

# Gold, an alternative to platinum group metals in automobile catalytic converters

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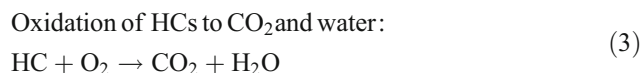
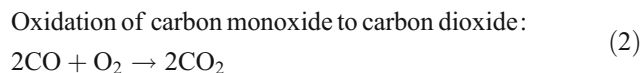
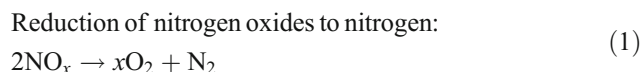
**Abstract** Catalytic converters based on the use of platinum, palladium and rhodium play a major role in the cleaning of automobile emissions. Gold, when dispersed as nano-sized particles, has demonstrated significant activity in the conversion of toxic components, including carbon monoxide, unburnt hydrocarbons and nitrogen oxides, in engine emissions and some advantages over the platinum group metals. Some research outcomes on the application of nano-sized gold for the conversion of these components are reviewed. Several key issues in relation to its performance and applicability in catalytic converters such as low-temperature activity and thermal stability and the possibilities of substituting platinum group metals for automobile emission control with gold are discussed.

**Keywords** Gold nanoparticles · Automotive catalytic converters · Selective reduction of nitrogen oxides · Catalytic oxidation of CO · Catalytic oxidation of hydrocarbons

## Introduction

Incompletely burnt hydrocarbons (HCs), CO and nitrogen oxides (NO<sub>x</sub>; including NO and NO<sub>2</sub>) produced by gasoline and diesel internal combustion engine vehicles are major air pollutants in cities [1]. To comply with current environmental protection legislation, highly efficient catalysts for the complete elimination of these compounds are needed

[1]. Since 1981, three-way catalysts (TWCs) have been used in vehicle emission control in many countries. Such catalytic converters have three simultaneous tasks [2]:



For the cleaning of exhaust from diesel engines, particulate matter, especially carbonaceous particulates, also need to be considered.

Commercial catalytic converters consist of three main components [3]:

1. The core, or substrate, which has a large surface area to support the catalyst and therefore is often called a catalyst support.
2. The washcoat, a very thin layer of paint or sealer on the catalyst support, is used to increase the core surface area by making it rougher and more irregular.
3. The catalyst itself. This is the key element in a catalytic converter and is composed most often of precious metals, i.e. platinum group metals (PGMs) including Pt, Pd and Rh [3]. Cerium, iron, manganese and nickel are also used, but each has its own limitations [3].

The annual global supply of Pt is only about 210 t [4]. The global Pt consumption has been doubled in the last decade, and production of automotive catalysts is the

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biggest consumer of it, accounting for over 50% of the total Pt demand [5]. The annual world production of Rh is only 7 to 8 t [6]. The rarity of these metals imposes a requirement for their sustainable consumption and eventual replacement with less scarce metals [7]. Au is more readily available and has a lower market price than Pt and Rh [8]. As a consequence, there has been an increasing interest in the application of Au in automobile emission control since it has demonstrated excellent catalytic activity when dispersed as fine particles [9, 10].

Apart from considerations regarding the availability and cost of PGMs, some other essential requirements for TWCs must be taken into account. First of all, as lean-burn engines (fuel burning in excess of air) are becoming more popular for economic reasons, simultaneous conversion of  $\text{NO}_x$ , CO and HCs under oxidising conditions with conventional TWCs becomes difficult without using complicated technology [11]. Secondly, as the low-temperature activity of TWCs is very limited, “cold-start” problems are likely to be encountered [12]. This review discusses the catalytic applications of nano-sized Au in the conversion of  $\text{NO}_x$ , CO and HCs reported in literature and the feasibility of substituting PGMs in automotive catalytic converters with Au. Some important considerations in the application of a nano-sized Au catalyst for emission control, including its low-temperature activity and thermal stability, and possible approaches towards overcoming its inherent limitations are highlighted.

### Catalytic conversion of pollutants in automobile emissions using Au nanoparticles

It has long been believed that gold is too inert to be useful as a catalyst [13]. Nevertheless, in the late 1980s, Haruta et al. [14] reported that a supported gold catalyst was able to catalyse the oxidation of CO to  $\text{CO}_2$  even at  $-70^\circ\text{C}$ . The catalyst they prepared consisted of gold dispersed as nanoparticles on a support, and the high catalytic activity was attributed to the small particle size of Au [14]. Compared to their bulk counterparts, gold nanoparticles (GNPs) often exhibit outstanding catalytic properties resulting from their nanometer size, which gives them increased surface-to-volume ratios and chemical potentials [15]. Following the pioneering study of Haruta, there has been significant research undertaken, and encouraging results have been reported on the application of GNPs to the removal of toxic components from automotive emissions.

