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# Low-temperature redox activity in co-precipitated catalysts: a comparison between gold and platinum-group metals

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## Abstract

We have identified two main mechanisms for inducing low-temperature activity in precious metal catalysts: normal-support activation (NSA) and active-phase enhancement (APE). The usual roles of a precious metal and its metal oxide support are reversed in NSA, resulting in highly active sites being created on the metal oxide. This applies when metallic gold is well dispersed within a defect-forming metal oxide (such as $CeO_2$ or even $ZrO_2$), and leads to formation of new sites for CO, NO and alkene conversion (to $CO_2$, $N_2$ and $H_2O$). In APE, established metal oxide catalysts can be deliberately made to operate at lower temperatures, by providing precious metal sites for oxygen activation. An example is iron(III) oxide, where incorporation of palladium leads to substantial lowering of the temperatures for CO oxidation, water-gas shift and oxidative dehydrogenation. Gold does not have the same effect, except for CO oxidation at high metal loading. However, the presence of gold or palladium in a hydroxylated metal oxide can lead to another route to low-temperature oxidation, in which highly reactive peroxide-like intermediates are believed to be formed on exposed metal surfaces. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Co-precipitates; Junction effects; Low-temperature activity; Peroxide intermediate; Precious metals

## 1. Introduction

In heterogeneous catalysis, the most effective catalysts are often comprised of two phases—a metal on a metal oxide support (for total oxidation, three-way catalysis, hydrogenation, dehydrogenation) or a mixed metal oxide (for partial oxidation of hydrocarbons to alkenes and oxygenates, and the ammoxidation of hydrocarbons to nitriles). Two generic theories have emerged to explain why binary materials can be so effective. Frost [1] has rationalised the high activity of some metal/support combinations in terms of a junction effect, arising from transfer of electrons from the support to the Fermi level of the adjacent metal, and giving rise to oxygen vacancies that become the active sites. In the case of mixed metal oxides, Weng and Delmon [2] have argued that one oxide needs to function as an activator and supplier of oxygen, while another needs to adsorb the co-reactant and receive the reactive oxygen species. Both theories are powerful because they can be applied predictively, whereas concepts such as SMSI [3] and the Mars-van Krevelen redox cycle [4] are generally used to explain established observations.

During the past 15 years, the number of known low-temperature heterogeneous catalysts has been steadily rising. In many instances, the active material is comprised of a metallic phase, which is highly dispersed on, or within, a metal oxide. Often the

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low-temperature activity is transitory [5,6], and only occurs after exposure of the catalyst to particular conditions, but it can also be achieved in fresh samples by using a specific composition [7] or preparative method [8]. Among low-temperature catalysts, gold is well represented as a key component [9]. Perhaps surprisingly, very little is known about the mechanisms by which catalytic reactions take place at low temperatures. Instead, most effort has been devoted to characterising the structure of the catalysts, particularly of those containing gold.

## 2. Terminology and reaction conditions

Some of the data presented below were generated during temperature-programmed tests in which the reactant feed was a simulated exhaust gas, which mimicked the type of exhaust produced by a gasoline-fuelled internal combustion engine during start up. The simulated exhaust gas contained 0.43%$H_2$, 0.72%$O_2$, 1.30%CO, 0.067%$CH_4$, 0.0223%$C_3H_8$, 0.0223%$C_3H_6$, 15%$CO_2$, 9.2%$H_2O$, 0.15%NO and 0.002%$SO_2$ (all mol%), with $N_2$ making up the balance. It is described as *net-reducing* because, although it contained both oxidising and reducing species, the latter were present in excess. In other tests, which were carried out under *net-oxidising* conditions, the gas-feed was a simple binary mixture of CO or butene in a large excess of air. In all cases, the precious metal loading in the catalysts used is expressed as a wt.%.

