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# The application of supported gold catalysts to automotive pollution abatement

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**Abstract**

A gold based catalyst was formulated for use as a three-way catalyst in gasoline and diesel applications. The catalyst was comprised of gold supported on cobalt oxide, which acted as promoter. The gold–cobalt oxide clusters had particle sizes of approximately 40–140 nm, and were supported on a mechanical mixture of zirconia-stabilised ceria, zirconia and titania. Under gasoline conditions at sub-stoichiometric and super-stoichiometric oxygen concentrations, fresh catalysts displayed a hydrocarbon $T_{50}$ of 240 °C, a CO $T_{50}$ of 85 °C and a $NO_x$ $T_{50}$ of 310 °C. After testing at temperatures of 500 °C over periods of up to 157 h, the activity of the catalyst decreased. 

*Keywords:* Gold catalysts; Three-way autocatalyst; Zirconia; Ceria; Titania

## 1. Introduction

The application of gold catalysts to the oxidation of carbon monoxide has been studied extensively, most notably by Haruta et al. [1,2]. A significant feature of gold-based catalysts is the low temperature oxidation of carbon monoxide, where the catalysts display activity at temperatures as low as −70 °C [3]. In general, these catalysts are comprised of gold particles with diameters between 2 and 5 nm supported on transition metal oxides which are thought to act as promoters [4]. In almost all cases, the transition metal is a first-row element such as titanium, manganese, iron or cobalt. For catalysts containing 1.2% gold supported on $Co_3O_4$, the activation energy ($E_{act}$) for CO oxidation is significantly lower, at 16.3 kJ mol$^{-1}$, than that measured for 0.66% gold on α-$Fe_2O_3$ ($E_{act}$ = 35.1 kJ mol$^{-1}$) or 1.0% gold on $TiO_2$ ($E_{act}$ = 29 kJ mol$^{-1}$) [1]. Catalysts containing $Co_3O_4$ as the promoter display the lowest temperatures for 50% conversion of methane, propene, trimethylamine and propane [5].

One application for which low temperature oxidation is important is automotive pollution abatement. The three major pollutants emitted by internal combustion engines are carbon monoxide, non-methane hydrocarbons and nitrogen oxides. Environmental legislation governing the emission of these pollutants is becoming increasingly stringent. Catalysts that are capable of removing these pollutants simultaneously are generally referred to as three-way catalysts (TWCs) and the design of these catalyst systems is continually evolving to meet lower emission requirements. Typically, these catalysts must operate in the presence of 10% $H_2O$ and 10–60 ppm $SO_2$ at temperatures ranging from 350 to 1000 °C and gas hourly space velocities ranging from 10 000 to over 100 000 h$^{-1}$ for the duration of 100 000 miles of operation [6]. All commercial TWCs in use at present are based on platinum, palladium and rhodium on a support comprised

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of zirconia-stabilised ceria, zirconia and γ-alumina. Additives include barium oxide and zinc oxide.

Catalyst efficiency is usually tested under simulated driving conditions using the standardised federal test procedure (FTP). A key problem identified in FTP tests is the liberation of unburned non-methane hydrocarbons during the cold start mode of the test when the catalyst monolith is at ambient temperature. As a consequence, the catalyst does not reach the hydrocarbon light-off temperature of about 300 °C until approximately 2 min after the start of the test. During this delay up to 50% of the total unburned hydrocarbons are emitted. Additionally, when the engine operates under prolonged idling conditions, the temperature at the inlet to the converter is typically 280 °C which is an accepted monolith temperature for a catalyst converter mounted approximately 80 cm from the exhaust manifold of a spark ignition engine of 1.8 l displacement [7]. This temperature is again below the light-off for hydrocarbons.

A gold catalyst with low temperature activity towards CO and hydrocarbon oxidation could be suitable in such an application, especially during the low temperature start-up and idling phases. In this work, catalysts containing cobalt oxide-promoted gold were tested under conditions that simulated the exhaust gases of gasoline and diesel automobiles.

## 2. Experimental procedures

### 2.1. Synthesis

The gold catalyst tested was comprised of three major components:

- The support: a mixture of zirconia-stabilised ceria (Rhone Poulenc HSA5), zirconia (Rhone Poulenc) and titania in the anatase form (Bayer).
- A promoter: cobalt in the form of $Co_2O_3$ and $Co_3O_4$. In addition, various additives such as rhodium, zinc oxide, magnesium oxide and barium oxide were present. All reagents were AR grade from Sigma Aldrich.
- The active catalytic phase: gold clusters.

The catalyst was prepared by impregnation of the promoter metal and the additives on the support mixture followed by gold precipitation on to the impregnated support. The composition of the catalyst is given in Table 1. Rhodium was added to the catalyst in order to promote the reduction of $NO_x$ species.

Table 1
Chemical compositions of typical catalysts used in this work

| Component | Concentration/% (m/m) |
|---|---|
| Cobalt | 1 |
| Gold | 1 |
| Rhodium | 0.1 |
| Zinc oxide | 2 |
| Barium oxide | 2 |

### 2.2. Impregnation

The support components were mixed in a mixer mill for 10 min prior to heating at 120 °C for 30 min. The heated support was then added to a solution containing appropriate concentrations of cobalt, barium, zinc and rhodium as the nitrate salts, at 80 °C. The pressure in the mixing vessel was reduced by means of a diaphragm vacuum pump and water was distilled off at a constant temperature of 65 °C over a 4 h period. The support slurry was dried at 120 °C for 2 h prior to crushing and sieving through a 35 μm mesh sieve. The prepared support was then calcined under air at 300 °C for 6 h.