There are two major concerns associated with the use of GNP-based catalysts for automobile emission control. On one hand, the cold-start temperature of an engine is insufficient to achieve a high catalytic efficiency for the

conversion of pollutants [16]. On the other hand, the normal temperature of the exhaust after the start-up period is too high for GNPs' stability [17]. Consequently, a large number of studies have focussed on the improvement of the low-temperature activity and thermal stability of GNPs catalysts. Numerous studies have shown that GNP catalysts can remove CO, HCs and  $\text{NO}_x$  simultaneously under proper conditions, and this is illustrated with representative literature results.

### Selective catalytic reduction of $\text{NO}_x$ with hydrocarbons and CO

TWCs used in modern cars can completely convert CO, HCs and  $\text{NO}_x$  emitted from traditional stoichiometric gasoline engines [18]. However, in lean-burn engines, particularly diesels that can provide better fuel economy, direct reduction of  $\text{NO}_x$  under lean conditions is practically impossible, although the oxidation of CO and HCs is fairly straightforward [19]. Control of  $\text{NO}_x$  from lean-burn engines demands an additional approach which may entail the use of a  $\text{NO}_x$ -storage catalyst (NSC) with periodic reductive regeneration, or selective catalytic reduction with ammonia ( $\text{NH}_3$ -SCR) or hydrocarbons (HC-SCR) [19].

NSC is based on periodic adsorption and subsequent reduction of  $\text{NO}_x$  [20]. The catalysts in such applications contain a precious metal such as Pt which promotes the oxidation of NO to  $\text{NO}_2$ . The resulting  $\text{NO}_2$  is then stored onto basic adsorbents, e.g.  $\text{Al}_2\text{O}_3$  and BaO. When the storage capacity is reached, rich exhaust conditions are established momentarily by engine management systems. As a result,  $\text{NO}_2$  desorbs from the adsorbent and is reduced by  $\text{H}_2$ , CO and HCs present in the exhaust gas [20]. However, a serious constraint of the NSC technique arises from the susceptibility of the basic adsorbents to sulphur poisoning [20].

In  $\text{NH}_3$ -SCR,  $\text{NO}_x$  are selectively reduced by ammonia to nitrogen over conventional TWCs [21] or  $\text{TiO}_2$  supported  $\text{V}_2\text{O}_5/\text{WO}_3$  catalysts [22]. The required ammonia can be produced *on board* by decomposition of urea. Pt-based catalysts are not effective for this purpose at moderate and high temperatures [21]. Also, discharge of nitric acid is another disadvantage of this process [21].

Under actual diesel exhaust conditions, only moderate  $\text{NO}_x$  conversion can be obtained with platinum catalysts through the HC-SCR approach unless high ratios of HCs to  $\text{NO}_x$  are used. However, in this case, the process will become uneconomic because of the amount of HCs consumed [19]. Also, the comparatively low temperature of the diesel exhaust, which is usually in the range  $100$ – $400^\circ\text{C}$ , makes the reduction of  $\text{NO}_x$  very difficult because of the low activities of conventional catalysts below  $200^\circ\text{C}$

[23]. Obviously, the most realistic and economic way to eliminate  $\text{NO}_x$  is to reduce them to  $\text{N}_2$  using the native HCs, CO or  $\text{H}_2$  in the exhaust gas under lean conditions. A variety of materials have been studied for their ability to catalyse these processes, and these include various kinds of zeolites, metal oxides and supported noble metal catalysts. Cu-ZSM-5, a copper ion-exchanged zeolite, has been reported to be a much more efficient catalyst for the elimination of NO than the earlier known catalysts for the catalytic reduction of this gas [24]. However, its activity decreases sharply with a decrease in the NO concentration, and it suffers from severe deactivation in the presence of oxygen or sulphur oxides [24]. In another study, it was found that Ga-ZSM-5 and In-ZSM-5 catalysts were highly active and selective for NO reduction by  $\text{CH}_4$ . It was shown that Ga-ZSM-5 was strongly inhibited by moisture, while In-ZSM-5 was fairly active even in the presence of 10% moisture [25]. In fact, most of the catalysts reported for this purpose so far are appreciably deactivated by moisture. Metal oxide catalysts show particular loss of NO reduction activity in the presence of moisture [26]. For practical applications to lean-burn exhausts, a catalyst should be capable of operating under the following conditions: an excess of  $\text{O}_2$  in the range of 2% to 10% (v/v), water vapour in the range from 10% to 15% (v/v), large hourly space velocities (the rate of exhaust gas fed per unit volume of catalyst) of greater than  $1 \times 10^5 \text{ h}^{-1}$  and a wide temperature range of 100–750°C [26].

The reactivity of Pt supported on a stable dealuminated Y zeolite for the selective catalytic reduction of NO by HCs has been investigated, but the reduction efficiency for NO was only 20–40% [27].  $\text{NO}_2$  was formed under the conditions studied, and it was preferentially reduced back to NO in the presence of the HCs [27]. The HC-SCR of lean  $\text{NO}_x$  at low temperatures below 200°C was remarkably improved using the Pt catalyst supported on mesoporous silica (Pt/MPS) [23]. These results were achieved with a stoichiometric amount of C6–C16 HCs over a wide temperature range from 170°C to 400°C; however, pulse injection of diesel fuel into the exhaust was found to be necessary in some practical applications [23].

