billion habitual smokers, already addicted to nicotine? Could modern catalyst technology destroy or at least decrease the biological activity of the toxins in tobacco smoke, while retaining a sufficient quantity of the nicotine and flavours required by a smoker?

The literature implies there may be a role for the platinum group metals to play in reducing tobacco-related disease. The prospect of exciting intellectual, ethical and commercial returns could encourage further work in this challenging area.

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# Oxygen Storage Capacity of Platinum Three-Way Catalyst

A three-way catalyst (TWC) converts the primary pollutants in exhaust gas from automobiles into carbon dioxide, water and nitrogen. The highest conversion efficiency can be achieved by maintaining a stoichiometric composition at the TWC. TWCs contain material which store and release oxygen ($O_2$) to aid this process. The $O_2$ storage/release capacity (OSC) of a TWC is a measure of its ability to reduce the negative effects of rich/lean oscillations in the exhaust gas composition by regulating the $O_2$ partial pressure via the $O_2$ storage material through its redox couple. Ceria-zirconia, which has oxygen vacancies, is frequently used as the $O_2$ storage component.

The OSC of a material can be measured by alternately pulsing a reducing agent (carbon monoxide (CO) or hydrogen ($H_2$)) and $O_2$ over the sample. The $O_2$ buffering capacity (OBC) is measured by pulsing $O_2$ in an inert gas, imitating mild reducing and oxidising conditions.

Now a team of scientists from the Università di Trieste, Italy and Universidad de Cádiz, Spain, have measured the OSC of a 0.58 wt.% Pt/$Ce_{0.68}Zr_{0.32}O_2$ catalyst at room temperature – where the creation of vacancies is unlikely (N. Hickey, P. Fornasiero, J. Kašpar, M. Graziani, G. Blanco and S. Bernal, *Chem. Commun.*, 2000, (5), 357–358). A feed stream was oscillated between reducing and oxidating conditions, using $H_2$ or CO as reducing agents. When $H_2$ was used significant dynamic-OSC values were measured at room temperature even on a redox-aged sample. This was not observed with CO as reductant or when the OBC method was used. Spillover of H seems to be a dominant factor contributing to the effectiveness of the $H_2$-OSC. Reduced Pt was required to promote $H_2$ activation.