### 2.3. Precipitation

Hydrogen tetrachloroaurate solution was added to a potassium hydroxide solution at pH 13. The temperature of the solution was increased to 60 °C and the preheated impregnated support was added to form a slurry. The pH was reduced to 8 by the addition of 0.1 M $HNO_3$. Magnesium citrate solution (six times the molar equivalent of hydrogen tetrachloroaurate) was added at a constant rate over a 30 min period in order to ensure adequate dispersion of the gold on the surface of the cobalt oxide promoter. The slurry was maintained at pH 8 and 60 °C for 60 min before being drained from the reactor and filtered. The filtered catalyst was re-slurried in de-ionised water and stirred for a further 30 min before being filtered and washed with water. The catalyst was dried at 120 °C under air for 2 h before being sieved to −35 μm and calcined at 450 °C under 5% $O_2$ for 3 h. The catalyst was stored prior to use.

### 2.4. Characterisation

Catalysts were characterised by means of transmission electron microscopy (TEM) for information on cluster size and element associations with elemental compositions determined by energy dispersive analysis by X-rays (EDAX). Surface area was determined by means of a BET isotherm and particle sizes were determined by means of laser diffraction. The catalyst surface composition and chemical state were probed by X-ray photoelectron spectroscopy (XPS).

### 2.5. Testing

Catalysts were tested in static bed quartz reactors containing 1 g of catalyst mixed with 1 g of silica. The reactors were heated by means of tubular heaters. Gas flow to the reactors was controlled by Brooks mass flow controllers. Feed gases to the reactors were intended to simulate the emissions of gasoline and diesel engines. The compositions of the gases used are given in Table 2. For simulated gasoline mixtures, tests were conducted under oxidising and reducing conditions, where the principal difference in the gas composition was the oxygen concentration: 0.6% under reducing conditions and 0.9% under oxidising conditions. For simulated diesel mixtures, the concentration of oxygen was significantly higher than under gasoline conditions at 7.5%. In addition, the concentration of CO in the diesel mix was significantly lower than in the gasoline system, at 0.03%.

Table 2
Gas mixture compositions for catalyst tests conducted under gasoline oxidising and reducing and diesel conditions

| Gas | Gasoline | | Diesel |
|---|---|---|---|
| | Oxidising | Reducing | |
| CO | 1.0% | 1.0% | 300 ppm |
| $O_2$ (%) | 0.9 | 0.6 | 7.5 |
| $CO_2$ | 10 | 10 | 10 |
| $C_3H_8$ (ppm) | 350 | 350 | 75 |
| $C_3H_6$ (ppm) | 350 | 350 | 25 |
| NO (ppm) | 1000 | 1000 | 300 |
| $SO_2$ (ppm) | 15 | 15 | 25 |
| $H_2O$ (%) | 2 | 2 | 2 |
| $H_2$ (ppm) | – | – | 100 |
| $N_2$ | Balance | Balance | Balance |

The reactor off-gases were analysed in a Rosemount NGA 2000 gas analyser system containing detectors for hydrogen, carbon monoxide, carbon dioxide, sulphur dioxide, oxygen, and nitric oxide.

Catalysts were tested between 25 and 500 °C under simulated gasoline and diesel exhaust conditions. Samples were tested for activity towards CO and hydrocarbon oxidation as well as nitric oxide reduction. Catalyst durability was established by maintaining the catalyst at 500 °C for periods up to 150 h. During the durability tests, catalyst stability was assessed by cooling to room temperature and determining catalyst activity by reheating to 500 °C at 10 °C $min^{-1}$. Gas hourly space velocities were maintained at 60 000 $h^{-1}$ for all tests.

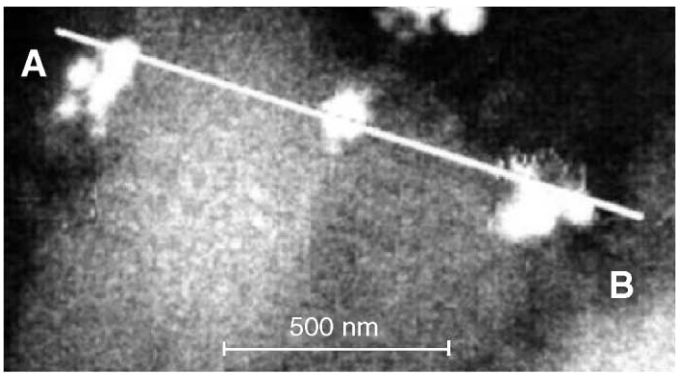


Fig. 1. TEM micrograph of a catalyst particle comprised of zirconia-stabilised ceria, zirconia and titania with three clusters comprised of cobalt oxide and gold. Note that the low resolution of the micrograph does not allow for the identification of individual gold clusters on the cobalt oxide surface. The line over the cross-section AB represents an EDAX line scan which is shown in Fig. 2.