The reaction kinetics of the reduction of NO with propene over Pt/MCM-41 (Pt-loaded MCM-41 zeolite) has been investigated in the temperature range from 150°C to 500°C [28].  $\text{O}_2$  exhibited a significant influence on the reduction. Small amounts of  $\text{O}_2$  (less than 0.4%) promoted the reduction whereas at higher  $\text{O}_2$  concentrations, the optimal NO conversion decreased substantially [28].  $\text{O}_2$  also reduced the  $\text{N}_2$  selectivity of the  $\text{NO}_x$  reduction, and an increase of space velocity was also found to have an adverse impact on the reduction efficiency [28].

The catalytic performance of Pt and Rh catalysts for the reduction of NO by propene in the presence of excess  $\text{O}_2$

has been investigated over catalysts supported on six different metal oxide carriers ( $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , yttria-stabilised zirconia,  $\text{ZrO}_2$  and  $\text{W}^{6+}$ -doped  $\text{TiO}_2$ ) [29]. It was found that the nature of the dispersed metal affects strongly the maximum NO conversion efficiency and the selectivity towards  $\text{N}_2$ . For a given support, Pt catalysts are always more active for both NO reduction and propene oxidation but are much less selective towards the formation of  $\text{N}_2$  compared to Rh catalysts. Rh catalysts are capable of selectively reducing NO, but their activity is suppressed by increasing the  $\text{O}_2$  feed concentration, possibly due to the formation of less reactive Rh oxides. The overall conversion efficiency of NO is low, and the  $\text{N}_2$  selectivity is unsatisfactory [29].

Dispersed Au catalysts have been studied for this purpose in recent years. Au supported on several metal oxides has been prepared with high dispersion by deposition–precipitation and co-precipitation methods [26]. These catalysts are active for the reduction of NO with  $\text{C}_3\text{H}_6$  in the presence of  $\text{O}_2$  and moisture [26]. The reaction temperature required for the reduction process varied depending on the type of the metal oxide support and increased in the order of  $\alpha\text{-Fe}_2\text{O}_3 \sim \text{ZnO} < \text{MgO} \sim \text{TiO}_2 < \text{Al}_2\text{O}_3$ . The highest conversion to  $\text{N}_2$  (about 70%) at 427°C was obtained over an Au/ $\text{Al}_2\text{O}_3$  catalyst with a gold loading of 0.1–0.2% (w/w). The conversion of NO to  $\text{N}_2$  over Au/ $\text{Al}_2\text{O}_3$  was slightly increased by the presence of water.  $\text{O}_2$  enhanced the conversion of NO. Taking into account that  $\text{NO}_2$  rather than NO reacted with  $\text{C}_3\text{H}_6$  at lower temperatures, it was suggested that the NO reduction could take place through the oxidation of NO to  $\text{NO}_2$  and the subsequent reaction of  $\text{NO}_2$  with  $\text{C}_3\text{H}_6$  [26]. In order to improve the catalytic activity of Au/ $\text{Al}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$ , which catalyses the NO oxidation to  $\text{NO}_2$ , was combined with Au/ $\text{Al}_2\text{O}_3$  through mechanical mixing [30]. The mixture was markedly active for the reduction of NO with HCs including ethene, ethane, propene, propane and methane in the presence of  $\text{O}_2$  and moisture at temperatures of 250°C to 500°C [30]. The performance of this catalyst is comparable to that of a Pt-loaded MFI zeolite at low temperatures, and it is considered as one of the most promising catalysts for practical emission control of lean-burn gasoline and diesel engines [30].

The effect of the gold precursor and reaction conditions on the catalytic activity of gold–alumina catalysts prepared by the sol–gel process was studied in detail by Seker and Gulari [31]. Gold catalysts prepared by the sol–gel method were found to be the most active catalysts reported in the literature with the Au/ $\text{Al}_2\text{O}_3$  catalyst showing the highest activity. Increasing the feed oxygen concentration showed many beneficial effects on catalytic activity and also resulted in the broadening of the catalyst's temperature window of activity. Interestingly, however, the  $\text{N}_2$  selectivity of the catalyst was

strongly dependent on the amount of water in the feed. The 100% N<sub>2</sub> selectivity at peak conversion, obtained under dry reaction conditions, decreased to 58% when there was only 2% water in the feed [31].

The reduction of NO by propene in the presence of excess O<sub>2</sub> over mechanical mixtures of Au/Al<sub>2</sub>O<sub>3</sub> with a bulk oxide has been investigated [32]. When mixed with Au/Al<sub>2</sub>O<sub>3</sub>, MnO<sub>x</sub> and CoO<sub>x</sub> and, to a much greater extent, CeO<sub>2</sub>, act synergistically with this catalyst, thus greatly enhancing its SCR performance [32]. In another study on HC-SCR of NO under diesel engine exhaust conditions, it was shown that an Au/Al<sub>2</sub>O<sub>3</sub> catalyst exhibited high activity and 100% selectivity towards the formation of N<sub>2</sub> in the temperature range of 300–350°C. At higher temperature, the NO conversion decreased due to competitive oxidation of the reductants. Addition of H<sub>2</sub> to the feed enhanced the catalytic activity for the NO conversion to N<sub>2</sub> [33].

