Low-Temperature Oxidation of CO in Smoke: A Review*

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CONTENTS

SUMMARY

The low-temperature catalytic oxidation of CO has been reviewed, targeting its possible application to cigarette smoke. The treatment of CO in smoke by using a filter-packed catalyst is extremely complicated by the presence of a variety of chemically active gaseous compounds, a particulate phase, the high velocity of pulsing smoke flow, and ambient temperature. The relevant mechanisms of catalysis and the catalyst preparation variables that could help to overcome these problems are considered. Possible contributors to the overall kinetics that must include variety of diffusion processes were briefly discussed. The chemisorption of O_2, CO and CO_2 on Pd, Pt and Au and on partially reducible supports, surface reactions and oscillations of the CO oxidation rate were analyzed. The effects of the surface structure and electronic properties of the catalyst support, preparation conditions and presence of a second transition metal on the projected CO oxidation activity of the catalysts in smoke are also discussed. The reviewed catalyst preparation approaches can solve the low-temperature catalyst activity problem. However, more work is required to stabilize this activity of an air-exposed catalyst to provide a necessary shelf life for a cigarette. The greatest challenge seems to be a particular phase - exclusive selectivity that would not contradict with the necessary fast diffusion of gases through the catalyst pores. [Beitr. Tabakforsch. Int. 22 (2006) 88–106]

ZUSAMMENFASSUNG

Es wurde die katalytische Oxidation von CO bei niedrigen Temperaturen im Hinblick auf eine mögliche Anwendung beim Zigarettenrauch untersucht. Die Umsetzung des Kohlenmonoxids (CO) im Rauch durch einen in den Filter eingepackten Katalysator wird durch die Vielzahl chemisch aktiver gasförmiger Verbindungen, die Gegenwart einer Partikelphase, die hohe Geschwindigkeit des pulsierenden Rauchstroms und die Umgebungstemperatur extrem erschwert. Die wichtigen Katalysemechanismen und die bei der Herstellung des Katalysators einfließenden Variablen, die bei der Überwindung dieser Schwierigkeiten helfen könnten, werden berücksichtigt. Mögliche Faktoren, die an der Kinetik der Abläufe beteiligt sind, einschließlich einer Vielzahl von Diffusionsprozessen werden kurz angesprochen. Die Chemisorption von O_2, CO und CO_2 an Palladium (Pd), Platin (Pt) und Au und an teilweise reduzierbarem Trägermaterial, Oberflächenreaktionen und Oszillationen der CO-Oxidationsrate wurden analysiert. Die Auswirkungen der Oberflächenstruktur und die elektronischen Eigenschaften der Katalysator-Trägersubstanzen, die Herstellungsbedingungen und die

Beteiligung eines zweiten Übergangsmetalls an der erwünschten Aktivität der CO-Oxidation des Katalysators werden ebenfalls diskutiert. Die beschriebenen Ansätze zur Herstellung des Katalysators können helfen, die bei niedrigen Temperaturen auftretenden Aktivitätsprobleme des Katalysators zu überwinden. Es ist jedoch zusätzliche Arbeit erforderlich, um diese Aktivität eines der Luft ausgesetzten Katalysators zu stabilisieren, um die Zigarette ausreichend lagerfähig zu machen. Die größte Herausforderung scheint hierbei eine spezielle Selektivität für die Phase zu sein, die nicht im Widerspruch zur notwendigen schnellen Diffusion von Gasen durch die Poren des Katalysators steht. [Beitr. Tabakforsch. Int. 22 (2006) 88–106]

RESUME

L'oxydation catalytique du monoxyde de carbone (CO) à faible température a été étudiée en vue d'une application potentielle à la fumée de cigarette. Le traitement du CO dans la fumée en utilisant un catalyseur chargé dans le filtre est particulièrement compliqué par la présence de multiples composants chimiquement actifs, une phase particulaire, une grande vitesse des flux d'air et la température ambiante. Les mécanismes pertinents de la catalyse et les variables de conception du catalyseur pouvant aider à résoudre ces problèmes sont pris en considération.

Des paramètres pouvant contribuer à la cinétique de réaction, y compris divers processus de diffusion, sont traités brièvement. La chimisorption de O_2, CO et CO_2 sur le palladium (Pd), le platine (Pt) et l'aluminium (Au) et sur des supports partiellement réductibles, des réactions à la surface et des oscillations du taux d'oxydation du CO ont été analysées. Les effets de la structure de la surface et les propriétés électroniques du support catalytique, les conditions de fabrication et la présence d'un deuxième métal de transition, sur l'activité prévue d'oxydation du CO dans la fumée sont également discutés. L'approche présentée pour préparer un catalyseur peut résoudre le problème d'activité du catalyseur qui se manifeste aux faibles températures. Plus d'études sont cependant nécessaires pour stabiliser cette activité de catalyseurs exposés à l'air pour garantir un bon fonctionnement à l'intérieur de la cigarette. Le défi le plus important semble être une sélectivité pour la phase particulaire qui ne serait pas en contradiction avec la diffusion rapide nécessaire du gaz à travers les pores du catalyseur. [Beitr. Tabakforsch. Int. 22 (2006) 88–106]

1   INTRODUCTION

A few percent by volume of CO is present in tobacco smoke, accompanied by a wide variety of compounds that could potentially react with it, including about 10% O_2 by volume. The undesirable CO could be eliminated from smoke by its chemisorption on transition metal complexes, hydrogenation and hydroformylation with H_2 and hydrocarbons, and by the water-gas-shift (WGS) reaction. These reactions could be conducted in a cigarette filter cavity at ambient temperature, where the high heat of CO oxidation could even elevate local temperature and accelerate catalysis. The same could also be detrimental if the cigarette filter

becomes too hot. Oxidation of CO by O_2 and/or by NO_x is the most common means for the abatement of CO, and will be addressed in this review.

Catalytic oxidative abatement of CO in gas mixtures, containing NO_x, H_2O, H_2 and hydrocarbons, has been studied extensively over a wide temperature range. These processes have been optimized for many industrial applications, including the purification of hydrogen for fuel cells (1), emissions control and other processes reviewed in (2,3). However, the elimination of CO from a variety of aerosol-containing streams, such as tobacco smoke, the complexity of which was reviewed by RODGMAN and GREEN (4), suffers from many additional complications (5). They include the presence of numerous reactive compounds, formed along with CO and described by BAKER (6), which would readily deactivate the catalyst active sites (6–8). This makes the selectivity of the applied catalyst particularly important. The selectivity to treat primarily CO should ideally be a combination of chemical selectivity, molecular size exclusive selectivity and selectivity to treat gas in the presence of a particulate phase. The objectives of this paper were to review the scientific literature on the catalytic oxidation of CO and identify systems that could be applicable to reducing CO yields in cigarette smoke. Since valuable information in this area relates mostly to the gas-phase catalysis, not complicated by the presence of particulate phase, we have considered many such examples, while trying to extrapolate results to the case of cigarette smoke.

2   BACKGROUND CONSIDERATION

Such restrictive control of catalyst selectivity, however, usually causes a decrease in activity towards the goal CO oxidation. For application inside a cigarette filter cavity, the temperature for sufficient conversion is required to be as low as ambient; hence, the activity of a catalyst must be extremely high. The pulsed profiles of CO and other smoke components and their high flow rates up to 10^6 h^{-1} through up to 1-mL catalyst bed are quite unusual for heterogeneous catalysis (the common in catalysis flow rate units "h^{-1}", which denote the volume unit of smoke per volume unit of catalyst during one hour, are used for comparison of the described catalysts).

Considering such a high smoke velocity, an additional complication arises from the necessity for a sufficiently low pressure drop on the cigarette filter loaded with a catalyst. This can be achieved on larger catalyst particles, whereas smaller catalyst particles are needed for avoiding external diffusion limitations in the catalyst bed. Instead of using the fine catalyst particles, one of the options could be an application of metal foam supported catalyst converters (9) or coated ceramic monoliths, capable of converting CO at up to 8×10^4 h^{-1} flow rates of gas (10). This approach can also help to dispense the heat of CO oxidation faster, the excess of which can adversely affect a cigarette performance.