## 3. Results and discussion

### 3.1. Catalyst characterisation

#### 3.1.1. Surface area

Fresh catalyst samples typically had a specific surface area of approximately $150\,m^2\,g^{-1}$. The area of used samples was found to be significantly lower at around $90\,m^2\,g^{-1}$. The large reduction in surface area suggests that the support had degraded, resulting in a loss of pore structure, which in turn encouraged the sintering of the gold after service at 500 °C. Particle sizes were $3\,\mu m < d_{90} < 5\,\mu m$.

#### 3.1.2. Electron microscopy

A low resolution TEM micrograph of a catalyst particle is shown in Fig. 1. Three clusters can be seen. An EDAX line scan across the catalyst particle reveals the presence of titanium, cerium, zirconium, cobalt and gold, as shown in Fig. 2. The spatial arrangement of the elements is given along the *x*-axis, which corresponds to the points along the line AB in Fig. 1.

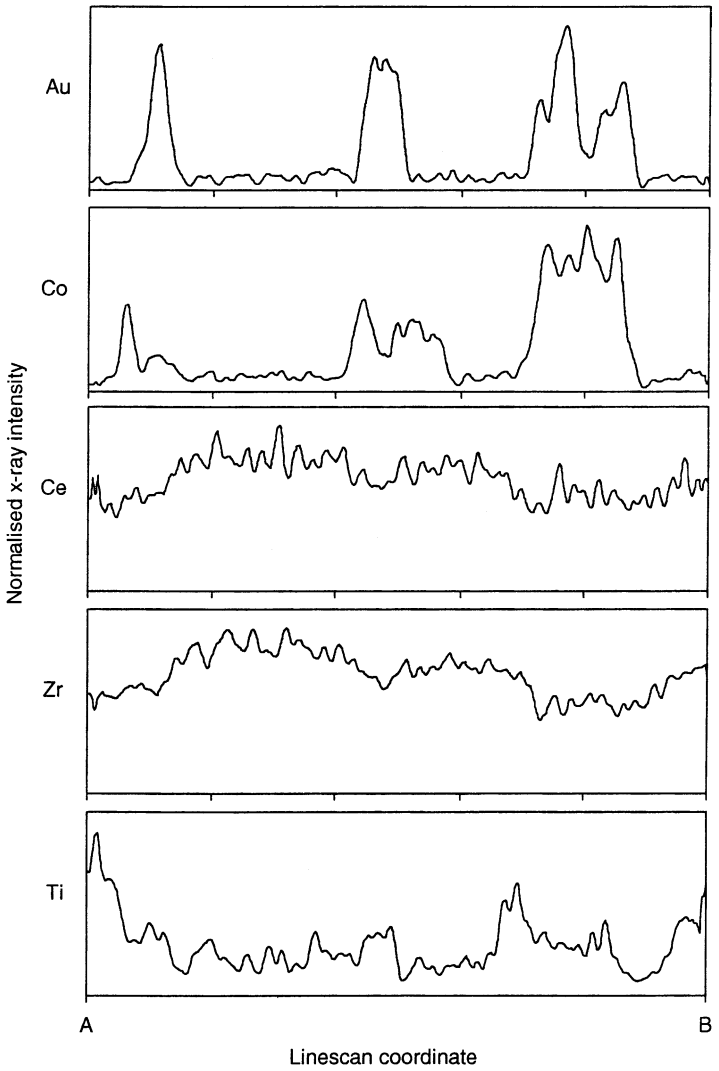


Fig. 2. EDAX line scans for Au, Co, Ce, Zr and Ti over a cross-section AB in the electron micrograph shown in Fig. 1.

Where the peak intensities for different elements overlap at a specific spatial point, it is reasonable to infer that the elements are associated. Large overlapping peaks occur for gold and cobalt in the positions of the three clusters in Fig. 1, suggesting that the metals are associated. The signals for titanium, cerium and zirconium are virtually constant over the length of the line scan, indicating that these elements do not form part of the cluster, but are rather part of the underlying support. The EDAX line scan data indicate that the catalyst particle is comprised of cobalt–gold clusters on a support made up of titania, ceria and zirconia. The size of the cobalt oxide–gold clusters is approximately 50 nm. The low resolution of the TEM image does not allow the identification of any individual gold cluster on the cobalt oxide.

### 3.1.3. XPS

Representative XPS spectra at the gold 4f and cobalt 2p binding energies are shown for fresh catalyst in Figs. 3 and 4, respectively. The Au(0) $4f_{5/2}$ and $4f_{7/2}$ doublet at 87.3 and 83.6 eV ($\Delta = 3.7$ eV) is seen clearly in Fig. 3. Clearly resolved peaks for Au(I) $4f_{7/2}$ and Au(III) $4f_{7/2}$ are not evident at the expected binding energies of approximately 86 and 88 eV, respectively. These data indicate that the major gold species on the fresh catalyst surface was metallic gold. However, it is possible that the Au(0) $4f_{5/2}$ peak at 87.3 eV overlaps the signals for the Au(I) and Au(III) $4f_{7/2}$ photoelectrons. Additionally, the Zn $3p_{3/2}$ peak at 90.1 eV would overlap with any Au(I) $4f_{5/2}$ and Au(III) $4f_{5/2}$ signals, which are expected at approximately 89.6 and 91.6 eV, respectively. While there are clear indications of Au(0) species, the presence of Au(I) and Au(III) species cannot be confirmed from these data.