A common problem with supported Au catalysts for the HC-SCR of NO<sub>x</sub> is that the maximum efficiency can only be reached when the temperature is above 300°C [30–33]. Therefore, improvement in their low-temperature performance remains a major challenge. It is noteworthy that other reductive components in the exhaust gas, such as CO and H<sub>2</sub>, are also capable of reducing NO<sub>x</sub> over supported Au catalysts. In one study, it was shown that under O<sub>2</sub>-free conditions, Au-based catalysts easily outperform those based on PGMs for the reduction of NO by CO. Considerable activity was observed even at 27°C with complete conversion of NO to N<sub>2</sub> occurring at about 150°C [34]. However, reduction of NO to N<sub>2</sub> under more efficient lean-burn conditions is more difficult [34]. The reduction of NO<sub>x</sub> by CO was also studied over Au catalysts supported on CeO<sub>2</sub> and CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, and the catalysts exhibited a high and stable activity and 100% selectivity towards the formation of N<sub>2</sub> at 200°C [35].

### Low-temperature oxidation of CO

Considerable amounts of pollutants in automobile emissions are generated within the first 5 min after starting the engine when the temperature of the catalytic converter is not high enough for efficient conversion to occur [16, 36]. The conversion efficiency of commercial catalytic converters declines very steeply at temperatures below 350°C and is practically zero during the starting and warming-up periods [37]. These cold-start emissions impose a serious pollution problem and require the identification of new catalysts that can operate at low temperatures to achieve their abatement [38].

Au-based catalysts have been shown to have the best low-temperature activity for CO oxidation of all catalysts [39], and at low temperatures, their activity exceeds that of

catalysts based on PGMs by about a factor of 5 [40, 41]. In most of these studies, the GNPs, which are generally between 2 and 10 nm in size, have been supported on various metal oxides. By loading Au on CeO<sub>2</sub>, CO was completely oxidised at 150°C [42]. A Au supported on FeO<sub>x</sub>/SiO<sub>2</sub> catalyst, prepared by a precipitation–deposition technique, achieved complete conversion of CO at 77°C [43]. GNPs supported on sodium titanate nanotubes produced a complete conversion of CO at –43°C [44]. In another study, Au was deposited onto a MnO<sub>x</sub> support by deposition–precipitation with urea. The activity of these Au/MnO<sub>x</sub> catalysts for CO oxidation strongly depended on the nature of the manganese oxide support and followed the order of Mn<sub>2</sub>O<sub>3</sub>>MnO<sub>2</sub>>Mn<sub>3</sub>O<sub>4</sub>. The Au/Mn<sub>2</sub>O<sub>3</sub> catalysts exhibited the highest activity, resulting in complete CO oxidation at –23°C [45].

It has been pointed out that the performance of a gold catalyst is determined by its particle size and the support material [46]. There is some disagreement on the catalytic performance achieved using different support materials, but the broad consensus is that reducible oxides of variable stoichiometry such as MnO<sub>x</sub>, TiO<sub>x</sub>, FeO<sub>x</sub> and CoO<sub>x</sub> contribute significantly to the catalytic activity of Au in the oxidation of CO, whereas oxides of fixed stoichiometry, such as Al<sub>2</sub>O<sub>3</sub>, do not [47]. Supported Au catalysts prepared on oxides of fixed stoichiometry (e.g. TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO) have also shown that reducible oxides (e.g. CeO<sub>2</sub>, TiO<sub>2</sub> and ZrO<sub>2</sub>) enhance the catalytic activity [48]. Au on Fe<sub>2</sub>O<sub>3</sub> is active for this reaction at temperatures as low as –76°C [14], a fact which alerted the wider scientific community to the unusual properties of GNPs. Excellent and sustained activity was also obtained when catalytic GNPs were combined with the already catalytic MnO<sub>x</sub>-CuO<sub>y</sub> mixtures [49].

It was also shown that the catalyst preparation technique has a significant impact on the performance of GNPs catalysts, and hence, research has focussed on the use of various techniques to prepare supported GNPs such as co-precipitation [41], chemical vapour deposition [50], impregnation [51], grafting [52], photo-deposition [53], physical mixing [54], low-energy cluster beam deposition [55], adsorption of Au colloids on metal oxides [56] and ion-exchange [57]. In general, GNP catalysts prepared with the deposition–precipitation technique exhibited the highest activity [41].