A solution to the problem of the unusually high catalyst activity required was suggested by WANG et al. (11) where CO was not necessarily all oxidized, but rather temporarily retained on a CO chemisorbent/catalyst during the puff and redirected between puffs from the mainstream smoke,

Table 1. General approaches and the case studies in CO oxidation catalysis

Catalyst types for CO oxidation	References
Complications in catalytic CO removal in smoke	1–5, 7, 8
Catalyst monoliths could be used for pressure drop decrease	9,1
Fe/TiO$_2$, Fe$_2$O$_3$ catalysts are used for CO abatement in smoke	9, 10, 14
CoO$_x$/CeO$_2$ catalysts have potential for low temperatures	19, 22, 23
La-Sr-Mn perovskites are for CO+NO and WGS at high temperature	30–32
Pt, Pd/zeolite are for CO+O$_2$; Ir/zeolite is for NO dissociation	33
NO is a co-catalyst for CO+O$_2$ on Rh, Pd-Au, Ag-Cu/C, zeolite	24, 34, 35
Characteristics of active supports (TiO$_2$, ZrO$_2$) for catalysts	36
Au is for low temperature, sensitive to water and CO$_2$; Pt, Pd - are resistant to those factors; Cu is for higher temperature; Ir is for high velocity	11, 13, 16–18, 21, 26

through the filter ventilation holes out of the cigarette. However, even this "CO pump" worked more efficiently when a high activity oxidation catalyst Ag/zeolite was applied. In one of the very few studies published, a complete and steady conversion of 1% CO in air at a flow rate of 5×10^5 h^{-1} on Au/Fe(OH)$_x$ at room temperature was observed by WU et al. (12). In a similar case, OKUMURA et al. (13) studied catalysts composed of TiO$_2$, Al$_2$O$_3$, SnO$_2$ or Fe$_2$O$_3$, supported at the 2% level iridium. Among them, the Ir/TiO$_2$ catalyst provided a complete CO conversion in a 2×10^4 h^{-1} flow of 1% CO gas at ambient temperature.

For CO oxidation in smoke the catalysis conditions would adversely affect such excellent results. Nevertheless, in the rare case of using the TiO$_2$-Fe$_2$O$_3$ catalyst, LI, HAJALIGOL et al. (7,14,15) reported successful removal of CO from cigarette smoke. In the absence of a noble metal, iron oxide catalyst showed an acceptable activity around 240 °C. The authors showed that supported iron on iron oxide can work even better (13,14) for simultaneous treatment of CO and NO in a cavity filter of a cigarette.

Copper, when it is the only active metal in the catalyst, could be very active when affected by a metal-support interaction (MSI) with, for example, ceria or samaria-doped ceria (11,16–18). ZHANG et al. (19) decomposed Cu pentanedionate complex on a support and prepared the Cu/CeO$_2$ catalyst, which was active at room temperature. It showed a very high sensitivity to moisture because of Cu(OH)$_2$ formation. Nevertheless, DEEVI and PALDEY (20) developed and patented similar catalyst for application in cigarette smoke. A more complex preparation procedure named "solvated metal impregnation", where copper was supported on CeO$_2$ from a toluene solution of evaporated Cu metal, was used by ZHANG et al. (21). This method produced a catalyst that was more resistant to the catalytic poisons, however it was not sufficiently active at ambient temperature.

The presence of mobile oxygen in Co$_3$O$_4$ makes cobalt an attractive transition metal for oxidation catalysts (22), even

though the existing catalysts require elevated temperatures for CO oxidation. Thus, the onset temperature of CO conversion was found to be around 100 °C for 15%CoO$_x$ on CeO$_2$ with an observed synergetic effect as reported by KANG et al. (23). A combination of the properties of copper and cobalt resulted in the efficient CeO$_2$-Al$_2$O$_3$–supported catalyst for selective oxidation of CO in the predominantly hydrogen atmosphere, as suggested by PARK et al. (24). However, up till now we could not find published results, which have suggested the application of cobalt- or copper-based catalysts in a cigarette filter.

AVGOUROPOULOS et al. (17) performed an experimental comparison of Pt/γ-Al$_2$O$_3$, Au/α-Fe$_2$O$_3$ and CuO/CeO$_2$ for CO oxidation in reaction gas that contained H$_2$. The Au catalysts performed better at low temperatures both in dry and slightly humid atmospheres, whereas the Cu catalysts became superior at higher temperatures. However, the Au catalysts appeared to be the most sensitive to water and CO$_2$ deactivation, while the Pt and Pd-Cu on Al$_2$O$_3$ were the most resistant to all these factors. In the latter cases, the high CO oxidation activity of the noble metals in the presence of water were linked to the high activity of these catalysts in the low-temperature WGS conversion of CO by water, as reported by KEGGI (25) and UTAKA et al. (26).

This paper will address the properties of the supported Pd and Au catalysts with Ag, Cu and other metals as catalyst promoters. Heterogenized PdCl$_2$-CuCl$_2$ Wacker-type catalysts are also considered which are known to be active at very low (below 0 °C) temperatures and may be transformed into highly dispersed Pd-Cu supported systems (8). It is noteworthy that such separation of the metal functions as to perform catalysis and promoting catalysis is conditional, especially in the latter example of the Pd-Cu complex. This definition has been used for convenience to specify which metal mostly carries the active sites and which metal mostly promotes them.

Most of the experimental results described here were obtained in smoke-free reaction gases, although the published works were selected to provide information, applicable to cigarette smoking conditions. Several recent literature reviews, written by COQ and FIGUERAS (27), TOEBES et al. (28), STAKHEEV and KUSTOV (29), are referenced here providing both useful ideas and discussions of many case studies. We have also highlighted some critical characteristics of CO oxidation catalysis that are applicable to a cigarette filter in Table 1. Many aspects of this problem are beyond the scope of our paper; as is whether direct oxidation during the room temperature filtration of cigarette smoke is the most feasible solution for selective CO removal. Being optimistic about the task, we think that comprehensive studies of catalysis in smoke are necessary. They will ultimately suggest a catalyst system that will possess high activity at room temperature, combined with the particle size and molecular selectivity and acceptable costs.

3   PALLADIUM AND PLATINUM CATALYSTS

The numerous available publications on supported Pt and Pd mono- and bi-metallic catalysts, used for low-temperature CO oxidation, often appear to provide valuable complementary data and will be discussed together.

Table 2. Catalysis features on Pd and Pt catalysts on active supports

Essentials of CO oxidation process	References
Pd is more tolerant to heteroatom compounds	37–39
TiO_2 increases oxygen mobility at the beginning of the reaction	16, 41–44
Reaction of lattice oxygen via surface formates and carbonates	16, 45–48
Spillover to the metal-support interface and CO oxidation on it	41, 49–53
Bridged CO vs. linear CO and surface coverage	10, 49, 54
Non-dissociative CO chemisorption, characteristic to Pd, is beneficial	27
Oxidation of CO by NO and O_2 is promoted by Fe, Mo, Mn, Cu, Cr	29, 55–57

However, the Pd catalysts seemed to be a better choice for a smoke application because they have a higher low-temperature catalytic activity and dispersion stability. In addition, some Pd catalysts, e.g., Pd on CeO_2 (37), are relatively tolerant to the sulfur compounds. This catalyst was found to be more resistant to catalytic poisons when modified with Co or Mo (38,39). Pd on NaZSM-5, where the zeolite may improve gas-phase selectivity in smoke, can be prepared providing 50% conversion of CO below 40 ˚C by tuning the calcination temperature high and reduction temperature low (40). Some of the important aspects of these catalysts' application in smoke are discussed below; others are referenced in Table 2.

3.1 Surface reactions

The network of reactions on the surface of Pd and Pt that leads to the formation of CO_2 in gas includes adsorption and activation of CO and O_2, surface diffusion and structuring of these chemisorbed molecules that may result in oscillations of oxidation rate, diffusion of oxygen deeper in and out of the crystalline lattice of the support, and desorption of the product CO_2. All these partial processes can be influential on the initial and steady-state activity of catalysts and on selectivity and sensitivity to the deactivating components of smoke.