## 3. Normal-support activation

It is well known that low-temperature activity can be induced in Pt-containing three-way catalysts by subjecting them to reducing conditions [5,10,11]. This enhancement in activity arises from a particular interaction between platinum and ceria. It can, however, be deliberately made to occur in a fresh catalyst by including the co-precipitation of Pt–$CeO_2$ (from a $Ce^{III}$ precursor) as a step in the preparative method [12]. The platinum in a highly active 0.9%Pt–$CeO_2$ formulation (Fig. 1), which has been prepared in this way, is almost undetectable on the catalyst surface, but seems to be dispersed as small metallic particles throughout the ceria (Table 1). During the preparation, the $Ce^{III}$ acts as a reducing agent, converting any $Pt^{IV}$ in its immediate vicinity to $Pt^0$, while itself being oxidised to $Ce^{IV}$. The small $Pt^0$ particles formed are left embedded in the $CeO_2$ that is formed.

In effect, co-precipitation leads to the reversal of the normal roles of the metal oxide and the precious metal, and encourages the formation of highly active sites on the phase that normally acts as the support. These sites are ‘triggered’ into activity by the presence of a net-reducing atmosphere (such as that produced

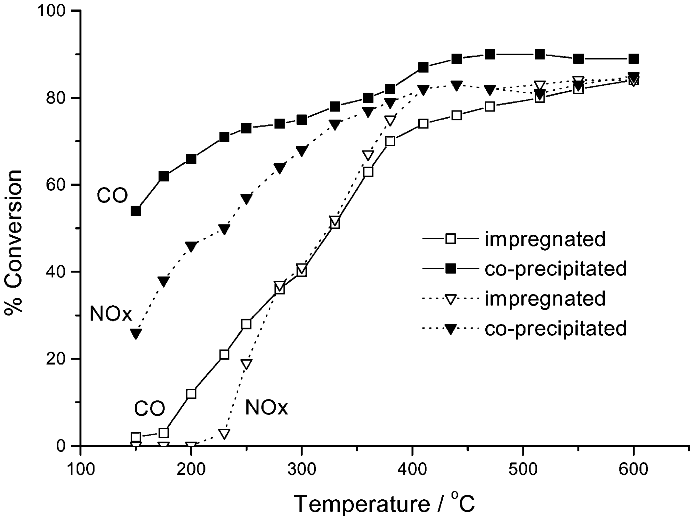

Fig. 1. Redox activity of 0.9%Pt–$CeO_2$ under net-reducing conditions (simulated exhaust gas at 1 l min$^{-1}$ $g_{cat}^{-1}$).

Table 1
Preparation and characterisation of M–$CeO_2$ with low-temperature activity under net-reducing conditions

| | |
|---|---|
| 0.9%Pt–$CeO_2$ | |
| Precursors | Chloroplatinic acid, $Ce(NO_3)_3{\cdot}6H_2O$ |
| Preparation | Aqueous precursors co-added to boiling NaOH; precipitate isolated, washed, dried and calcined (air, 500 °C) |
| Characterisation | CO/M = 0.08; BET surface area = 130 $m^2\,g^{-1}$; STEM: no Pt resolved at $25 \times 10^6$ magnification; EXAFS: 70%$Pt^0$, 30%$Pt^{IV}$, XPS: Pt/Ce = 0.002 |
| 0.9%Au–$CeO_2$ | |
| Precursors | $HAuCl_4$, $Ce(NO_3)_3{\cdot}6H_2O$ |
| Preparation | Aqueous precursors co-added to boiling NaOH; precipitate isolated, washed, dried and calcined (air, 500 °C) |
| Characterisation | CO/M = 0; BET surface area = 125 $m^2\,g^{-1}$; XPS: electron-enriched surface gold (Au $4f_{7/2}$, $E_b$ = 82.8 eV); Au/Ce = 0.003 |

by a gasoline engine during start up), and are particularly effective at catalysing CO oxidation, alkene oxidation and NO reduction. The role reversal, which we describe as normal-support activation (NSA), also occurs when platinum is replaced by gold or palladium. The preparative method using co-precipitation (summarised for gold in Table 1) gives rise to a material in which the metal is again largely invisible, but which possesses similar catalytic activity to the Pt analogue (compare data for co-precipitated catalysts in Figs. 1 and 2).