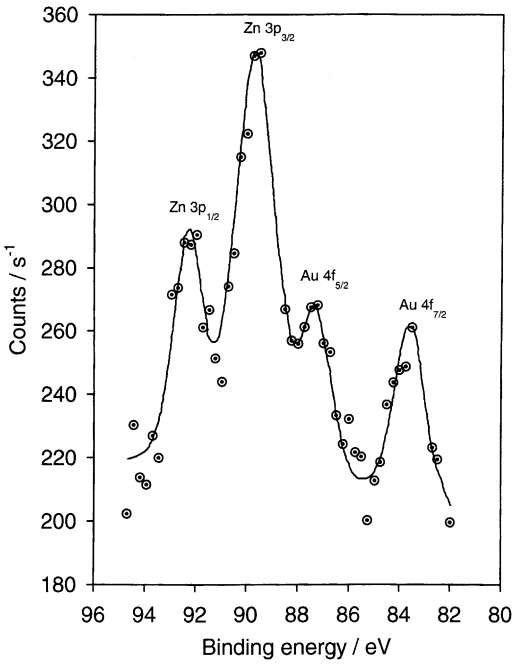


Fig. 3. High resolution XPS spectrum for gold 4f photoelectrons.

For cobalt, the Co(II) and Co(III) $2p_{3/2}$ peaks at 780.7 and 780.0 eV, respectively, overlap the Ba $3d_{5/2}$ peak at 780.6 eV, as shown by the single convoluted peak in Fig. 4. Additionally, $\Delta = 15.2$ eV for the Co $2p_{1/2}$ and Co $2p_{3/2}$ photoelectrons and $\Delta = 15.3$ eV for the Ba $3d_{3/2}$ and Ba $3d_{5/2}$ photoelectrons. This makes any definitive identification of the electronic state of cobalt very difficult.

## 3.2. Catalyst testing

The principal tests applied to the catalysts in this work were the measurements of carbon monoxide (CO) conversion to carbon dioxide, hydrocarbon (HC) oxidation and nitric oxide (NO) reduction. Specific tests included the measurement of conversion as a function of temperature to give catalyst activity, the measurement of conversion as a function of time at constant temperature to give catalyst durability, and the measurement of conversion as a function of time and temperature to give catalyst stability. Catalyst performance was assessed in terms of the $T_{50}$ temperature, defined as the temperature at which 50% conversion had occurred.

## 3.3. Gasoline applications

### 3.3.1. Catalyst activity

Under oxidising conditions, CO $T_{50}$ occurred between 75 and 85 °C, as shown in Fig. 5. CO oxidation was complete at temperatures above 120 °C. Hydrocarbon oxidation occurred in two phases: propene was oxidised at temperatures approximately below 250 °C while propane was oxidised up to the experimental temperature limit of 500 °C. The HC $T_{50}$ was 240 °C, with complete conversion occurring at 470 °C. Under

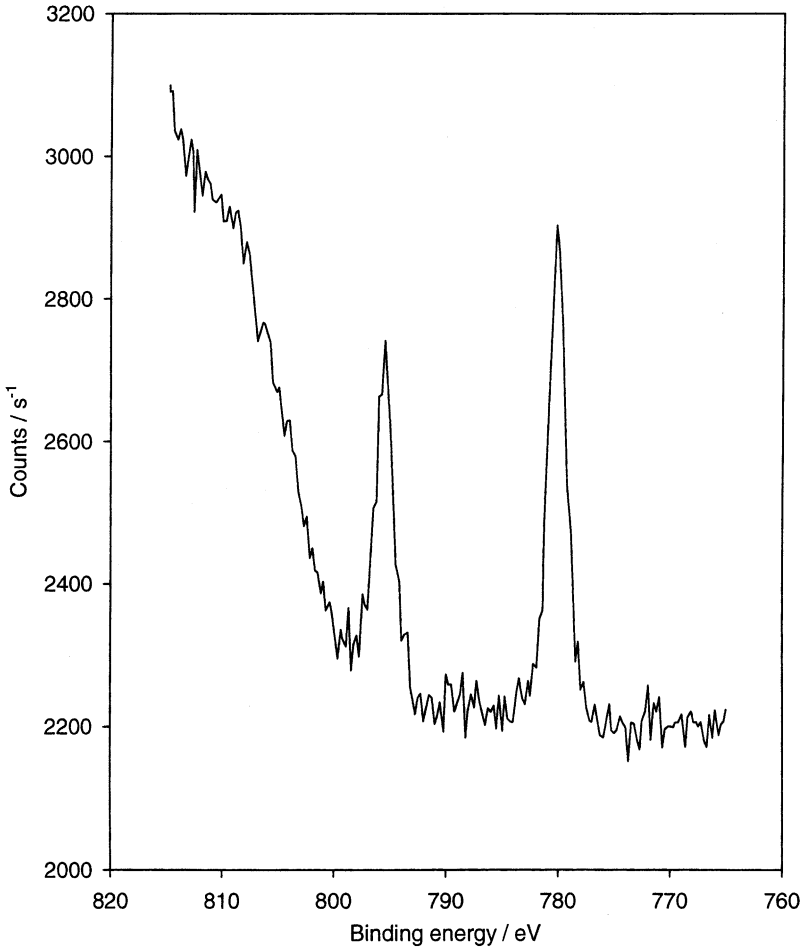


Fig. 4. High resolution XPS spectrum for cobalt 2p photoelectrons.

the oxidising conditions imposed on the catalyst, virtually no nitric oxide reduction occurred. The activities for CO and hydrocarbon oxidation as well as NO reduction are shown in Table 3.