A successful application requires a catalyst not only to show high catalytic activity but also good thermal stability against sintering. In this respect, GNPs catalysts often fail because they lose much of their activity after calcination at high temperature [17]. It is generally recognized that the deactivation of the catalyst is caused by the growth of GNPs and sintering of the support [17]. Therefore, stabilisation of GNPs remains a challenge in developing

Au catalysts. It has been demonstrated that the support material and the preparation approach play a major role in determining the thermal stability of Au catalysts [17]. A  $\text{La}_2\text{O}_3$ -doped  $\text{Fe}_2\text{O}_3$  support was prepared by co-precipitation, and Au was loaded by deposition–precipitation. The thermal stability of the Au catalyst was enhanced considerably by  $\text{La}_2\text{O}_3$  doping. Even after calcination at  $500^\circ\text{C}$  for 12 h, a  $\text{La}_2\text{O}_3$ -doped catalyst could convert 90% of CO at  $28.9^\circ\text{C}$ , whereas a catalyst without  $\text{La}_2\text{O}_3$  achieved the same conversion efficiency at  $43.5^\circ\text{C}$  [17].

To overcome the low activity problem of Au catalysts prepared by impregnation, a two-step procedure was developed [58]. The resulting GNPs supported on  $\text{Al}_2\text{O}_3$  had an average size of 2.4 nm. The reactivity for CO oxidation at room temperature was comparable to that for catalysts prepared by deposition–precipitation. These catalysts were stable to hydrothermal sintering, with average particle size around 4 nm after sintering in 10 mol%  $\text{H}_2\text{O}$  at  $600^\circ\text{C}$  for 100 h [58]. The activity of  $\text{Au}/\text{Al}_2\text{O}_3$  and  $\text{Au}/\text{MO}_x/\text{Al}_2\text{O}_3$  ( $\text{M}=\text{Cr, Mn, Fe, Co, Ni, Cu}$  and  $\text{Zn}$ ) was studied for low-temperature oxidation of CO and  $\text{CH}_4$  [59]. Generally, addition of  $\text{MO}_x$  to  $\text{Au}/\text{Al}_2\text{O}_3$  has been found to stabilise the small Au particles present initially on the support in heat treatments involving temperatures of up to  $700^\circ\text{C}$ . Unfortunately, the activity of the catalysts for low-temperature oxidation of  $\text{CH}_4$  was very low [59].

The oxidation behaviour of CO in the presence of HCs can be quite different. In general, CO oxidation is less efficient in the presence of HCs at low temperatures. For example, it was observed that the presence of acetylene strongly inhibited the oxidation of CO, but CO was readily oxidised once acetylene was completely oxidised [57]. It was assumed that this inhibition was caused by the favoured adsorption of  $\text{C}_2\text{H}_2$  over CO on the catalyst [57]. Therefore, low-temperature oxidation of HCs is essential for the conversion of CO. The influence of metal oxides (e.g.  $\text{CeO}_2$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$ ) as a support for GNPs on the activity of the corresponding catalysts for the oxidation of CO and  $\text{C}_2\text{H}_2$  was investigated. By using  $\text{Au}/\text{CeO}_2$ , complete oxidation of CO and  $\text{C}_2\text{H}_2$  in their mixture was achieved at  $200^\circ\text{C}$  and  $180^\circ\text{C}$ , respectively, whereas much higher temperatures were needed for their complete oxidation with  $\text{Au}/\text{TiO}_2$  or  $\text{Au}/\text{ZrO}_2$  catalysts [60]. This clearly indicated the possibility of low-temperature oxidation of both CO and HCs by using proper support materials. It is noteworthy that under lean-burn conditions, the emission of CO is minimal, implying that more attention needs to be paid to the oxidation of HCs [61].

### Catalytic oxidation of hydrocarbons

There are two classes of unburnt hydrocarbons in exhaust gas, namely small molecules that produce intermediate

combustion products resulting from the breaking of the C–C chain and larger molecules that are formed by pyro-synthesis in hot, fuel-rich zones (e.g. benzene, toluene, xylene and various polycyclic aromatic hydrocarbons). Small molecules are usually difficult to oxidise and are the main products of incomplete combustion [57].

GNPs have displayed significant activity in the combustion of these organic compounds [62]. High-surface area  $\text{CeO}_2$  prepared by precipitation and calcination at low temperatures showed high-surface oxygen reducibility and high activity for benzene oxidation at low temperature [63]. The performance of Au supported on high-surface area  $\text{CeO}_2$  for the oxidation of a mixture of CO and benzene is superior to that of Au supported on  $\text{TiO}_2$ , despite the excellent activity of the latter for low-temperature CO oxidation. At  $250^\circ\text{C}$ , both CO and benzene conversion were greater than 90% on  $\text{CeO}_2$  supported GNPs. Moisture is beneficial for the oxidation activity of  $\text{CeO}_2$ -supported Au catalysts, which further improves their suitability for automobile emission control [63]. Another study showed that loading of GNPs onto a  $\text{FeO}_x/\text{TiO}_2$  support significantly improved the  $\text{CO}_2$  selectivity (with  $\text{CO}_2$  as the final oxidation product) in the oxidation of toluene [64]. A similar effect was observed for the oxidation of propene [65]. A study on the oxidation of CO, hexane and benzene by air with Au supported on  $\text{CeO}_2$  and  $\text{ZrO}_2$  showed that 100% conversion of hexane was obtained with  $\text{Au}/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$  at  $300^\circ\text{C}$  and that full conversion of benzene was reached at  $250^\circ\text{C}$  with  $\text{Au}/\text{CeO}_2$  [66]. These HCs inhibited the oxidation of CO, whereas CO promoted the oxidation of the HCs [66].