The way in which the support changes during NSA becomes clear from temperature-programmed reduction (TPR). Normally, unmodified $CeO_2$ reduces in two steps [13], the first of which corresponds to removal of several top layers of anions, and the second to removal of bulk anions to form $Ce_2O_3$. The addition of Pt to $CeO_2$ by impregnation lowers the temperature of the first step, but the same effect is not observed when the platinum is replaced by gold (Table 2). However, when either metal is incorporated by co-precipitation with a $Ce^{3+}$ precursor, the *reducibility* of the ceria surface is dramatically increased. Hydrogen spillover does not seem to be the cause—there are few exposed spillover sites available, and the enhanced reducibility is observed even in the absence of gas-phase hydrogen. The observations seem more consistent with a ‘junction effect’ [1] arising from the contact between the ceria and a metal with high work function. As a result of this

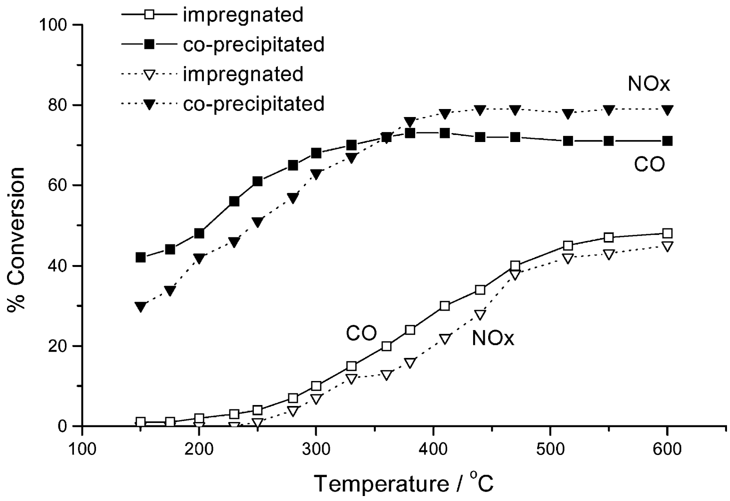

Fig. 2. Redox activity of 0.9%Au–$CeO_2$ under net-reducing conditions (simulated exhaust gas at 1 l $min^{-1}$ $g_{cat}^{-1}$).

Table 2
Reducibility of ceria as measured by temperature-programmed reduction (using $10\%H_2/N_2$)

| Material | Peak temperatures ($H_2$ consumed/mmol $g_{cat}^{-1}$) |
|---|---|
| $CeO_2$ | 450 °C (0.84), 860 °C (0.36) |
| $0.9\%Pt/CeO_2$ (impregnated) | 180 °C (0.85), 800 °C (0.33) |
| $0.9\%Pt–CeO_2$ (co-precipitated) | −5 °C (0.75), 410 °C (0.15), 840 °C (0.31) |
| $0.9\%Au/CeO_2$ (impregnated) | 450 °C (0.85), 880 °C (0.38) |
| $0.9\%Au/CeO_2$ (co-precipitated) | 120 °C (0.83), 810 °C (0.32) |

interaction, the anions at the ceria surface are easily removed during exposure to a net-reducing atmosphere, and the resultant oxygen vacancies become the active sites for CO, NO and alkene conversion.

NSA can also occur when Pt, Pd or Au is co-precipitated with oxides that are inherently much less reducible than ceria. In the case of $ZrO_2$, e.g., the loading of precious metal needs to be relatively high, and a reducing agent (such as sodium formate) needs to be added during the co-precipitation to ensure that highly dispersed metallic particles are formed within the support [12]. TPR of the calcined co-precipitate confirms that the surface of the $ZrO_2$ is easily reduced (at 100 °C) to form oxygen vacancies, consistent with the low-temperature activity observed under a net-reducing simulated exhaust gas (Fig. 3).

## 4. Active-phase enhancement

Co-precipitation of a precious metal and a metal oxide can also lead to the formation of another type of low-temperature catalyst, which functions under net-oxidising conditions (such as those generally used for partial or total oxidation reactions). Although the preparative method is similar to that used for NSA, the precious metal loading generally needs to be higher, to ensure that oxygen-activating sites are exposed at the surface, while the metal oxide needs to be intrinsically active for the desired catalytic reaction. If these conditions are met, the resultant material can show comparable catalytic performance to that of the unmodified metal oxide, but at much lower temperature. We refer to this effect as active-phase enhancement (APE).

