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# Investigation of the effect of the preparation method on the activity and stability of Au/$CeZrO_4$ catalysts for the low temperature water gas shift reaction

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## ABSTRACT

The impact of the preparation method on the activity and stability of gold supported on ceria–zirconia low temperature water-gas shift (WGS) catalysts have been investigated. The influence of the gold deposition method, nature of the gold precursor, nature of the washing solution, drying method, Ce:Zr ratio of the support and sulfation of the support have been evaluated. The highest activity catalysts were obtained using a support with a Ce:Zr mole ratio 1:1, $HAuCl_4$ as the gold precursor deposited via deposition precipitation using sodium carbonate as the precipitation agent and the catalyst washed with water or 0.1 M $NH_4OH$ solution. In addition, the drying used was found to be critical with drying under vacuum at room temperature found to be most effective.

DRIFT spectra of CO adsorbed at room temperature over the range of catalysts synthesized showed that the Au–CO band area (major species: metallic gold) varied with preparation method and could be correlated with the observed activity of the catalysts under the WGS feed.

## 1. Introduction

Gold based catalysts have been shown to be active for a wide range of catalytic reactions [1,2]. The performance of gold catalysts is closely related to the size of the deposited nanoparticles with finely dispersed gold particles in intimate contact with the support believed to be crucial to obtain high activity for gold based water-gas shift (WGS) catalysts [3]. Consequently, the gold nanoparticles preparation and stabilization are highly sensitive to the preparation method employed. Haruta and co-workers have shown that co-precipitation (CP) or deposition–precipitation (DP) techniques allow the preparation of active Au catalysts for CO oxidation [4]. Active Au catalysts have also been prepared from co-sputtering [5], chemical vapour deposition [6], adsorption of colloidal gold onto metal oxides [7], or supporting gold phosphine complexes as precursors for Au metal particles [8]. In addition to the method of loading Au onto the support, a number of other parameters, can influence the activity of Au catalysts such as the nature of the gold precursor, the gold loading, the nature of precipitating agent, the pH during preparation, the washing solution, the calcination atmosphere and temperature all being reported to exert a strong influence on the activity of supported Au catalysts [9–15].

The nature of the support also plays a vital role in determining the activity of gold catalysts [16]. In the case of WGS catalysts, gold supported on $Fe_2O_3$ [11,17,18], $TiO_2$ [19–21], ZnO [22], $ZrO_2$ [22], zeolites (NaY, Na-mordenite and Na-ZSM-5) [23], $CeO_2$ [24–31] and doped $CeO_2$ [32] have all been reported to show activity for the WGS reaction. Additional modification of supports by sulfation have also been tested resulting in improved WGS activity for Au supported on sulfated $ZrO_2$ catalysts [33–35]. Gold supported on ceria–zirconia has been shown to be highly active for the WGS reaction [36] and is generally more stable than $Fe_2O_3$ based catalysts [37]. Addition of zirconia to the ceria has been reported to improve the oxygen storage capacity of ceria, which is considered important for redox processes in reactions such as CO oxidation [38–40] and WGS [37].

While there have been major developments in optimising the preparation of active Au catalysts for the WGS reaction there is still a need to improve the stability of these catalysts to allow their commercial application [41,42]. In the case of gold supported on ceria–zirconia, deactivation under the feed has been proposed to be due to the loss of metal/support interaction with the feed conditions (amount of water, $CO_2$ in the feed and the pretreatment) as well as the thermal history of the catalyst all shown to influence the stability of the catalyst. For example, increased water concentration and/or elevated temperatures have been shown to result in loss of activity and this has been proposed to be due to the gold nanoparticle becoming detached from the oxide support [42,43]. The active form of the gold in low temperature WGS Au/ceria–zirconia catalysts has been investigated by XAS, XPS and

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DRIFTS [41–43]. Therein, *in situ* DRIFTS was used to correlate the rate of change of the Au–CO bands with time on stream with the deactivation rate of the catalysts and demonstrated that the majority of the WGS catalyst activity following initial deactivation could be ascribed to zero valent gold sites.

In this study we have investigated a number of catalyst preparation parameters which influence the activity and stability of WGS Au/ceria–zirconia catalysts. Preparation parameters including gold precursor deposition method (Deposition–Precipitation (DP), Co-Precipitation (CP), Urea Gelation Co-precipitation (UGC)), the concentration and composition of the washing solution, the nature of the gold precursor ($HAuCl_4$, $AuBr_3$), the drying method, the Ce:Zr mole ratio in the support, the calcination temperature and the sulfation treatment employed have been varied to determine their effect on WGS activity and stability of the resultant catalysts. In each case the vibrational spectrum of CO adsorbed on the supported gold at room temperature as a function of preparation method has been used to characterise the surface composition in terms of the gold oxidation state and relative number/strength of the adsorption sites. These have been compared to the Au–CO species observed under the WGS feed.