3.1.1 *State of active oxygen and CO*: The role of oxygen stored in the support lattice is fundamental in the mechanisms of CO oxidation on supported Pd and was investigated in (58,59). In addition to the CO chemisorption on Pd, the Pd-support interaction was found to further promote the transfer of active oxygen from sub-surface layers to the reaction. This conclusion was supported by the fact that, in oxygen-free surroundings, CO caused a significant agglomeration of 1–2 nm Pt clusters on TiO_2 even at room temperature (59). The mechanism of O_2 adsorption and its state on the surface of Pt/TiO_2 was studied by UNER et al. (45), where O_2 was found to be chemisorbed in the molecular form first on the carrier and then on Pt upon saturation of the catalyst surface. Until then, oxygen was found to be atomized to some extent that also agreed with the fact that the oxygen adsorption heat decreased with increased O_2 pressure. The genesis of the oxygen atoms from CO and O_2 (air) was elucidated when Pt/CeO_2 was studied by ERTL (46) in CO

combustion under the transient conditions of cold start of a car, and when oxidation on a similar catalyst was conducted in the presence of H_2 and H_2O (16). During low-temperature CO oxidation, the catalysts were covered predominantly with CO molecules. The oxygen atoms of CO remained for a longer time in the catalyst than the carbon atoms; that was explained by formation of carbonate on ceria and subsequent exchange of its oxygen with the ceria lattice. Formation of formate, carbonate and bicarbonate structures in CO/H_2 gas on titania, zirconia and ceria was found and investigated by MA et al. (47) and by IIDA et al. (48). These results emphasize the importance of chemisorption on noble metal and spillover, or transfer of CO on active support and its reaction with the surface oxygen outside the transition metal clusters.

The term "active support" has become common in catalysis to denote the supports that can both activate some of the interacting gas molecules, and affect the electronic structure and activity of the metal clusters on them. Thus, the ZrO_2-CeO_2 support was found to be the most active promoter for Pt, followed by the individual oxides of Ce and Zr. The results in (16,41,42) suggest that the generated oxygen species could both spill over to the metal particles and react directly with the reducing CO molecule in gas or on the metal surface, which is more commonly considered. The authors of (42,43) found an increased reducibility of both CeO_2 and PdO in similar catalysts as a result of incorporation of TiO_2. This synergism in the binary oxide support resulted in an increased oxygen mobility, particularly at the beginning of the reaction, and would be beneficial for catalysis in smoke under puffing conditions.

A noble metal oxide layer surrounding the supported metal particles was found to form as a result of oxygen diffusion from the support. The content of this two-dimensional phase on the Pt/SiO_2 catalyst varies with the surrounding conditions, particularly with the different content of the reaction gas (49). The resulting synergism between oxide phases was explained by WENG and DELMON (50) as a spillover, or surface diffusion of dissociatively adsorbed oxygen onto the metal/metal oxide interface and its reaction with the chemisorbed CO. This is consistent with a "non-competitive" Langmuir-Hinshelwood mechanism, discussed by WOOTSCH et al. (41).

The migration of an excessive oxygen from the reducible support to the transition metal could even block the CO active sites as found by MIRKELAMOGLU and KARAKAS (51) for the Na-promoted Pt/SnO_2. Unlike the SnO_2-supported catalysts (51,52), the extensive kinetic study by BOURANE and BIANCHI (53) indicated no synergism for the Pt/Al_2O_3 catalyst. A low-temperature CO oxidation on this catalyst involved a non-competitive chemisorption of CO and O_2 on Pt and a Langmuir-type surface reaction between linearly adsorbed CO and weakly adsorbed oxygen.

The state of reacting CO is determined primarily by the multiplicity of its sorption. Linearly adsorbed CO appears to be the surface state prior to the oxidation act on a Pt/Al_2O_3-type catalyst, whereas the bridged CO just occupied the oxygen activation sites. AHLUVALIA et al. (10) showed that the rate of low-temperature oxidation of CO was limited by the removal of the bridged CO. This slow liberation of the Pt^0 site is necessary to allow formation of weakly adsorbed oxygen that requires an induction period

of several seconds. Therefore, the situation with the Pt surface initially covered with CO is not acceptable for a cigarette filter application, where the whole reaction must have been completed in a fraction of a second. Although this seemed not to be the case in a cigarette because of a long-term initial exposure of the catalyst to air, other volatile molecules could adsorb and block oxygen in a similar or stronger manner.

In a situation where CO and O_2 on the metal surface are localized in separate domains, the reaction between chemisorbed molecules is expected to take place only on the boundaries of these domains (49). In the reversed situation that is more characteristic of a cigarette, when O_2 saturates the Pd surface, the subsequent adsorption of CO may take place at the top (54). Further uptake of CO can also compress the oxygen layer into the domains. The electron acceptor oxygen on the Pd surface in the neighborhood of CO can reduce the net electron transfer from the metal to the CO ligand and thereby weaken the metal-CO bond that must facilitate the catalytic oxidation as shown in (60) for Pd/CeO_2. This surface "fill-up" model, which is effective when a reducible CeO_2 support is used, seems to be potentially applicable and beneficial for a cigarette filter.

3.1.2 *Kinetic oscillations*: An approximately two-second puff profile of CO production within the cigarette burning zone imposes certain requirements on the starting activity of the catalyst. Besides, this the catalytic activity must be high, and it should not have even a second-long induction period. Additionally, the catalytic oxidation of other volatile organic compounds, present in smoke, may also experience similar oscillations (61) that can further complicate the process. Therefore, the kinetic oscillations, which are a well-known and thoroughly studied feature of CO catalytic oxidation in other than smoke environments, will be addressed in this review.

The phenomenon is partially caused by a competitive sorption of O_2 and CO on a noble metal crystal and on the support, and involves interaction between chemisorbed molecules (46,62). The authors of (63,64) experimentally investigated the kinetics of the CO+O_2 reaction. Some of the mechanisms of this process have been established, particularly the chemisorption of CO and O_2 on different adsorption sites. An asymmetric inhibition of the process by CO was found to be a part of the oscillation mechanism. Thus, whereas the dissociative O_2 chemisorption was strongly inhibited by the presence of preadsorbed CO, the chemisorbed oxygen atoms formed open ad-layers that did not significantly affect the additional CO uptake.

The oscillations of the CO oxidation rate typically occur within a relatively narrow range of CO concentration of around 1%, which is an average CO level in cigarette smoke that in maximum can reach a few percent. The kinetic models of the entire process including the rate oscillations and formation of adsorbate patterns on surfaces of Pt, Pd and Ir were analyzed in detail by KURKINA, ZHDANOV *et al.* (65,66) and more recently by YAN *et al.* (67). These models were derived from the Langmuir-Hinshelwood mechanism, which was found to be sufficient to explain the oscillation kinetics. Thus, at low CO pressure the Pt surface was largely covered with adsorbed oxygen and the reaction rate usually was proportional to CO

pressure. When CO coverage became so high that it started to inhibit O_2 adsorption, further increase of CO pressure decreased the reaction rate, which now became limited by O_2 adsorption. The decrease of the rate with increasing CO pressure became steeper at lower surface temperatures, caused by a drop in the reaction heat.

The reaction rate oscillations on the noble metal catalysts are also associated with a periodic variation of the atomic structure of the surface. Thus, a clean metal surface, e.g., Pt with a 1×2 structure reversibly transforms into the 1×1 structure if the CO surface coverage exceeds about 20% (66,58) or even less if transformation is promoted by the reaction heat (67). This heat overcomes the 1.1 kJ/mol of difference in the energies between 1×1 over 1×2 arrangements on Pt. On the other hand, the probability of adsorption is larger on the 1×1 phase than on the 1×2 phase, which promoted the removal of CO after the 1×2 to 1×1 transfer.

The oscillation phenomenon was thoroughly investigated for polycrystalline supported noble metal by ZHDANOV and KASEMO (66) and provided practical information for a catalyst development. The authors showed the influence of the metal cluster, indicating that the probability of oscillations diminishes with Pt crystal sized below 4 nm. The oscillation mechanism comes into play on Pd at low pressures, whereas on Pt it happens at higher pressures (46). This may provide some reference for design of the catalyst for a cigarette that would be less complicated with the rate oscillations.

Typically the period of one rate oscillation is 1 to 2 seconds, which matches the duration of a single puff of a cigarette. The puff most likely starts with the all-surface configuration 1×2 being covered with oxygen and should end with the noble metal surface partially reconstructed into the 1×1 symmetry. During this time the O_2 adsorption is the rate-limiting stage as concluded by the studies (46, 69–72). On the 1×1 patches thus formed, more O_2 will be adsorbed and react with adsorbed CO, so that the coverage by CO drops below the critical value, which provides stability of the 1×1 phase. The surface structure, therefore, transforms back to 1×2 where the O_2 sticking coefficient is smaller and the CO coverage may build up again, repeating the process. This model suggests that the actual CO oxidation in a cigarette filter may reach a significant rate later in the puff or even after the puff when the reaction will proceed with already chemisorbed CO. This provides an estimate of about 1 mg for the needed CO capacity of the catalyst bed in the filter or for the CO delivery within a single puff. In the following paragraphs we will discuss the source of oxygen to oxidize CO and to restore the original state on the catalyst.