Our best examples of APE involve the use of palladium to enhance the low-temperature activity of iron(III) oxide [14] and bismuth molybdate [15] (Table 3). The optimum palladium loading seems to lie between 2 and 10%—at lower loadings, there is insufficient exposed palladium; at higher loadings, the materials behave like supported-Pd catalysts. In both Pd–Fe–O and Pd–Bi–Mo–O, the exposed palladium is initially present mainly as $Pd^{2+}$ ions, which appear to form the active sites for oxygen activation at low temperatures. By maintaining a supply of reactive and selective oxygen species, the presence of palladium allows the metal oxide to function catalytically

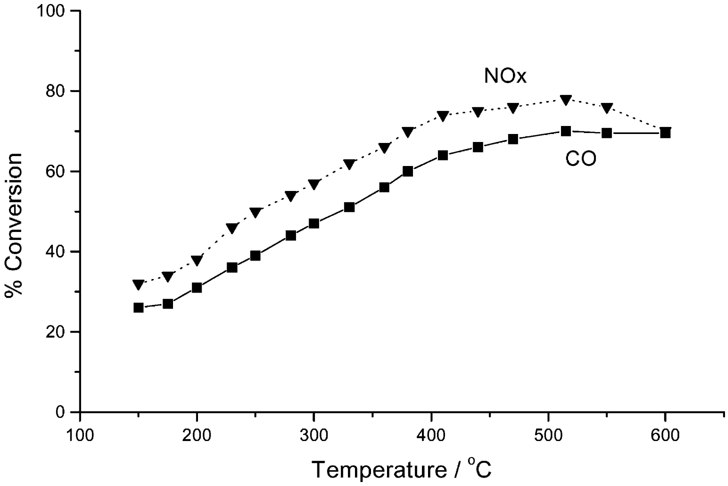

Fig. 3. Redox activity of chemically reduced co-precipitated $4\%Au–ZrO_2$ under net-reducing conditions (simulated exhaust gas at $1\,l\,min^{-1}\,g_{cat}^{-1}$).

Table 3
Preparation and characterisation of Pd–M–O catalysts with catalytic activity at lower temperatures than the parent metal oxides

| | |
|---|---|
| 4%Pd–Fe–O | |
| Precursors | $Pd(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$ |
| Preparation | Aqueous $Na_2CO_3$ added to aqueous mixture of precursors; addition stopped at pH = 8.5; precipitate isolated, washed and dried; calcination optional (air, 500 °C) |
| Characterisation | XRD: no crystalline phases; XPS: Pd in +2 state (Pd $3d_{5/2}$, $E_b = 337.3$ eV), Fe in +3 state (Fe $2p_{3/2}$, $E_b = 710.6$ eV) |
| 10%Pd–Bi–Mo–O | |
| Precursors | $Pd(NO_3)_2$, $Bi(NO_3)_3 \cdot 5H_2O$, ammonium molybdate |
| Preparation | Ammonium molybdate (dissolved in aqueous ammonia) added dropwise to solution of mixed Pd and Bi precursors (dissolved in 30%$HNO_3$); pH adjusted to 7.4; precipitate isolated, washed, dried and calcined (air, 500 °C) |
| Characterisation | TPR: low temperature reduction of PdO; XRD: two crystalline phases ($Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$) |

at temperatures where oxygen mobility (through the lattice) would normally be a limiting factor. In this way, the operating temperature of iron(III) oxide can be lowered by 250 °C for CO oxidation, water-gas shift and oxidative dehydrogenation, while the operating temperature for oxidative dehydrogenation over bismuth molybdate can be lowered by 150 °C. (Although bismuth molybdate is renowned as a catalyst for the conversion of propene to acrolein [16], APE cannot be used to enhance this reaction as dramatically because desorption of the product becomes limiting at lower temperatures.)