The performance of unpromoted and promoted with  $\text{MO}_x$  ( $\text{M}$ : alkali, alkaline earth, transition metals or cerium)  $\text{Au}/\text{Al}_2\text{O}_3$  catalysts has been studied for combustion of saturated hydrocarbons including methane and propane [67]. Temperatures above  $400^\circ\text{C}$  are required to oxidise  $\text{CH}_4$ , compared to temperatures of only above  $250^\circ\text{C}$  for  $\text{C}_3\text{H}_8$ . The addition of various  $\text{MO}_x$  to  $\text{Au}/\text{Al}_2\text{O}_3$  improved the catalytic activity in both methane and propane oxidation. For methane oxidation, the most efficient promoters of the catalytic activity of  $\text{Au}/\text{Al}_2\text{O}_3$  were found to be  $\text{FeO}_x$  and  $\text{MnO}_x$ . These results and the results obtained by other authors suggest that the role of the alkali or alkaline earth metal oxides is related to the stabilisation of the GNPs, whereas transition metal oxides and  $\text{CeO}_2$  may be involved in oxygen activation [67].

The research outlined above has shown that complete oxidation of hydrocarbons requires higher temperatures than that for CO and  $\text{NO}_x$ . In general, unsaturated hydrocarbons are easier to be oxidised than saturated hydrocarbons. For instance, by using an alumina supported Au catalyst, complete oxidation of ethylene occurs at  $300^\circ\text{C}$ , while complete oxidation of ethane can only be achieved at

700°C [38, 57]. Of the saturated hydrocarbons, methane is the most resistant to complete oxidation [68]. Usually, a temperature of at least 500°C is needed for its complete oxidation [1, 67]. However, some promising results have been reported on the oxidation of saturated hydrocarbons at lower temperatures. In one study, Au catalysts on oxide supports for the total oxidation of methane, ethane and propane were prepared by co-precipitation with  $\text{CoO}_x$ ,  $\text{MnO}_x$ ,  $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CeO}_2$ ; deposition–precipitation with  $\text{TiO}_2$  or impregnation with  $\text{CoO}_x$  and  $\text{MnO}_x$  [38]. Many of the oxide supports act as active alkane activation catalysts at high temperatures (e.g.  $\text{MnO}_x$  and  $\text{CoO}_x$ ). The addition of Au to these active materials for alkane combustion has led to a substantial increase in the catalytic activity in all cases investigated [38]. Au/ $\text{CoO}_x$  was identified as the most effective catalyst for alkane oxidation and was found to retain a constant high activity over a 48-hour test period. Interestingly, no correlation between alkane oxidation and CO oxidation was established in these studies, indicating that different mechanisms of oxygen activation and/or different active sites were involved [38]. It was shown that 95% of  $\text{CH}_4$  was oxidised at 300°C which was much better than with the other catalysts hitherto reported. Oxidation of higher alkanes is more easily achieved than that of  $\text{CH}_4$ . For example,  $\text{C}_2\text{H}_6$  and  $\text{C}_3\text{H}_8$  were completely oxidised at 250°C and 200°C, respectively, using Au/ $\text{CoO}_x$  [38]. These results imply that complete combustion of HCs in exhaust gases could be readily achieved with the aid of a proper Au catalyst once the temperature of the catalyst has reached a suitable level (~300°C).

### The use of supported gold alloys for catalytic conversion of engine emissions

While GNP catalysts have displayed several advantages over conventional TWCs, the use of gold alloys can be expected to further improve automobile emission control. The structural and catalytic properties of  $\text{SiO}_2$ - and  $\text{TiO}_2$ -supported Pt–Au bimetallic catalysts prepared by co-impregnation were compared with catalysts of similar composition, synthesized from a  $\text{Pt}_2\text{Au}_4(\text{C}\equiv\text{CBut})_8$  cluster precursor [69]. The smallest metal particles were formed when the bimetallic cluster was used as a precursor and  $\text{TiO}_2$  as the support. The cluster-derived  $\text{Pt}_2\text{Au}_4/\text{TiO}_2$  catalysts exhibited low-temperature CO oxidation activity [69].