Under reducing gasoline conditions there was still sufficient oxygen for CO oxidation to occur, as shown in Fig. 6. The CO $T_{50}$ remained unaffected at 75–85 °C. The HC $T_{50}$ increased to 310 °C, with approximately 90% conversion at the temperature limit of 500 °C. At the lower oxygen concentration present under reducing gasoline conditions, complete conversion of nitric oxide to nitrogen occurred at approximately 330 °C with $T_{50}$ = 300 °C. When rhodium was excluded from the catalyst composition, the NO $T_{50}$ value increased approximately by 80 °C. The rapid increase in nitric oxide reduction corresponded to complete utilisation of oxygen in the feed gas stream by CO and hydrocarbon oxidation. However, there appears to be competition between CO and the hydrocarbons for oxygen, as shown by the higher hydrocarbon $T_{50}$. This is evident from the transient reduction in CO conversion at approximately 300 °C.

Table 3
Activity of fresh catalyst under oxidising gasoline conditions

| Gas | $T_{50}$ (°C) | $T_{100}$ (°C) |
|---|---|---|
| CO | 75 | 170 |
| HC | 240 | 470 |
| NO | – | – |

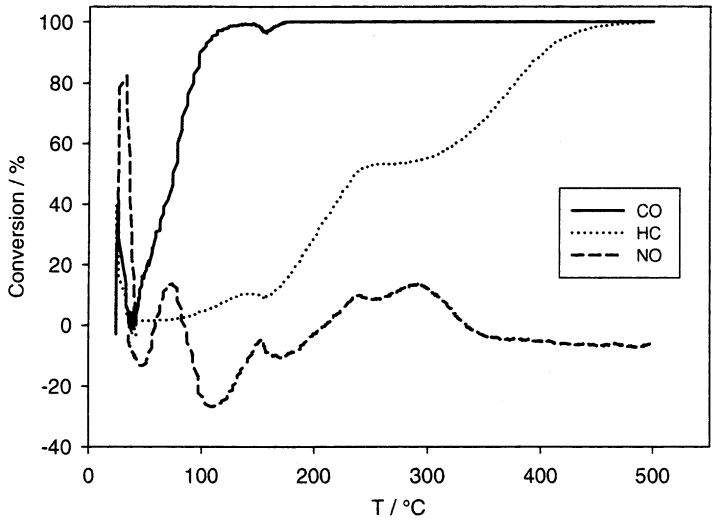


Fig. 5. Fresh catalyst activity under oxidising gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

The activities under reducing gasoline conditions are given in Table 4.

Table 4
Activity of fresh catalyst under reducing gasoline conditions

| Gas | $T_{50}$ (°C) | $T_{100}$ (°C) |
|---|---|---|
| CO | 85 | 200 |
| HC | 310 | >500 |
| NO | 300 | 330 |

### 3.3.2. Durability and stability

The durability and stability of the cobalt–gold catalysts were tested at temperatures of 500 °C for periods of up to 150 h. The durability data are shown in Figs. 7 and 8 for oxidising and reducing conditions, respectively. As discussed earlier, it is clear

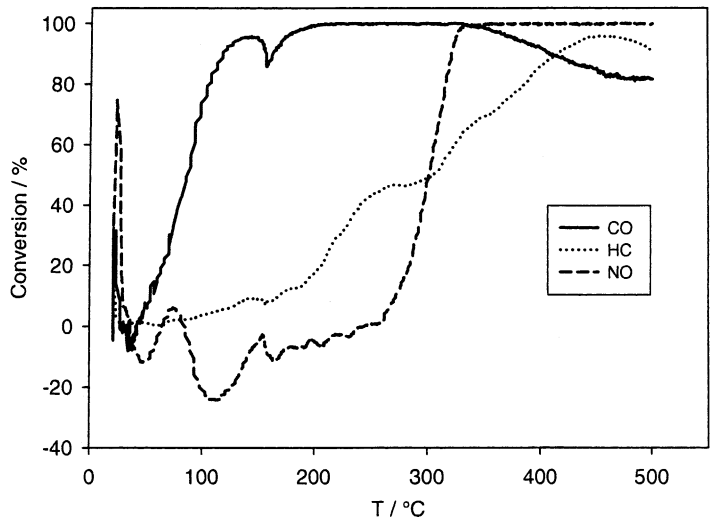


Fig. 6. Fresh catalyst activity under reducing gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