## 2. Experimental

### 2.1. Catalyst preparation

To prepare the pure ceria support, $(NH_4)_2Ce(NO_3)_6$ (Sigma–Aldrich) and urea were dissolved in deionised water. An aqueous solution of $NH_4OH$ was added dropwise and the mixture was heated to 100 °C under constant stirring for 8 h. The precipitate was filtered and washed with water and then dried for 12 h at 100 °C before being calcined at 400 °C for 4 h. In the case of zirconia, $ZrO(NO_3)_2 \cdot xH_2O$ (Sigma–Aldrich) was dissolved in deionised water and the hydroxide precursor was precipitated under constant stirring by adding an aqueous solution of $NH_4OH$ with the pH kept constant at 9.0 (TitraLab 856 pH Stat Titration Workstation, Radiometer Analytical). The precipitate was thoroughly washed and then dried at 100 °C overnight before being calcined at 500 °C for 4 h. For the mixed ceria–zirconia, supports ($Ce_{1.5}Zr_{0.5}O_4$, $Ce_{0.5}Zr_{0.5}O_4$, $Ce_{0.5}Zr_{1.5}O_4$) were prepared via a sol–gel method using the corresponding mole ratios of $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot xH_2O$ dissolved in deionised water. An aqueous solution of $NH_4OH$ was added under constant stirring until the pH reached a value of 9.0. The resulting gel was then filtered, dried overnight at 100 °C and calcined at 500 °C for 4 h.

Three methods of gold deposition were employed – DP, CP and UGC. In the case of DP typically the support was slurried in deionized water and warmed to 60 °C under constant stirring. The pH was adjusted to 8.0 by the addition of 0.05 M aqueous solution of $Na_2CO_3$. An aqueous solution of $HAuCl_4$ or $AuBr_3$ (~1.2 mM) was added slowly to the support slurry (~1 $cm^3\,min^{-1}$). During this operation, the pH was maintained at 8.0 by addition of an aqueous solution of $Na_2CO_3$. After the addition of the gold precursor solution, the slurry was stirred for 1 h at 60 °C, recovered by filtration and thoroughly washed (washing solutions tested included: water, 0.1 M $NH_4OH$, 5 M $NH_4OH$ or 0.1 M $Na_2CO_3$) to remove soluble halide. The precipitate (from $HAuCl_4$ precursor) required washing with 175 $cm^3$ water per gram of precipitate to remove all the $Cl^-$ from the catalyst. The filtered solid was then vacuum dried at room temperature for 6 h. Alternative drying methods were also explored *vide infra*; these included rotary evaporation (at 70 °C for 6 h), freeze drying (coolant; acetone and dry ice, 6 h), and oven drying (100 °C for 6 h).

For the CP prepared catalysts, aqueous solutions of $HAuCl_4$ (~1.2 mM), $(NH_4)_2Ce(NO_3)_6$ (0.3 M) and $ZrO(NO_3)_6 \cdot xH_2O$ (0.3 M) were mixed under continuous stirring. The mixture was then heated to 60 °C and an aqueous solution of $Na_2CO_3$ was added while maintaining a pH of 8.0. The precipitate was then aged at 60 °C for 1 h, filtered, washed with deionized water and dried using the different drying processes as described above for the DP method.

Urea gelation co-precipitation has also been used. In this case aqueous solutions of $HAuCl_4$ (~1.2 mM), $(NH_4)_2Ce(NO_3)_6$ (0.3 M), $ZrO(NO_3)_6 \cdot xH_2O$ (0.3 M) and urea (4 M) were mixed and heated to 80 °C under continuous stirring. An aqueous solution of $NH_4OH$ was added drop wise and the resulting precipitate was aged at 80 °C for 8 h, filtered, washed with deionized water and dried using the different drying processes described for the DP method.