Mixed-metal Au/Pt catalysts were also prepared by means of polyamidoamine dendrimers [70]. Removal of the organic dendrimer by heating at 300°C under an oxygen stream, followed by treatment at 300°C under flowing hydrogen, gave intimately mixed Au/Pt catalysts with metal

particle sizes of <4 nm. The stabilised nanoparticles were then adsorbed onto oxide supports (e.g.  $\text{SiO}_2$  or  $\text{TiO}_2$ ) and thermally activated to produce supported mixed-metal catalysts. The resulting  $\text{Au}_{16}\text{Pt}_{16}/\text{SiO}_2$  catalyst had a light-off temperature of ~30°C, whereas the equivalent  $\text{Au}_{32}$  catalyst lighted off at ~130°C and the equivalent  $\text{Pt}_{32}$  catalyst at ~80°C [70]. The catalytic activity of this catalyst was investigated in CO oxidation, toluene hydrogenation and the reduction of NO by propene.

Low-temperature CO oxidation over a Pd/Au nanoalloy catalysts supported on silica was studied. A mixture of Pd (90%)/Au (10%) (72.5%) and Pd (31%)/Au (69%) (27.5%) was found to be remarkably active at 27°C while at the same time this catalyst was more stable than a pure Au catalyst [71].

A computational study of the catalytic activity of Pd atoms incorporated into Au(111) facet showed that the Pd monomer, dimer and trimer exhibited high activity for the oxidation of CO according to Eq. 4 which proceeded via an association mechanism in which the intermediate OOCO was formed [72].



Significantly, a low-energy barrier (0.19–0.32 eV) was found for the formation of OOCO. The atomic oxygen produced by this reaction (Eq. 4) was removed by another CO on a Pd-decorated Au cluster via Langmuir–Hinshelwood or Eley–Rideal mechanism. This study indicated that Pd ensembles incorporated into Au(111) facet markedly improved the catalytic activity of the gold nanoclusters [72]. These results indicate improved catalytic performance, and some examples may also show a decrease in the cost of the alloyed catalysts relative to pure Au catalysts.

### A practical example: a GNPs catalyst for the cleanup of diesel engine emissions

Although there are numerous publications on the application of GNPs in the elimination of individual pollutants or some of their bi-component mixtures emitted from automotive engines, reports on the elimination of mixtures of  $\text{NO}_x$ , CO and HCs are scarce. A major obstacle to achieving this goal is the lower thermal stability of GNPs which is dictated by the low melting point of Au of 1,068°C, compared to 1,769°C for Pt. It is assumed that this probably means that GNPs may not be suitable for use in TWCs that operate at high temperatures (>600°C) [73].

Nevertheless, Nanostellar Inc., a USA-based company, has announced a diesel emissions cleaning technology with the introduction of Au as an oxidation catalyst [73]. The gold-based catalyst, NS Gold™, is now in production with one of the four largest European diesel car manufacturers

[74]. It is reported that this catalyst enables manufacturers of light- and heavy-duty diesel engines to reduce noxious emissions by as much as 40% more than with Pt catalysts at the same cost [75, 76]. When compared to Pt–Pd catalysts, the use of NS Gold™ can potentially increase HCs oxidation activity by 15–20% at equal precious metal cost. With a tri-metal formulation of Au, Pt and Pd, NS Gold™ allows the proportions of each metal to be adjusted to meet engine-specific performance targets and stabilise the overall cost of diesel catalysts, despite fluctuations in the price of precious metals [75, 76]. It is reported that NS Gold™ is potentially suitable for treating all lean-burn exhausts. Applications include, but are not limited to, treating particulates and hydrocarbons in soot filters, stationary-source volatile organic compound emissions and ammonia slip in SCR systems [75, 76].

### Future directions and challenges

As mentioned above, major concerns in the application of Au-based catalysts in automobile emission control include their low-temperature activity and thermal stability. These may be the main challenges and focuses in any future study. Diesel engine emissions have lower temperatures than those produced by petrol engines [77]. This could be the main reason that GNPs are more applicable to diesel engine emissions. Practical applications of GNPs catalyst in the treatment of exhausts from gasoline engines have not yet been reported. However, such catalysts have some unique properties compared to their PGM-based counterparts. PGM-based TWCs lack low-temperature start-up activity and exhibit problems during prolonged idling, resulting in the catalyst monolith not operating until a light-off temperature of about 300°C (at this temperature a catalytic converter achieves a 50% conversion) required for the oxidation of HCs. GNPs catalysts have better low-temperature activity [73]. In particular, they have shown activity for the reduction of NO<sub>x</sub> in lean-burn exhaust at both high and relatively low temperatures, although their low-temperature activity remains to be improved [30].

To compensate for the unsatisfied low-temperature activity of catalytic converters, several potential solutions for the cold-start problem have been proposed. One strategy is based on quickly bringing the catalyst to working temperature, including close-coupled or manifold mounted catalysts [75], electrically heated catalysts [78], exhaust gas ignition (EGI) [79, 80] and combustion heated catalysts [81]. A variety of heat storage devices have also been suggested, all of which work on the principle of retaining heat from the time of the last car's shutdown until the following cold start [82]. Another strategy is to trap hydrocarbons during cold start for release after the catalyst

has reached operating temperature [79, 83]. In general, all of these cold-start solutions benefit further through the application of improved catalyst technology (so-called low-light-off catalysts) which allows the catalyst to operate at lower temperatures and with leaner starting engines (with the exception of EGI). These engines provide an exhaust with less unburnt HCs and more oxygen at start-up [36].