3.1.3 *Subsurface oxygen and desorption of CO_2*: The oscillation phenomenon causes a clockwise reaction rate hysteresis if the CO pressure is continuously increased and decreased again, similar to that in the puff-by-puff smoking. Such a clockwise hysteresis was also observed at low and variable O_2 pressure but was found to change to counter-clockwise as O_2 pressure was increased. This additional mechanism was attributed to the participation of oxygen atoms, dissolved below the surface (50,73). If the surface is largely covered with oxygen atoms, they will penetrate below the surface,

leaving the surface less active and the oxygen-sticking coefficient reduced. As a consequence, the surface may become predominantly covered by CO, creating conditions for subsurface oxygen atoms to move back to the surface from the reservoir until the initial situation is reestablished and one oscillation cycle is completed.

The importance of sub-surface oxygen in catalysis diminished when the size of a transition metal oxide cluster increased, as described in detail by CIMINO and STONE (74). However, the sub-surface oxygen is also present in the partially reducible supports, like titania or ceria, which causes the O_2 activation mechanism to be influential in catalysts of the Pd/CeO_2-type. A direct interaction of CO with the oxygen from ceria-zirconia was shown experimentally by BAORO et al. (75) to be a major contributor in catalysis under unsteady-state experimental conditions.

Based on similar models, LIU (76) and SIRIJARUPHAN (77) with co-authors found that, for Pt/Al_2O_3, addition of iron oxide provided oxygen for oxidation of CO adsorbed on Pt, thereby creating a dual-site non-competitive mechanism for catalysis. This approach of accumulating active oxygen for further CO or hydrocarbon oxidation was utilized by BERNDT and LANDRI (78) to design a layered catalyst structure, in which a lower layer or substrate serves as an oxygen activator. The important feature of such catalysts (77) was an enhancement of the catalytic activity for selective CO oxidation in hydrogen streams, and therefore might have potential for application in smoke.

The authors of (79,80) investigated the Ag_2O surface layer with oxygen both above and below the surface. In this situation, CO acted as a chemical regulator of the dissolved oxygen atoms in the near-surface region. The maximum oxygen capacity of the sub-surface oxide layer corresponded to its full reduction (81–83). If we consider 100-mg loading of a catalyst in cigarette filter that carries about 1 m^2 of reducible oxide, than we estimate that all oxygen in this monolayer may oxidize about 1 mg CO. This amount approximately represents CO in smoke from one puff of 35-mL volume under Federal Trade Commission (FTC) smoking conditions. If we further assume that the catalyst can "recharge" its oxygen during a minute between puffs from gas, then the source of active oxygen for the 2-second puff will be totally internal. Therefore, the CO oxidation rate may not necessarily be limited by chemisorption and activation of O_2 from gas. Supporting this estimation is the finding by BEDRANE et al. (83) that the process of a noble metal-assisted oxygen penetration into the ceria and ceria-zirconia-supported noble metal catalysts appeared to be fast.

The mechanism of CO_2 participation in the oxidation process must be considered for a cigarette filter application because of the high concentration of CO_2 in smoke and the following literature data. NIJHUIS et al. (84) investigated desorption of CO_2 from the Pt catalyst below 150 ˚C and found that CO_2 formation was faster than its desorption, and its rate therefore should be taken into account for the descriptive kinetics. A similar rate-limiting step was found also by BOULAHOUCHE et al. (85) on Au/TiO_2 at sub-ambient temperature and by CIMINO and STONE (74) on Co/MgO catalysts at higher temperatures. These findings may agree with other studies where CO_2 desorption was found to be fast (53,73) if this adsorbed CO_2 is considered

in terms of the OC-O surface complex, just formed from CO_{ads} and O_{ads} according to (86). Besides, the CO_2 desorption rate was found to relatively decrease with decreased temperature (87) that makes this process kinetically influential for room temperature catalysis in smoke.

3.2 *Preparation of catalysts*

Application of molecular sieves or, more specifically, zeolites or clays for smoke filtration may improve selectivity of the catalysts (88,89). Since the structures and applications of zeolites have been thoroughly discussed in the literature, we will only highlight a few expected complications emerging in smoke. One of them is clogging and deactivation of the pores by mostly polar molecules and particles. Since the task of keeping water and other highly polar molecules out of the catalyst surface is quite difficult, a more feasible solution could be an application of a larger aperture size zeolite. Thus, a 5Å zeolite was found to provide access for CO molecules to the cavities until it gets hydrated in open air, whereas the 9Å zeolite gained better sieving properties after long term storage in a humid air (8).

Another feature of zeolite-supported metal catalysts appears to be their relatively low stability in a redox surrounding. Reduction of metal oxide can move the metal ions within or out of the cavities even at temperatures below 100 ˚C, whereas oxidation may partially redistribute it back. Such metal transfer was found to be more significant for the catalysts with high metal loadings. An excessive reduction in CO and sintering of Pd or Fe in a ZSM-5 matrix could overfill zeolite cavities and make them inaccessible for gas molecules, as shown by LOBREE et al. (90,91). Since these processes are faster at elevated temperatures, the room temperature cavity filter-type applications of zeolite-supported metals would work better for cigarettes.

Specially prepared carbons, such as industrial-scale activated carbonized wood, bitum or coconut shells, or sophisticated materials such as nanotubes and fullerenes can successfully be used for low-temperature CO oxidation catalysts. The activated carbons will be discussed along with the very interesting Wacker catalysts, because the carbon support appears to be a part of almost all catalysts of this type. However, application of carbon-supported catalysts for cigarette smoke filtration is rigorously limited by a non-selective adsorption activity of carbon in smoke. Therefore, catalysts on carbon-type supports are not discussed in this review.

3.2.1 *Co-precipitation and precipitation*: The preparation of supported small clusters of noble metals with necessary catalyst characteristics can be done in a variety of ways, among which the co-precipitation and precipitation on the support, followed by thermo-treatments and reduction, seem to be most practical and provide good results. The catalysts, built on these principals in the zeolite cavities, would have even more advantages for a selective treatment of gas molecules in the presence of particulate in smoke.

The catalysts from the co-precipitation method are usually characterized by a narrow distribution of metal particles from 1 to 3 nm. These particles may be relatively stable in an inert or, preferably, oxidative atmosphere at elevated temperatures, which are applied for decomposition of an intermediate

complex. Heat treatment in a reducing atmosphere often causes sintering, most likely due to the formation of intermediate PdH_x. A co-precipitation procedure of the catalyst, preceding the heat treatment, is important in arranging the necessary metal-metal and metal-support interactions to control sintering. A variety of starting materials, e.g., $PdCl_2$, $Pd(NH_3)_4Cl_2$, $Pd(acac)_2$, $(C_2H_5O)_4Si$, along with temperatures, pH, solvents (alcohols, acetone, aqueous ammonia), reactive or inert atmospheres, and other variables was considered in detail in (28,92).

Thus, by simply controlling the pH of aqueous $Pd(NO_3)_2$, the isolated complex $Pd(H_2O)_4^{2+}$ can be formed at pH < 1 whereas small PdO colloidal particles of 1.7–1.8 nm can be prepared by hydrolysis at pH > 2 (28). This situation appeared different in the presence of stronger ligands. The presence of ammonia yielded the complex ion $Pd(NH_3)_4^{2+}$, stable in quite basic environment, whereas the chloride ion formed a complex $PdCl_4^{2-}$, which was stable in a neutral solution. All these surface compounds must be considered specifically with a selected support in terms of an optimal strength of the interaction between precursors. The co-precipitated catalysts usually require much higher temperatures for formation of reduced noble metal (92), compared to those precipitated on a solid support, which could adversely affect the catalyst structure.

The advantages of supporting noble metal on an already preformed matrix are the better control of the catalyst structure and the usually lower temperature, which is necessary for producing dispersed reduced metal particles. Supported metal can be prepared by the addition of an aqueous solution of, for example, $Pd(NO_3)_2$, to a stirred slurry of the support in an aqueous solution of NaOH, followed by washing, drying around 110 ˚C and reduction in H_2. The dispersion of Pd in the prepared catalyst was found to be independent of the reduction temperature up to 400 ˚C. SHEN and MATSUMURA (93) found that this procedure, applied to the CeO_2 support, led to the presence of a rather high surface concentration of Pd^{2+} ions, even after reduction at 500 ˚C. The high pH values facilitated strong interaction of the metal ions with the surface. As could be expected, the catalysts prepared with $PdCl_2$ as a precursor showed a significantly higher Pd^{2+} concentration than those prepared from nitrate salt.