When palladium is replaced by platinum or gold, APE is either much more limited or not apparent at all. Exposed Pt sites are highly effective for total oxidation, and the effect of their presence on the surface of a partial oxidation catalyst is to increase conversion at the expense of selectivity. Using gold, we have been able to induce low-temperature oxidative dehydrogenation activity in iron(III) oxide, but only temporarily. As shown in Fig. 4, a dried co-precipitate of 4%Pd–Fe–O ($Pd^{2+}$ in an amorphous $Fe^{3+}$ matrix [15]) converts 1-butene to 1,3-butadiene at temperatures well below the minimum of 300 °C required by conventional iron(III) oxide catalysts [17]—we have recorded starting temperatures as low as 80 °C when Pd is present. Although the activity of the Pd–Fe–O declines slightly with time on line,

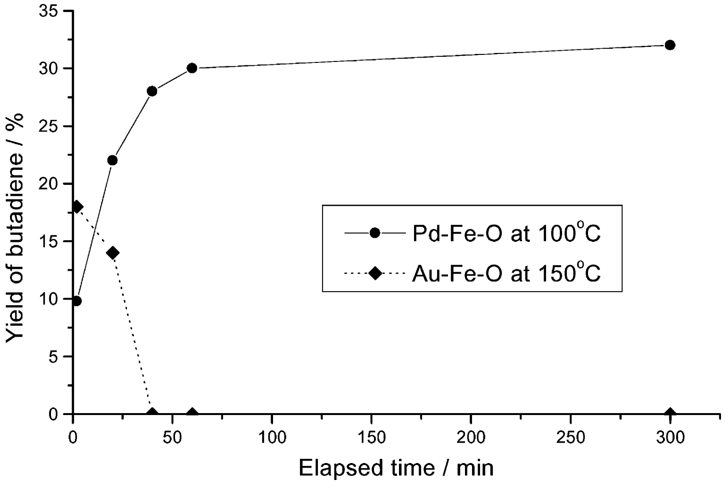

Fig. 4. Low-temperature oxidative dehydrogenation of butene under net-oxidising conditions (14%butene/air at 100 $cm^3\,min^{-1}\,g_{cat}^{-1}$).

there is a compensating rise in selectivity, resulting in a gradual increase in yield of butadiene over the first few hours of operation. Although the analogous gold catalyst shows activity at temperatures as low as 150 °C, the reaction ceases within 40 min of the gas-feed being introduced (Fig. 4).

Unlike NSA, where Au, Pd and Pt are virtually interchangeable in producing the effect, APE is best achieved by Pd. In our view, palladium is capable of providing and maintaining a shortcut in the normal Mars-van Krevelen mechanism (a redox cycle involving solid-state transport of oxide ions) by which single metal oxide catalysts function [15]. By contrast, Pt activates oxygen into a non-selective form, while gold initially provides selective oxygen species but cannot maintain their supply. In essence, palladium behaves like the ‘donor phase’ in the mechanism proposed by Weng and Delmon [2] for selective partial oxidation over mixed metal oxides. The key difference is that palladium performs this function at much lower temperatures than the best oxides (such as $Sb_2O_4$ or $Bi_2O_3$) can achieve.

## 5. Peroxide-like intermediates

For CO-oxidation under net-oxidising conditions, we find that a relatively high gold loading is required to produce low-temperature Au–MO catalysts. Typically, the loading is between 4 and 8%, but sometimes higher loadings are required for reproducible behaviour. In some of our formulations, such as 5%Au–ZnO (prepared by inverse precipitation), gold is present on the surface in the form of 4–5 nm metallic particles, which fall within the range now widely considered to be the optimum for low-temperature CO-activity [18]. However, some of our most active materials, such as uncalcined 5%Au–Fe–O (again prepared by inverse precipitation) have a quite different morphology. In our best Au–Fe–O formulations, the surface gold is predominantly in the form of Au(III) on a hydrated support.