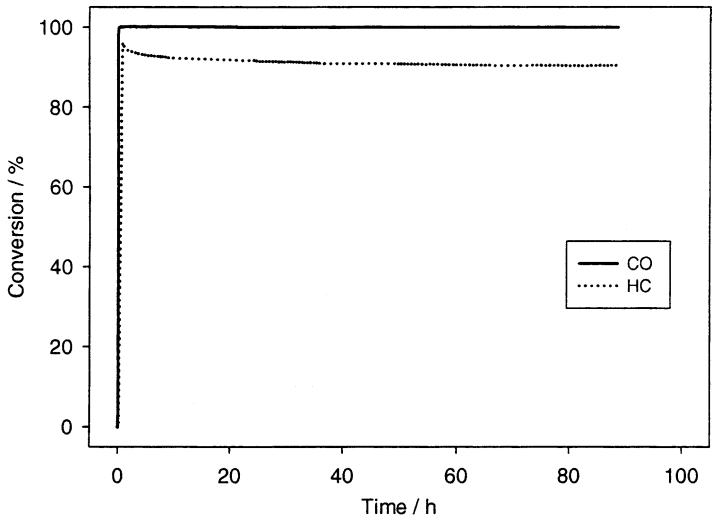


Fig. 7. Catalyst durability under oxidising gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

that, even under oxidising conditions, there is competition between CO and the hydrocarbon components in the gas mixture for any available oxygen. Hydrocarbon oxidation decreased with time, stabilising at approximately 90% conversion, while CO oxidation remained unaffected at 100% conversion. No nitric oxide conversion was detected.

Under reducing conditions, CO oxidation and NO reduction occurred at 100% conversion, while hydrocarbon oxidation decreased rapidly from 100% conversion, eventually stabilising at approximately 60% conversion.

In terms of catalyst stability, the $T_{50}$ for CO oxidation under oxidising gasoline conditions increased

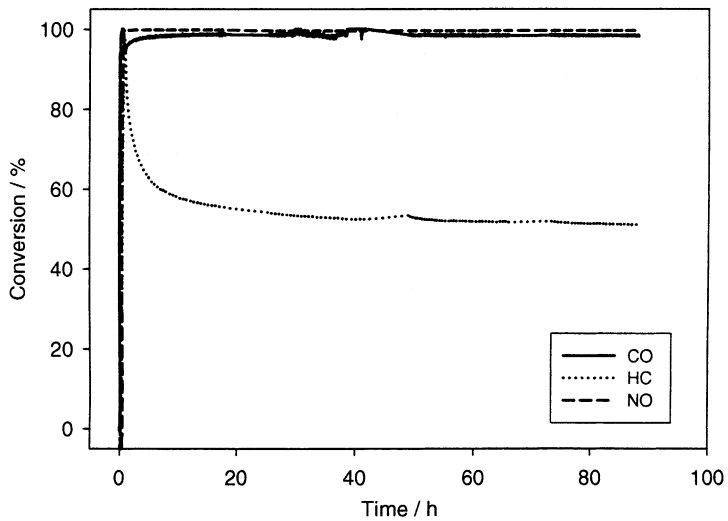


Fig. 8. Catalyst durability under reducing gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

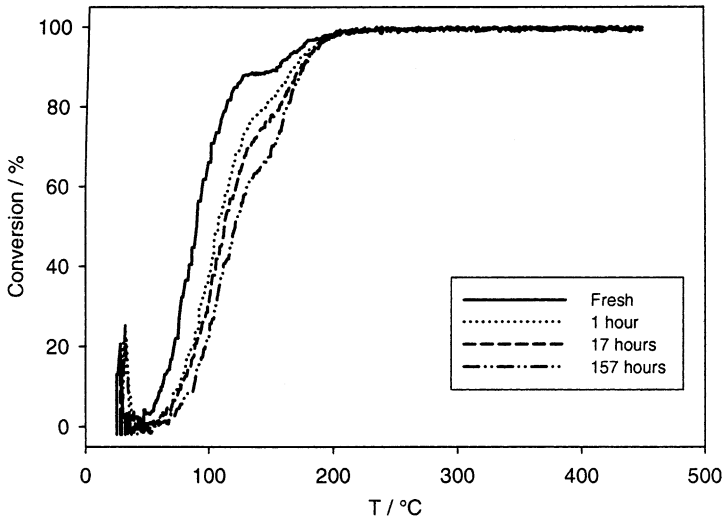


Fig. 9. Catalyst stability with respect to CO oxidation under oxidising gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

slightly with increasing time online, from 90 °C for fresh catalyst to 121 °C for the same catalyst after 157 h online at 500 °C (Fig. 9). At temperatures above 200 °C, CO oxidation was stable at 100% conversion, regardless of time online. As shown in Fig. 10, the $T_{50}$ for hydrocarbon oxidation displayed a similar trend to that for CO. The $T_{50}$ for fresh catalyst was 270 °C and increased to 310 °C after 157 h online. Complete hydrocarbon oxidation was not achieved at temperatures below 500 °C. These data are confirmed by the durability data shown in Fig. 7.