Instead of precipitation in ionic form, the metals can be reduced in close vicinity to the support surface, which is especially suitable for the production of noble metal catalysts because of their favorable reduction potentials. Thus, a metal can be directly applied onto the support by introduction of a soluble reducing agent to a suspension of support material in a solution of the active metal. As a useful example, the reduction of palladium in a complex of non-aqueous solution of the reducing agent ethanol appeared to be a slow process. Hence, the duration of this reduction could be used to control the mean particle size of the metal.

A "ship-in-bottle"-type synthesis of catalyst sites in spatially hindered cavities, described by ICHIKAWA (94), can help to increase selectivity towards gas phase of smoke. This technique was used to make Pt carbonyl clusters, nanowires, and nanoparticles in micro- and mesoporous materials that was described by FULUOKA et al. (95). Reductive carbonylation of metal ions impregnated in NaY zeolite or in mesoporous silica FSM-16 selectively formed the platinum carbonyl clusters; decarbonylation of these clusters yielded 1 nm-size naked Pt nanoparticles.

Similar nanoparticles in FSM-16 were prepared by a direct H_2 reduction of H_2PtCl_6/FSM-16 at 300 ˚C to form 2.5 nm metal particles in 2.7 nm pores. The same diameter Pt nanowires (length 50–300 nm) were obtained by photoreduction of H_2PtCl_6/FSM-16 in the presence of water/isopropyl alcohol vapor. The catalysts exhibited unique properties in CO chemisorption and in WGS reaction due to their morphology in the mesoporous channels of FSM-16, which could be studied by monitoring the unusual magnetic properties of these Pt wires.

3.2.2 *Catalyst promotors*: In this part we will discuss several case studies of promotors to the noble metal catalysts that can beneficially control their properties that are relevant to the cigarette filter application. In most bimetal catalysts, described in the literature, the CO oxidation active area was considered to be in closest proximity to the border between the prime metal cluster and the second metal. MARGITFALVI et al. (96,97) found that the catalyst systems Pd^{2+}/Cu^{2+}, Au^+/Au^0 and Sn^{4+}/Pt were principally the redox couples, which showed activity as long as some charge difference between two metals was maintained. CuO is readily reducible and can form different phases in the catalyst $PdCu/Al_2O_3$. COLEN et al. (98) and MERGLER et al. (99) showed a large synergetic increase in the activity of similar catalysts that they also explained in terms of the properties of the noble metal to Cu interface. KHANRA and MENON (100) showed that the content and distribution of the metal and metal oxide phases and, therefore, the catalyst properties strongly depend on the order of Pd and Cu introduction on the carrier.

Furthermore, the surface content of this bimetal particle was controlled by the presence of CO/H_2 and O_2 in the gas, which could enrich the surface with Pd and Cu respectively. This result was consistent with the adsorbate-adsorbent bonding energies, provided by ROCHEFORT and FOURNIER (101). Computational modeling suggested that CO and NO are more strongly bound to Cu atoms on Pd-Cu alloy than on pure Cu and less strongly bound to the Pd atoms on alloy than to those of pure Pd. Similar gas-solid interaction mechanisms can apply to the iron oxide on Pt/TiO_2, investigated by SHOU et al. (102). It is noteworthy that the prepared catalyst provided 70% conversion of CO at 40 ˚C in a flow of 15,000 h^{-1}. The authors also obtained good results for flow rates up to 36,000 h^{-1} by using ceria and alumina as a support for a Fe-Pt catalyst.

A synergistic promotion of CO oxidation was found for several catalyst systems, such as Pt and Pd on SnO_2, Sb_2O_4 or coprecipitated $SnO_2+Mn_2O_3$, which conducted the oxidation reaction under the conditions where the components alone were catalytically inert (85,96,103–105). To explain this effect we will consider two kinetic regions, which were observed during CO oxidation (46,106).

At low CO concentration the oxidation reaction appeared to be first order with respect to CO and practically temperature-independent, whereas at high CO concentrations the reaction rate was zero order with respect to CO and temperature-dependent. Synergism was usually observed for the second region or for the high CO partial pressures that seem to be

characteristic in cigarette smoke, where this pressure may reach 40 torr. The synergism in this region is believed to be driven by the oxide component of the catalyst. This suggests promotion of active catalysis on SnO_2, modified by Pd via its solution with PdO (107). In support of this model, SnO_2 on activated carbon was found to be active towards CO binding as shown by IUKE, AL-KHATIB et al. (107,108) and in their earlier papers on the kinetics of CO adsorption.

Many other heteroatoms have been found to facilitate oxidation on Pt and Pd. Thus, incorporation of rubidium by KONSOLAKIS et al. (106) enhanced the catalytic activity of Pt by a factor of 100 in the reduction of NO by CO over Rb-promoted Pt/γ-Al$_2$O$_3$ catalysts. The effect of K-promotion of the noble metal was found to be less pronounced (109). The observed promotional effects were ascribed to the alkali-induced changes in the chemisorption bond strengths of CO, NO and NO dissociation products.

Deposition of submonolayer quantities of Au onto a Pt surface was applied by CHANDLER and PIGNOLET (110). In the case of Pd catalysts on SiO_2, formation of Au-Pd alloys resulted in a dramatic increase in CO oxidation activity when Pd concentration exceeded 50% in the study by VENEZIA et al. (111). They showed that gold decreased the adsorption of O_2 and lateral diffusion of adsorbed CO that could favorably shorten the induction period of CO oxidation in a cigarette filter at the start of a puff. The advantageous differences in catalyst activities and selectivities were attributed primarily to geometric effects.

3.2.3 *Selectivity of deposition*: Deposition of a metal precursor on the support can be non-selective or selective, depending on whether the interaction between noble and the second metal precursors during the deposition was prearranged. In the first case, the interaction between each precursor and solid surface must be stronger than that between precursors. The selectivity of deposition, therefore, can be controlled by surface diffusion of both metals to yield bimetallic aggregates during activation as discussed by COQ and FIGUERAS (27). We will illustrate the principal of selective deposition with a few case studies.

Deposition by exchange of a surface ion to another metal-carrying charged species, such as Pd(NH$_3$)$_4$Cl$_2$ or PdCl$_4$K$_2$ was found by RADKEVICH et al. (112) to be driven by electrostatic interaction. Such an ion exchange in aqueous solutions usually yields the nano-sized particles after activation. The final dispersion of Pt on SiO_2, however, strongly depends on the drying conditions, and is particularly determined by the possibility of melting of intermediate complex [Pt(NH$_3$)$_4$(OH)$_2$]$_n$ clusters around 100 ˚C as studied in detail by GOGUET et al. (113).

A similar ion-exchange approach was used by YANG et al. (114) to prepare the [AuCl$_4$]$^-$ complex on the silica, functionalized with positively charged groups. However, the authors found that the Au particles, formed upon reduction with NaBH$_4$, showed low resistance to sintering already at 100 ˚C and relatively low catalytic activity. This was explained by lack of metal-support interaction (MSI) in this system that, therefore, can be improved either by strongly interacting supports or by a second metal-promotor on the same inert support.

A combination of the two above methods for preparation of Au and Pd or Pt catalysts could provide a good result. Thus,

RIAHI et al. (115) described how bimetallic PdAu nanoparticles located in the supercages of Y zeolite could be obtained from the co-exchange of HY zeolite with Pd(en)$^{2+}$ and Au(en)$_2$$^{3+}$. The ethylenediamine ligand performed the *in-situ* reduction of Pd and Au in an inert atmosphere without significant sintering. Ion exchange on the surface becomes grafting in the case of organometallic complexes, which can react with surface hydroxyl groups with the removal of organic ligands like acetylacetonate, cyclopentadiene or π-allyl, as shown by CRABB and MARSHALL (116). Bimetallic catalysts, such as PtPd/Al$_2$O$_3$ and PdCu/C, can also be prepared by using a reductant, e.g., hydrogen, which preadsorbed selectively on the parent metal. The ions of the second metal are then reduced by this reagent, and the metals interact.