Of the precious metals, gold (which has the highest activation energy for $O_2$ dissociation) is predicted to be the best catalyst for $H_2 + O_2$ conversion to $H_2O_2$ [19]. It is perhaps not surprising, therefore, that gold catalysts are capable of epoxidising propene in the presence of oxygen and hydrogen [20]. This occurs only at temperatures high enough for gold to dissociate the hydrogen (30–120 °C), but still low enough to avoid dissociating adsorbed oxygen molecules. At lower temperatures and in the absence of hydrogen, peroxide-like intermediates could still be formed, by the reaction of adsorbed $O_2$ (on the gold) with hydroxyl species (on the support). If these intermediates are indeed the most

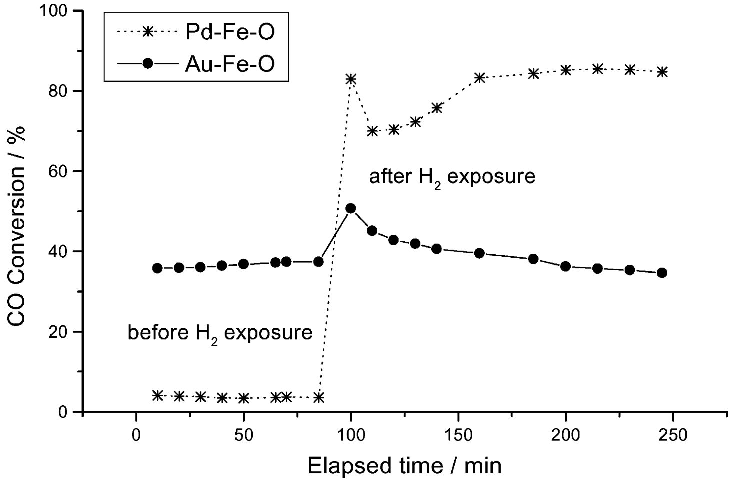

Fig. 5. CO-oxidation activity of 10%Au–Fe–O and 20%Pd–Fe–O at 0 °C, under net-oxidising conditions (1%CO/air at 400 $cm^3\,min^{-1}\,g_{cat}^{-1}$). Elapsed time was measured from when stable activity was reached. After 85 min, the catalyst was exposed to $H_2$ for 10 min at 10 °C, and flushed with $N_2$ for 5 min, before restarting the CO/air feed.

active oxidants of CO at low temperatures, it would explain

- (i) the importance of moisture to maintaining activity [18],
- (ii) why calcination (or even excessive drying) of the catalyst is detrimental [9],
- (iii) the poisoning effect of $SO_2$, which preferentially adsorbs on the support [21].

It is tempting to suggest that gold is exceptional in its ability to form highly reactive intermediates that allow it to convert CO so effectively at low temperatures. Comparing our best co-precipitated Au–Fe–O catalyst (10%Au) with our best Pd–Fe–O catalyst (20%Pd) in an isothermal reactor at 0 °C seems to confirm this impression. The activity of the freshly prepared (dried but uncalcined) gold catalyst is 10 times that of the palladium analogue. The activity of the Pd–Fe–O can be dramatically enhanced, however, by a short low-temperature exposure to hydrogen without any subsequent thermal treatment (Fig. 5). Initially, we ascribed the improvement to reduction of $Pd^{2+}$ ions to metallic palladium, but later found that using alternative reductants did not produce the same effect [22]. Instead, the enhanced activity appears to be related to the condition of the iron oxide, which is almost certainly left in a highly hydroxylated state after the low-temperature exposure to hydrogen. The gold catalyst is not affected in the same way, presumably because the iron oxide is already in a hydroxylated state when the catalyst is prepared.

## 6. Conclusions

In the present study, we show that the Frost junction effect theory (originally used to explain the activity of methanol synthesis catalysts [1]) can be applied to several gold-containing formulations, in which highly dispersed metallic gold is embedded in a reducible metal oxide. However, the junction effect does not seem to occur in catalysts where the gold is deposited in discrete locations on the surface of the support. Nor do these latter catalysts conform to the Delmon model, unlike their palladium-containing analogues, which can exhibit sustainable partial oxidation activity at exceptionally low temperatures. In the absence of convincing mechanistic information, we consider that the circumstantial evidence points to the formation of peroxide-like intermediates on the surface of exposed gold particles. We propose that these intermediates, which are particularly effective for CO oxidation at the lowest temperatures, originate at the interface between the gold and a hydroxylated support, and are formed by the reaction of adsorbed molecular oxygen with the nearby hydroxyl species. Gold does not appear to be unique in forming these highly reactive intermediates, though. Hyperactive Pd–MO catalysts, comparable in performance to the best gold formulations, can be prepared by deliberately pre-hydroxylating the oxide surface.

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