Two methods of sulfating the $Au/CeZrO_4$ catalysts were utilised. A $Ce(OH)_4$–$Zr(OH)_4$ hydroxide gel was used as the starting material adapting from the method reported by Kuperman and Moir [33]. The gel was prepared by the CP method using $(NH_4)Ce(NO_3)_6$ (0.1 M) and $ZrO(NO_3)_2 \cdot xH_2O$ (0.1 M) aqueous solutions and $NH_4OH$ as the precipitant. The gel was dried at 110 °C for 12 h and then sulfated by addition of a 0.5 M $H_2SO_4$ solution (with constant stirring for 1 h) to achieve 0.09 mol of pure $H_2SO_4$ per gram of the gel. The sulfated gel was then dried at 120 °C for 3 h and calcined at 650 °C for 4 h to form CZS-I. Following formation of CZS-I, gold deposition, via the DP method, followed by vacuum drying was used to form the final catalyst. For support CZS-II, a similar method as the one described for the CZS-I was adopted except that all the starting materials: $(NH_4)Ce(NO_3)_6$ (0.1 M), $ZrO(NO_3)_2 \cdot xH_2O$ (0.1 M) and 0.5 M $H_2SO_4$ were mixed prior to precipitation/formation of the hydroxide gel. $NH_4OH$ was used to precipitate the gel, thereafter the precipitate was filtered, dried at 120 °C for 3 h and calcined at 650 °C for 4 h before deposition of the Au again by DP.

### 2.2. Catalyst characterisation

The gold content was measured by ICP-OES (Optima 4300 DV, Perkin-Elmer) and the specific surface area and porosity by BET (Micromeritics ASAP 2010). XRD analysis of the catalysts was performed using a PANalytical X'Pert Pro X-ray diffractometer using Cu Kα X-ray source with a wavelength of 1.5405 Å.

### 2.3. Activity testing

The catalyst activity was tested in a plug flow tube microreactor held in a temperature controlled furnace with a thermocouple measuring the temperature in the middle of the bed. Typically, 150 mg of catalyst was heated at 1 °C $min^{-1}$ to 100 °C under He and then from 100 °C to 200 °C under the WGS feed. The feed consisted of 2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$ (total flow 100 $cm^3\,min^{-1}$; gas flow controlled by Aera mass flow controllers). The purity of the gases was >99.95% (supplied by BOC). A stable flow of water vapour was established by passing the feed (CO, $CO_2$ and $H_2$) through a saturator/condenser system. The temperature of the saturator was maintained slightly above the temperature required to give a water vapour pressure of 7.5 kPa with the excess water vapour removed in a glass condenser. Both reactants and products were analysed by GC (Perkin Elmer; Auto System XL ARNEL) equipped with a thermal conductivity detector.

### 2.4. DRIFTS study of CO adsorption at room temperature

The DRIFT spectra of the adsorption of CO over the supported gold catalysts (50 ± 5 mg) were recorded using a Bruker Equinox 55 spectrometer using an average of 128 scans and a resolution of 4 $cm^{-1}$. The DRIFTS setup consisted of an *in situ* high temperature diffuse reflectance IR cell (Spectra-Tech) fitted with ZnSe windows which was modified in house to behave as a plug flow reactor, the details of which have been previously reported [44]. The back-

**Table 1**
Comparison of the % CO conversion at 200 °C under the WGS feed (2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$) for 2 wt% Au/$CeZrO_4$ catalysts prepared by co-precipitation, urea gel co-precipitation and deposition precipitation methods with the catalyst slurry dried using different methods – oven at 100 °C for 6 h, rotary evaporator at 70 °C for 6 h, vacuum dried at room temperature for 6 h and freezing using a acetone/dry ice bath for 6 h.

| Preparation method | Drying method | % CO conversion at 200 °C |
|---|---|---|
| Co-precipitation | Oven | 18.6 |
| | Rotary evaporation | 15.0 |
| | Vacuum | 5.2 |
| | Freeze | 6.8 |
| Urea gel co-precipitation | Oven | 26.0 |
| | Rotary evaporation | 24.1 |
| | Vacuum | 3.3 |
| | Freeze | 1.8 |
| Deposition precipitation | Oven | 78.0 |
| | Rotary evaporation | 94.0 |
| | Vacuum | 92.9 |
| | Freeze | 88.0 |

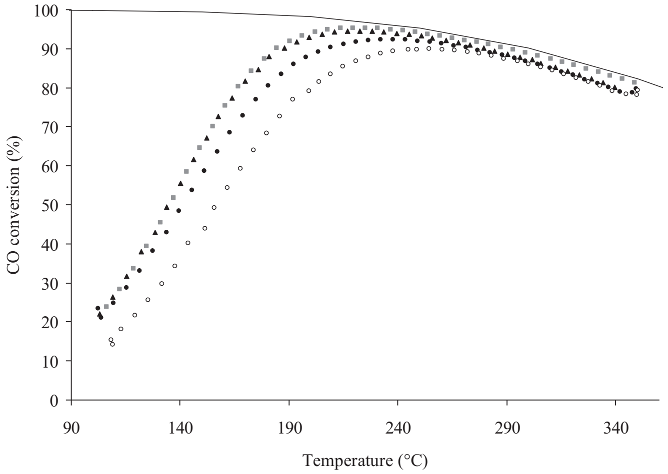

**Fig. 1.** 2 wt% Au/$CeZrO_4$ catalysts prepared by deposition precipitation of the Au, comparing the WGS activity at increasing reaction temperature (feed = 2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$), for catalysts dried under vacuum at room temperature (grey squares), oven dried at 100 °C for 6 h (open circles), dried by rotary evaporation for 6 h (black triangles) or freeze dried for 6 h in an acetone/dry ice bath (black circles). Solid line shows the equilibrium CO conversion with increasing temperature.