Under reducing gasoline conditions, there was a significant increase in the CO $T_{50}$ from 94 °C for fresh catalyst to 158 °C after 63 h online, as shown in Fig. 11. At temperatures above 250 °C, approximately 98% of the CO was oxidised, irrespective of time

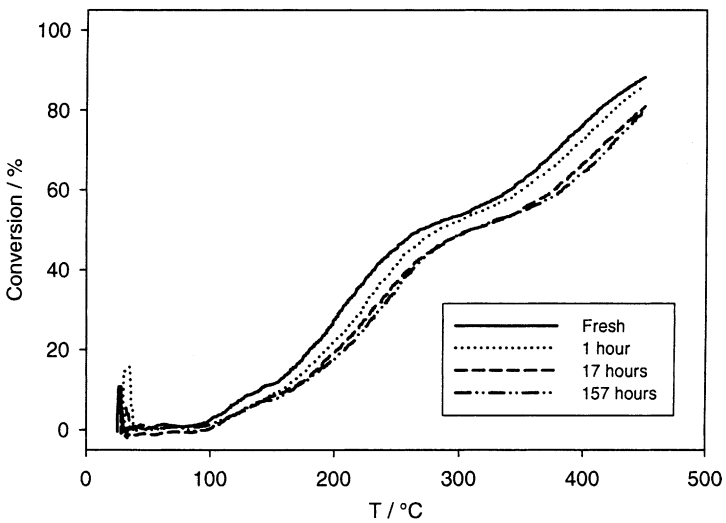


Fig. 10. Catalyst stability with respect to hydrocarbon oxidation under oxidising gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

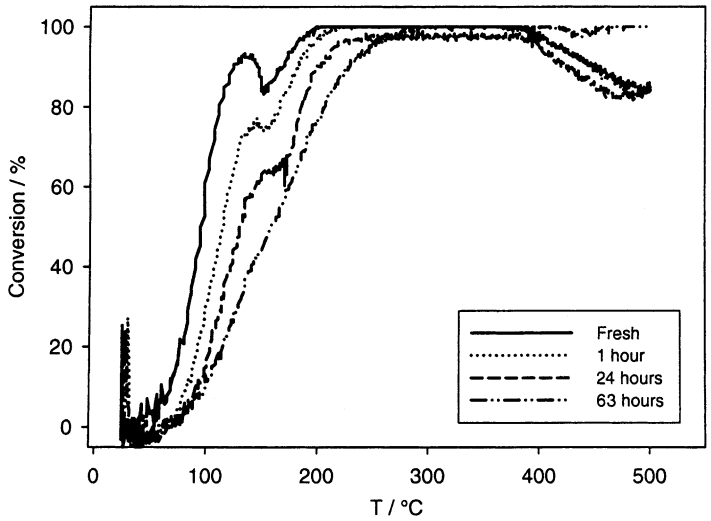


Fig. 11. Catalyst stability with respect to CO oxidation under reducing gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

online. Similarly, as shown in Fig. 12, the hydrocarbon $T_{50}$ increased from 350 °C for fresh catalyst to 370 °C after 63 h.

The oxidation of hydrocarbons was significantly more erratic when compared to the oxidising gasoline conditions. This behaviour is believed to be due to competition between CO and hydrocarbons for oxygen. Under oxygen-deficient conditions, nitric oxide reduction is favoured, especially at temperatures above 300 °C, where oxygen is consumed by the CO and hydrocarbon oxidation reactions. This behaviour is shown in Fig. 13. The nitric oxide $T_{50}$ for fresh catalyst was 330 °C, increasing to 340 °C after 63 h. Complete conversion occurred at temperatures above 400 °C.

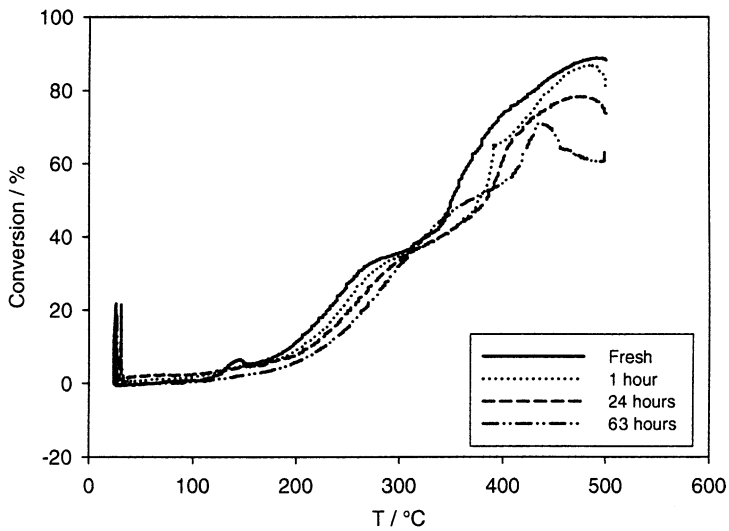


Fig. 12. Catalyst stability with respect to hydrocarbon oxidation under reducing gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

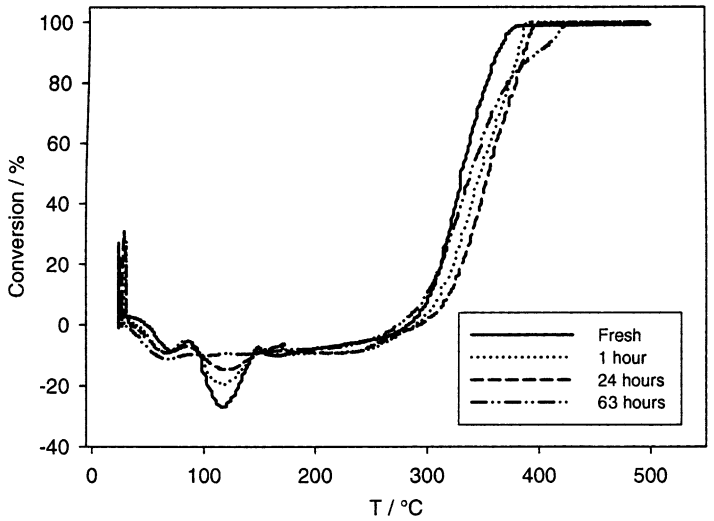


Fig. 13. Catalyst stability with respect to NO reduction under reducing gasoline conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