A practical strategy to rapidly elevate the catalyst's temperature in the start-up period is to oxidise CO quickly and heat the catalyst using the heat released from this reaction [36]. As mentioned above, Au catalysts have excellent low-temperature activity in the oxidation of CO. However, some HCs are capable of strongly inhibiting this oxidation process [57]. A novel technology combining a HCs trapping system and ambient temperature CO oxidation has shown an excellent performance in the cold-start engine emission treatment using a Pd–Pt catalyst [36]. It can be assumed that such a combined technology is also feasible for Au catalytic systems. Further improvement of the low-temperature activity of Au catalysts for the reduction of NO<sub>x</sub> and the oxidation of HCs may be the most economic solution to this issue.

There are also reports on the improvement of the thermal stability of GNPs based on different approaches. An Au/SiO<sub>2</sub> catalyst was prepared by growing 2.5 nm GNPs on a fused silica support using the physical vapour deposition technique of magnetron sputtering. The resulting catalyst was thermally stable up to at least 500°C when annealed in an oxygen containing environment [84]. This high thermal stability was attributed to the absence of residual impurities, ensured by the halide-free production method and a strong bond (about 3 eV per bond, estimated by density functional theory calculations) between gold and defects at the silica surface. The Au/SiO<sub>2</sub> catalyst has been found to be less active for CO oxidation than Au/TiO<sub>2</sub> catalysts. However, it can be regenerated far more easily, thus allowing full recovery of its activity after deactivation [84]. The addition of different metal oxides (MO<sub>x</sub>) to Au/Al<sub>2</sub>O<sub>3</sub> catalysts, used for the total oxidation of methane, has shown that MO<sub>x</sub> stabilise GNPs on Al<sub>2</sub>O<sub>3</sub> and the resulting catalysts are thermally resistant up to 700°C [59]. Improvement in the thermal stability of GNPs-based catalysts has been also achieved by doping with La<sub>2</sub>O<sub>3</sub> [17]. It is evident that further improvement of the overall performance of Au catalysts will be mainly decided by the use of the best support materials [17, 26, 48, 85].

Although the thermal stability of GNPs catalysts seems to be quite limited due to their low Tammann temperature of 395°C, where atomic surface mobility becomes significant [86], a modification of the mechanical manifold for the delivery of the exhaust emission to the catalyst may provide a possible way of optimizing the temperature of the catalyst and its efficiency. For example, direct introduction of the exhaust gas through the catalyst during the start-up

period and leading the exhaust to the catalyst through a cooling manifold after the start-up period may maximize the activity of the catalyst during the start-up period and minimize the high temperature effect on the catalyst's stability afterwards.

Poisoning by sulphur compounds is also a significant concern in catalytic converters. There have been reports on the development of sulphur-resistant catalysts based on supported GNPs [87]. Results show that the developed Au/FeO<sub>x</sub> catalyst can remove CO completely at –22°C and has a high resistance to humidity and sulphur poisoning [87]. The addition of CeO<sub>2</sub> to an Au/Al<sub>2</sub>O<sub>3</sub> catalyst improved the sulphur tolerance for CO oxidation [88]. A support for a catalyst for controlling exhaust emissions which contained a high-surface area  $\gamma$ -alumina with a monomolecular layer of a second oxide (e.g. TiO<sub>2</sub>, CeO<sub>2</sub> or ZrO<sub>2</sub>) was reported [89]. It was claimed that catalysts prepared by using this support displayed outstanding thermal stability and resistance to sulphur poisoning [89]. A method was also described for preparing GNPs supported on CoO<sub>x</sub> which exhibited high resistance to SO<sub>2</sub> and H<sub>2</sub>O and high catalytic activity for the selective oxidation of NO at a relatively low temperature of 120°C [90]. Interestingly, it was found that SO<sub>2</sub> enhanced the catalytic activity of Au/CoO<sub>x</sub> in the oxidation of NO [91]. However, development of catalysts with high sulphur resistance remains a challenge.

In summary, it is well-known that very low amounts of NO<sub>x</sub> are produced during the start-up stage of engines and these oxides can be reduced with HCs after this stage in the presence of excess O<sub>2</sub> and H<sub>2</sub>O when supported GNPs are used. Also, numerous results have shown that GNPs can catalyse the oxidation of HCs below the Tammann temperature of gold. By doping some metal oxides such as La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, MnO<sub>x</sub> and CoO<sub>x</sub>, one can further improve the thermal stability and the catalytic activity of GNPs in the abatement of NO<sub>x</sub>, CO and HCs. In addition, by using combined technologies, such as HCs trapping systems in combination with low-temperature CO oxidation, one can largely overcome the inherent drawbacks of GNPs. Thus, it seems reasonable to assume that GNPs can become a viable substitute for PGMs in the treatment of automobile emissions.

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