A very active version of a similar zeolite-supported Pt-Fe catalyst for work in a hydrogen stream was prepared by KOTOBUKI et al. (55) by a conventional sequential exchange of Pt^{2+} and Fe^{3+} on Na-type mordenite, followed by annealing and reduction in H$_2$ at 300 ˚C. This catalyst demonstrated a very strong synergetic effect between Pt and Fe, thus providing selective activity at nearly ambient temperature at gas velocity of about 10^5 h^{-1}, or at the conditions similar to those in a cigarette filter.
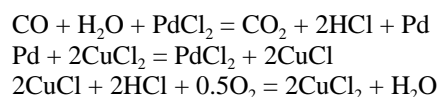
3.3 *Heterogenized homogeneous catalysts*

Unlike many heterogeneous Pd catalysts that are good for CO oxidation but sensitive to deactivation by water in the reaction gas, the homogeneous PdCl$_2$-CuCl$_2$ catalysts require water for their activity at ambient temperature. FARRAUTO and BARTHOLOMEW (117) described the Wacker processes of low-temperature oxidation of olefins, efficiently performed on a homogeneous catalyst, which was a combination of PdCl$_2$ and CuCl$_2$. This catalyst was modified with activity-promoting additives Mo, W and V by NOWINSKA et al. (118). In spite of the high activity at room temperature, these catalysts do not appear to be pyrophoric.

The immobilized Pd-Cu and other metal-based homogeneous oxidation catalysts were discussed systematically in an extensive review by DE VOS et al. (119). Typically, a heterogenized homogeneous catalyst retains its complex structure and remains active, being built in a thin film of solution spread on an inert support. Carbon has been reported to be superior to other supports for such a catalyst (120,121). This use of activated carbon remains a major obstacle for application of this type of catalyst for smoke filtration, since carbon can adversely affect the smoke taste.

The uniqueness of carbons as carriers is their hydrophobicity, since water does not fill their pores thus introducing diffusion limitations for a feed gas that must be critical for smoke. Further promotion of high catalyst activity was achieved by WU and CHANG (122) by using even more hydrophobic porous styrene divinylbenzene copolymer. Considering a possible adverse effect of carbon on the smoke taste, use of a porous polymer could make a good substitute to carbon for use in cigarette filter.

Another advantage of the Wacker-type catalysts is that, being homogeneous complexes, they had been extensively studied and are well understood. The redox reactions, discussed by PARK and LEE (121), involved in the catalysis, are the following:

$$CO + H_2O + PdCl_2 = CO_2 + 2HCl + Pd$$
$$Pd + 2CuCl_2 = PdCl_2 + 2CuCl$$
$$2CuCl + 2HCl + 0.5O_2 = 2CuCl_2 + H_2O$$

WU and CHANG (122) suggested that the catalyst oxidation site consists of Pd^{2+} with chlorine and carbonyl ligands and solid $Cu_2Cl(OH)_3$ particles. During catalysis most of $CuCl_2$ was reduced to Cu^+ species coordinated with Cl^-, Pd^0 and Pd^{2+} (123,124). Addition of $Cu(NO_3)_2$ facilitated the formation of the active Cu^+ complex and, therefore, promoted catalysis. A larger than stoichiometric amount of $CuCl_2$ relative to $PdCl_2$ was required for high activity of the carbon-supported catalyst.

4   GOLD CATALYSTS

Gold-containing catalysts have recently attracted great interest for their largely unexpected activity at below room temperatures as discussed by BOND and THOMPSON (125,126). Similar to the more traditional Pt and Pd catalysts, gold is capable of catalyzing a wide range of reactions of carbon and nitrogen oxides, water and hydrocarbons (127). Unlike most transition metals, bulk Au does not chemisorb CO at room temperature (128), whereas Au nanoparticles were found to exhibit high catalytic activity at and below room temperature (129,130). The importance of the surface steps and kinks on this dispersed gold for CO chemisorption at room temperature and its activity in its oxidation was observed by PICCOLO et al. (131).

The results obtained by GIORDANO and WANG et al. (132,133) provide comparison between adsorption and catalysis properties of rutile-supported Au, Pd, Cu and Ag, and help to position gold among catalytically active transition metals. Thus, the latter two metals (Cu, Ag) were found to interact strongly with the bridging oxygens of TiO_2, donating electrons to the 3d state of Ti, whereas Au and Pd formed covalent polar bonds with the support. This similarity in the bonding properties of Au and Pd could be explained by the high ionization potential of Au (interaction with Ti without charge transfer) and also by the ability of Pd to hybridize the 4d and 5s atomic levels and to form bonds with the 3d level of Ti. Therefore, not only the strength of metal-support interaction but also its covalent nature may be important in forming the active Au or Pd catalysts.

The choice of support for gold has been found to be critical. A necessary strong metal-support interaction (SMSI) for a highly dispersed thermally stable Au catalyst was readily provided by TiO_2, ZrO_2 or CeO_2 (130,134–141), but Al_2O_3 and other more inert supports were also used (142–144). These catalysts showed high activity at ambient temperature when basic alumina, silica and titania were used as catalyst supports, whereas the acidic supports (alumina-silica and activated carbon) resulted in much lower CO oxidation activity of gold. The other strongly interacting supports could be used in the form of freshly prepared hydroxides as was done in the case of the gold phosphine complexes. The preparation of these catalysts will be described below in more detail because the resulting catalysts demonstrated record-high activities at room temperature.

4.1   Mechanisms of CO oxidation

Similar to the catalysis model by DERROUICHE and BIANCHI (145) on Pt and Pd, the catalysis on Au has been described as the Langmuir-Hinshelwood-type by GOTTFRIED and CHRISTMANN (146). The activation energy was found by MANUEL et al. (147) to be as low as 57 kJ/mol on the gold catalyst, which is about half of that found, for example, for Ph/Ce-Zr-O. This more flat temperature dependence of the reaction rate on Au can be beneficial for a cigarette filter application when a low-temperature active catalyst is exposed to smoke. Thus, a large exothermic effect of CO oxidation must cause some initial increase in the filter temperature. This can escalate oxidative catalysis of other molecules and an uncontrolled growth in temperature that will not happen if the activation energy of oxidation on this catalyst is low.

SCHUMACHER et al. (148) found that adsorption of hydrogen on Au provided competition for CO, consequently changing the order for CO from 0.35 to 0.9. This competition may impose a complication for using Au catalysts in smoke containing hydrogen and other active gas molecules. However, the situation may change when other, active or reducible, supports are used for the Au catalyst. Thus, Au/ZnO was found to be activated for $CO+O_2$ reaction by the presence of H_2 in the reaction gas. MANZOLI et al. (149) suggested that hydrogen could prevent poisoning of the catalyst by suppressing the formation of stable carbonate-like species on the metal oxide at ambient temperature.

A similar carbonate mechanism of deactivation was suggested for the water-gas shift (WGS) reaction on Au/CeO_2, where partially reduced Ce^{3+} facilitated formation and deposition of carbonates and formates on active sites (135,150,151). Sensitivity of the supported gold catalyst to this poisoning activity of CO can be controlled by transition metal additives, such as Fe and Mn for the Au/MgO catalyst, as shown by MARGITFALVI et al. (152). In the case of tobacco smoke, a tiny amount of Fe in it could even be a promotor of gold catalysts in the filter.

Another useful property of gold catalysts is that the presence of water on the surface of some gold catalysts can strongly promote their activity by actually creating the active sites. This active site was found by COSTELLO, KUNG et al. (142–144) to be a metallic Au cluster and a cationic Au with a hydroxyl group. The active Au/Au^+ redox couple helped to explain why heat treatment of uncalcined Au/Al_2O_3 at 100 ˚C in the humid hydrogen atmosphere activated the catalyst by creating mixed Au states, whereas H_2 or H_2O alone did not provide such activation.

4.1.1 State of metal clusters: Gold catalysts, such as Au/TiO_2, are characterized by a strong metal-support interaction and by the presence of the perimeter interfaces between Au particles and the support (142) that are controlled by the preparation conditions, as discussed by HARUTA and DATE (153). Thus, it makes a difference for the state of Au cluster whether it is positioned on the oxidized surface or on the oxygen vacancies of TiO_2. In the latter case, considered by LOPEZ and NORSKOV (136), electron transfer from Au particle to the TiO_2 surface caused geometric changes in metal particles.