### 3.4. Diesel applications

A brief investigation of catalyst activity under diesel conditions was conducted. Durability and stability tests were not undertaken. The activity of fresh catalyst is given in Table 5 and shown in Fig. 14. The CO $T_{50}$ of 60 °C is favourable as is the hydrocarbon $T_{50}$ of 170 °C. These $T_{50}$ figures are not unexpected

Table 5
Activity of fresh catalyst under diesel conditions

| Gas | $T_{50}$ (°C) | $T_{100}$ (°C) |
|---|---|---|
| CO | 60 | 120 |
| HC | 170 | 420 |
| NO | 250 | – |

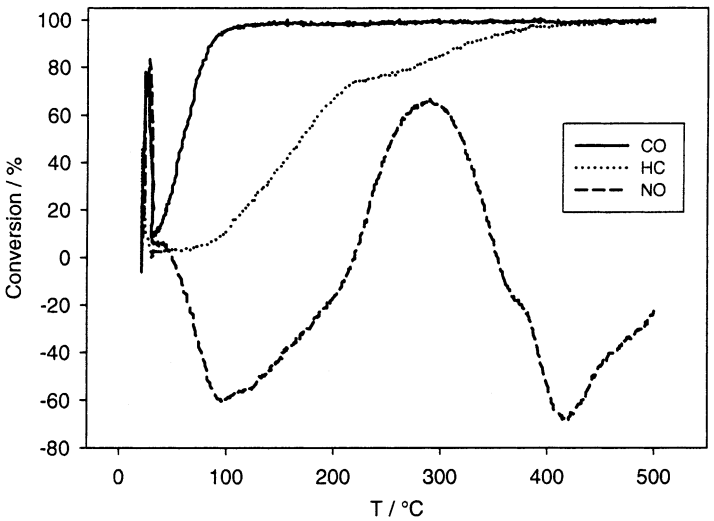


Fig. 14. Fresh catalyst activity under diesel conditions. Gas composition is given in Table 2. GHSV = 60 000 $h^{-1}$.

owing to the high oxygen concentration of 7.5% and the low concentrations of CO and hydrocarbons in the feed gas (Table 2). The reduction of nitric oxide is interesting in that a "window of activity" was observed at temperatures between 220 and 350 °C, displaying a maximum conversion of 66% at 290 °C. At temperatures above and below the conversion band, a significant release of NO into the reactor was noted, as can be seen from the negative conversions recorded by the online detector.

## 4. Conclusions

While the existing PGM-based TWCs operate efficiently at temperatures greater than approximately 300 °C on gasoline engines, they display poor HC conversions at temperatures below the HC light-off of approximately 300 °C. Under cold start and idling conditions, the temperature of the catalyst bed is usually less than 280 °C. Gold catalysts have shown potential as low temperature TWCs—the hydrocarbon $T_{50}$ for a fresh catalyst is 240 °C, while for CO, the $T_{50}$ is 85°C. After approximately 157 h online at 500 °C, the $T_{50}$ temperature increased to 310 °C for HC conversion and 120 °C for CO conversion. Conversion of NO was more stable, with the $T_{50}$ increasing from 330 °C for fresh catalyst to 340 °C after 63 h online at 450 °C.

A significant hurdle for the gold-based TWC is the high operating temperature requirements imposed by gasoline engines. Typically, a catalyst must be able to withstand a temperature of 1100 °C for at least 12 h. The gold-based TWC cannot survive under such conditions and it is accepted that gold will not be able to match the high temperature performance of the PGM-based TWCs. However, a relatively simple system in which PGM- and gold-based catalysts operate in parallel can be envisaged, where the gold catalyst is in use at low temperatures but is bypassed in favour of the PGM catalyst at higher temperatures. In this way, maximum conversion activity can be maintained both at low temperatures using the gold catalyst and at high temperatures using the PGM catalyst.

Under diesel conditions, CO and HC oxidation is favoured, with $T_{50}$ values of 60 and 170 °C, respectively. Under the highly oxidising conditions encountered in the diesel gas stream, reduction of NO is not expected. A NO conversion window is observed at temperatures between 220 and 350 °C, with a $T_{50}$ value of 250 °C. However, large NO absorption bands are observed at temperatures above and below the conversion window.

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## References

[1] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.
[2] M. Haruta, Catal. Today 36 (1997) 153.
[3] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[4] G.C. Bond, D.T. Thompson, Catal Rev.-Sci. Eng. 41 (1999) 319.
[5] M. Haruta, Now Future 7 (1992) 13.
[6] R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, Chapman & Hall, London, 1997, p. 580.
[7] R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, Chapman & Hall, London, 1997, p. 596.