The influence of SMSI on the parameters of metal clusters increased at low coverages of TiO_2 with Au, which correlated with unusually high dispersion and catalytic activity of nano-scale gold catalysts. An opposite electron transfer from TiO_2 to Au was found experimentally in Au/TiO_2 with high Au loading (137). This promoted chemisorption of oxygen on an excessive negative charge. Interestingly, pre-chemisorption of hydrogen, possibly protonated on the surface, can also activate Au/TiO_2 for CO oxidation (145) and may help in keeping the catalyst active in H_2-containing smoke.

A completely disordered layer of chemisorbed CO at sub-ambient temperatures was found by GOTTFRIED et al. (154). This suggested that the previously discussed oscillation-type behavior, characteristic of Pd and Pt catalysts, should not be the same for Au catalysts. However, CO pressures above 20 mbar were found to cause a surface reconstruction of Au particles (128). This CO concentration is typical of cigarette smoke and makes the consideration of such a low-temperature displacement of Au atoms and destabilization of the surface structure important.

COSTELLO, KUNG et al. (142) concluded that CO_2 forms from decarboxylation of either hydroxycarbonyl, or bicarbonate surface structure on the Au^+/Au site, stabilized by hydroxyl groups. This model successfully explained several key features of Au catalyst performance, i.e., reversible deactivation at dehydration or overoxidation of gold particles. According to this model, an attempt to form the catalyst above 100 °C, especially, in the presence of O_2 must fail, because such treatment would destroy the active site Au^+-OH (130).

The presence of strong ligands, including water in the reaction gas, can stabilize Au^+ complexes in $Au/M(OH)_x$ catalysts (138,152). Thus, the $Au/Fe(OH)_3$ and $Au/Ti(OH)_4$ catalysts remained active in the low-temperature CO oxidation after calcination much above 200 °C. The authors, however, stated that O_2 activation was exclusively performed on the gold particles, whereas involvement of support in this process was ruled out. This conclusion seems to be debatable, because other studies show an active role of reducible oxide supports in the oxygen activation process, while it is generally agreed that CO adsorption on the support may be insignificant (155).

4.1.2 Composition of active site

4.1.2 *Composition of active site*: The composition of the CO chemisorption site including Au^{n+} and Au^0 as well as the boundary of Au particles on a variety of supports was proposed based on spectral analysis (156,157). Several CO adsorption forms were experimentally detected on the supported Au catalysts with the desorption energies from 8 to 38 kJ/mol (154). The inclusion of Au^{n+} in the active site has been debated by GOOSSENS et al. (158). The authors did not observe Au ions in the Au/TiO_2 undergoing catalysis by Mossbauer spectroscopy. However, this may not contradict the more common model of randomly distributed Au^+-containing active sites, since this method could not detect concentrations as low as 0.001% of possibly working and unstable Au^+ in the catalyst (139,156).

The active site that involves the boundary of Au particles and support was discussed by BOCCUZZI et al. (140). The reversible adsorption of CO on Au particles, irreversible adsorption of O_2 at the perimeter interface with formation of superoxide O_2^- as a rate-determining step and the fast formation of the OC-Au-O intermediate to produce CO_2 on the perimeter

interface were reported. The formation of peroxide and hydroxide oxygen on ZrO_2 and TiO_2 from atomic oxygen, activated by Au particles, and their reactions with CO/Au to form surface formates were studied in (141,159,160).

In agreement with this, CHANG et al. (161) showed that the adsorption of CO and O_2 on the working Au/TiO_2 catalyst was not competitive and O_2 activation was conducted by the support. Therefore the experimentally observed superoxide species on both metal and support in the $Au/Ti(OH)_4$ system studied by HAO et al. (162) could only be explained by O_2^- diffusion on the Au particles. In contrast, the O_2^- species were found to result from O_2 interaction with electrons trapped on the missing oxygen sites, or on the Ti^{3+} centers. Molecular orbital calculations almost excluded a possibility of O_2^- formation from O_2 on the Au cluster, but rather suggested O_2^- formation on and from TiO_2, followed by surface diffusion on gold.

Such support reduction was found to be promoted by Au particles, so that for example, the temperature of CeO_2 reduction decreased by almost 300 °C when Au was imbedded (163,164). In contrast to the reducible oxides, in the case of SiO_2 as a support, the O_2 chemisorption on and under the Au surface was a main source of active oxygen (132,165) that appears to be a rate-limiting reaction. As a result, the turnover number (rate of surface reaction) can be independent of the Au particle size for active supports like CeO_2, TiO_2, Fe_2O_3; whereas for the "inert" supports the turnover number is dependent on particle size (111,164).

4.1.3 Different supports for gold

4.1.3 *Different supports for gold*: Large amounts of molecular O_2 can be adsorbed and activated on Fe_2O_3, NiO_x, CoO_x and ZnO (164,166–168), and this could provide an oxygen supply during the reaction on Au catalysts under smoking conditions. Among these the ZnO-supported catalyst was found to be tolerant to water in the reaction gas (168). For these supports the authors suggested a similar dominant reaction pathway involving adsorption of O_2 on the support in O_2^- form, dissociation at the interface, and reaction on the Au particle and/or at the interface with CO on Au.

Usually the addition of zirconia to ceria increased the oxygen storage capacity, as well as reducibility and oxygen mobility in support as investigated by KOZLOV et al. (169). BULGAKOV et al. (170) explained this phenomenon by a decrease in the local Ce-O coordination number from 8 to 7 with ZrO_2 addition. A further improvement of the individual or mixed oxides could be their support on more stable non-reducible oxides with a developed pore structure. For example, an additional benefit from using CeO_2 on Al_2O_3 as a support for gold was studied by CENTENO et al. (171). It was shown that ceria enhances the final dispersion and thermostability of Au particles.

We believe that the molecular sieves are attractive for smoke treatment because they must be selective towards the gas phase. Preparation of Au in Y-type zeolite was developed by LIN et al. (172,173). Prior to incorporation of Au, the zeolite was treated with $NaNO_3$ solution at pH 6, which ultimately increased the activity and stability of the catalyst. However, application of a relatively low surface area zeolite may impose a limitation on the concentration of Au in catalyst, because excessive gold may form large particles of a low activity on exterior surface, which are prone to sintering (173).

These catalysts were promoted by incorporation of Fe in zeolite along with Au by BULUSHEV et al. (174). The catalyst design could be similar to that described above for Au on reducible oxide, except the active Au-Fe-O groups were built in the zeolite cavities. The authors found that along with a higher activity the catalysts with iron demonstrated lower long-term stability, probably because of sintering of the reduced metal and/or deposition of carbonate-like species. However, considering the short catalysis time required in a cigarette filter application, this may not be a critical obstacle. TIBILETTI et al. (16) found that iron incorporation into the Au catalyst on carbon fibers instead, resulted in a significant increase in both initial activity and stability of Au particles in catalysis. This catalyst type may work better in the presence of water and hydrogen and that would be preferable for smoke applications.

4.2   Preparation of catalysts

Among a variety of methods for preparation of highly dispersed Au catalysts, we will highlight several procedures, developed in more detail for Au on an active/reducible support, which usually form more active catalysts than the non-reducible carriers (175,176). Although alumina and silica were reported by IVANOVA et al. (177) to form very active gold catalysts, we do not discuss their preparation here as they are less likely candidates for a cigarette filter application at present.

The preparation techniques can be summed-up as a co-precipitation of $HAuCl_4$ and a second metal salt, deposition-precipitation-reduction of Au compound on support, and chemical vapor deposition procedure consisting of adsorption and decomposition of gold complexes onto metal oxide. These methods have been developed for preparation of 1–5 nm size Au particles, resistant to sintering and active in catalysis at temperatures around ambient (151,178). The other, less extensively used precipitation technique was a sol-gel method, which also produced 2.5 nm Au clusters in 74 m^2 TiO_2 matrix, active at temperatures as low as 50 ˚C (179). In many cases, the catalyst precursors were calcined at high temperatures (up to 800 ˚C) to strengthen the metal-support interaction, for example, in Au/TiO_2 catalysts prepared by a spray method (180).

A similar Au/TiO_2 (181) catalyst, which showed high activity at room temperature, was prepared by a deposition-reduction method, where an aqueous solution of $HAuCl_4$ was adsorbed on the support and reduced by $NaBH_4$. The higher pH of the $AuCl_3$ solution (up to 10.5) gave LIN et al. (182) better results because of facilitating formation of the surface ensembles Au-O-Au. The solid was calcined around 200 ˚C that provided a delicate balance between Au^0 and Au^+-OH^- as an active site for CO oxidation, as also was recently suggested by PILLAI and DEEVI (130) for the CeO_2-supported gold.

However, the balance could be easily disrupted both by over-reduction of gold, as well as by its excessive oxidation, which is in agreement with the findings on Au/Fe_2O_3 catalysts by WANG et al. (183). In agreement with these results, LI et al. (184) suggested skipping the calcination step, which only decreased the activity of Au/TiO_2. Remarkably, they also found that the wet impregnation of TiO_2 with $HAuO_4$ and complexation with NH_3, produced a similarly active catalyst for CO oxidation below 25 ˚C.

The mixed Au^+/Au^0 active sites were developed for a differently prepared Au/Fe_2O_3 catalyst (87,185). Co-precipitation by Na_2CO_3 from aqueous solution of $HAuCl_4$ and $Fe(NO_3)_3$ produced a very active and stable catalyst. It is noteworthy that unlike the above-mentioned sol-gel catalysts, these samples exhibited poor activity after calcination at 400 ˚C for 3 h whereas uncalcined materials, which were only dried at 120 ˚C for 16 h, exhibited a far greater activity. The dried materials consisted of uniformly dispersed assembles of a mixed $AuOOH \times xH_2O$ and Au^0, whereas the calcined materials were comprised of 3–5 nm cuboctahedral metallic Au particles supported on 20 nm diameter well-crystalline α-Fe_2O_3 particles.

The effect of gold on the properties of the support was usually found to be beneficial. In addition to the electronic interactions, HUTCHINGS et al. (186) reported that the presence of Au in the co-precipitated Au/CuO and Au/ZnO samples suppressed crystallization of the supports. A similar phenomenon was assumed in the cases of the just precipitated $Fe(OH)_3$ and $Ti(OH)_4$ supports. Interestingly, the process of Au crystal growth was found not to be completely thermo-activated, but to have a point of stability at the atomic level, so that some particular size Au cluster may become more energetic and more active than its atomic precursor (187).

The dispersion and resistance of Au clusters to the thermal sintering were found to be determined by the supporting crystalline surfaces. The TiO_2 (1×1) and (1×2) surface structures were found to promote growth of 3 and 0.1 nm Au particles, respectively. Those metal clusters were found to be stable up to 460 ˚C (137). The problem with Au agglomeration in such catalysts was essentially solved by using a TiO_2/SiO_2 substrate instead of pure titania (188), which stabilized 2–3 nm Au clusters and consequently increased the catalyst activity.

Many published studies have focused on application of phosphine complexes of gold as on the unique precursors of ultimately fine Au clusters. Phosphine as a ligand was found to inhibit the formation of large Au^0 particles because of its high ligating affinity (189). A method for the preparation of exceptionally active, supported Au catalysts involves the use of as-precipitated wet amorphous metal hydroxides as support precursors for the incorporation of the $AuPPh_3NO_3$ complex precursor from organic media (160,190). In $AuPPh_3NO_3$ coordination, the nitrate anion bond is much weaker than that of the triphenylphosphine ligand, hence the release of the NO_3^--ligand from the complex $AuPPh_3NO_3$ on $Fe(OH)_3$ and $Ti(OH)_4$ was done at room temperature. A subsequent temperature-programmed calcination in air at 400 ˚C finally produced 3% $Au/M(OH)_x$ catalyst, active at room temperature (190).

A catalyst less critical to the state of support, but with about the same activity was prepared by CHOUDHARY et al. (191). The authors applied another gold complex $[Au_6(PPh_3)_6](BF_4)_2$, which formed gold clusters of 5 nm size on the surface of titania. TiO_2 was calcined at 500 ˚C prior to interaction with a CH_2Cl_2 solution of a gold complex. This catalyst was more stable than the one obtained from a gold nitrate complex. To conclude this discussion we will just mention that the gold heterogeneous catalysts are still relatively new and provide many problems to study. Some important features of them along with the references are collected in Table 3.

Table 3. Parameters affecting catalysis on Au catalysts; comparison with Pd and Pt catalysts

Subject	Essentials	References
Au, compare to Pd, Pt	Bonding of Au on TiO_2 is similar to that of Pd	132, 133
	Rate oscillations on Au are similar to that of Pd, Pt	128
	Activation energy on Au is much lower than on Pd	147
Supports and ligands	Pros and cons of Au on CeO_2, Al_2O_3, zeolite and C	168, 171–174
	Basic supports give stronger MSI and better activity	128, 134, 145
	SMSI in Au/TiO_2 is greater at low Au loading	137, 142, 153
	Strong ligands stabilize Au dispersion	138, 142
	Preparation of Au/TiO_2-type catalysts	30, 31, 33, 36, 141, 182
	Preparation of Au/Fe_xO_y catalysts	12, 87, 183–185
	Detrimental effect of Cl^- on catalyst activity	139
	PH_3 ligand and complexes in catalyst preparation	160, 190, 191
Catalysis	Active species on ZrO_2 and TiO_2 are OH and O_2^-	141, 160, 162
	H_2 and water are beneficial for CO oxidation on Au	135, 146, 148, 149
	Water promotes $Au/Au+$ active site for CO oxidation	139, 142–144, 154, 156

Table 4. Potential application of the Au, Pd and Pt catalysts in smoke

Smoke application of the catalysts	Supporting references
Advantages	
Usually Pd is more poison-resistant than Pt; and Co or Mo make this resistance even better; examples of transition metal catalysts for smoke	37–39, 192
Addition of Fe promotes the Pd, Pt and Au for work in the presence of H_2	77, 78, 152
Synergism in binary oxide support, e.g., CeO_2+PdO, increases the initial oxygen mobility, which is beneficial for puffing regime	43, 44
Oscillations of the CO oxidation rate on Pd and Au catalysts may help to expend the catalysis beyond a 2-s puff by first collecting CO and then oxidizing it	128, 154
The amount of "subsurface" oxygen may be enough for oxidation of one-puff CO	81–83
Molecular sieves (zeolites, clays), along with the "ship-in-bottle" technique, may help to improve selectivity in smoke	88, 89, 95
The temperature dependence of catalysis on Au is less steep than on Pd, Pt that can be beneficial for using the Au catalysts in the filter cavity	145–147
CO can be temporarily adsorbed within a puff and released between puffs, or oxidized at higher temperatures that can decrease the necessary amount of adsorbent/catalyst by a factor of 10	7, 14, 15
The Wacker catalysts $PdCl_2+CuCl_2$ on carbon efficiently work in water vapor at room temperature	117–121
Complications	
Establishing the "working" chemisorption equilibrium of CO and O_2 on Pd and Pt catalysts could be too slow for the filter application	10, 54, 60
Oscillations of the CO oxidation rate may cause a slow surface reconstruction to limit the cigarette filter application	54, 60–67
Enabling the "subsurface" to participate in CO oxidation could also be too slow	161, 165
Oxidation rate on Au showed greater order in respect to CO in the presence of H_2 that may complicate its use in smoke, which contains much of reducing compounds along with hydrogen	148, 149
The Wacker catalysts can provide an adverse effect of carbon support on the smoke taste; however, should be substituted with some polymer, e.g., porous styrene divinylbenzene resin	118–122

CONCLUSIONS

Many compounds in smoke are capable of oxidizing (O_2, H_2O, NO_x, SO_2) or hydrogenating (H_2, hydrocarbons) CO on similar catalysts, necessitating the collection and analysis of the world literature data in this area. The present review is limited to the catalytic oxidation of CO with respect to a few problems provided by the nature of tobacco smoke. The complexity of the kinetics of this process in the presence of highly reactive gaseous compounds in smoke, together with the particulate phase would be stressed by the high flow rate of a pulse stream through the catalyst bed and the large concentration gradients that exist inside a burning cigarette.

The state of active oxygen and carbon oxides on Pd and Au catalysts, mechanisms of their activation, role of support, its interaction with the transition metal clusters, role of interface area between them, transfer and storage of oxygen for CO oxidation reaction, catalyst promotors and the methods of preparation of the most active and selective catalysts have been reviewed.

The conclusions about the basic advantages and complications in using the Au, Pd and Pt catalysts in the cigarette filter are listed in Table 4. The results, referred in this Table and the discussed above catalysis approaches, can lead to a relatively easily solution in the part of low-temperature catalyst activity. However, the greatest challenge seems to

be a particular phase-exclusive selectivity that would not contradict with the necessary fast diffusion of gases through the catalyst pores. Much more work is also required to stabilize high activity of the in-air packed catalyst to provide a necessary shelf life for a cigarette.

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