ground was recorded with a fresh catalyst under Ar at 25 °C prior to introduction of 2% CO in Ar (total flow 50 $cm^3$ $min^{-1}$). All DRIFT spectra are displayed as Log 1/$R$ where $R$ is the relative reflectance ($R$ = reflectance recorded under 2% CO in Ar/reflectance recorded under Ar) [45].

All spectra have been corrected for contributions due to unreacted gas-phase CO and the electronic transition from the reduced ceria–zirconia which was recorded following the desorption of CO [46–48]. However, no electronic transition was subtracted from the sulfated-$CeZrO_4$ supported catalysts since the Au–CO band intensities were very low and there was no evidence of a band/shoulder at 2125 $cm^{-1}$ on the main Au–CO band (see supplementary information). This is consistent with sulfated Pt/$Ce_xZr_{1-x}O_2$ catalysts where the electronic transition band was not observed at temperatures below 150 °C under $H_2$ [49].

## 3. Results and discussion

### 3.1. Activity data

### 3.1.1. Effect of Au deposition method and precipitate drying method

Table 1 reports a comparison of the CO conversion at 200 °C for 2% Au/$CeZrO_4$ catalysts prepared by co-precipitation (CP), urea gel co-precipitation (UGC) or deposition precipitation (DP) methods where the slurry obtained during the preparation has been dried either in an oven at 100 °C for 6 h, a rotary evaporator at 70 °C for 6 h, vacuum dried at room temperature for 6 h, or freeze dried using an acetone/dry ice bath for 6 h. Of the preparation methods explored, the deposition precipitation method gave the most active catalysts irrespective of the drying method employed (Fig. 1). Catalysts prepared by the CP and UGC methods were significantly less active than the catalysts prepared by DP with maximum CO conversions of 50% and 60% at 340 °C for the CP and UGC methods, respectively. Regarding the impact of the drying method on the catalysts prepared by the DP method, the vacuum method gave the best results followed by the rotary drying and the freeze drying with CO conversions of 94, 93 and 88% at 200 °C, respectively. Oven drying for DP prepared catalysts gave the lowest activity (∼78% CO conversion at 200 °C) compared with the other drying methods, however this drying method gave the best results for the catalysts prepared by the CP and UGC methods (Table 1). The difference in behaviour between the DP and the CP or UGC preparation methods stems from the different catalysts architectures obtained. In the case of the DP method, the gold is deposited on a pre-formed oxide surface and the drying method will impact on the gold-oxide surface interaction. In the case of the CP or the UGC methods, both the oxide formation and the gold incorporation occur during the catalyst preparation process which leads to a different catalyst architecture than that obtained by the DP method. For example, core-shell structure or gold encapsulation may be obtained. The drying method will, therefore, affect both the gold and the oxide. It is, therefore, not surprising that for the same drying procedure different results are obtained in the case of the CP or UGC compared to the DP preparation method.

For the DP method, while the vacuum drying gave the catalyst with the highest activity, the vacuum drying was carried out at room temperature while the other methods were performed at higher temperatures (70–100 °C). To probe the effect of temperature on the drying method, the vacuum and oven drying were also carried out at 70 °C using either an oil bath or a microwave oven to heat the sample. Fig. 2 shows the performance of the catalysts dried under vacuum at room temperature and 70 °C using an oil bath as well as the activity of the catalysts dried in an oven at 70 or 100 °C. Vacuum drying the DP catalyst at 70 °C using an oil bath led to reduced activity compared with the material obtained after room temperature treatment while drying using a microwave oven led to a totally inactive catalyst. The results obtained with the microwave oven are consistent with results reported for Au/$Fe_2O_3$ catalysts where reduced activities have been observed following drying using microwave irradiation compared with the catalysts obtained using more conventional drying method [17]. When the catalyst was dried in the oven at 70 °C, higher activity was obtained compared with the catalyst formed after drying at 100 °C. In this case the activity was similar to that of the catalyst vacuum dried at room temperature.

The results obtained for both the vacuum and oven drying method are consistent with the need to decrease the contact of water at high temperature in order to maintain the gold–support interaction. As reported in [42] water has been proposed to cause deactivation of the catalyst on stream and methods to reduce the water retained on the catalyst after the washing step could affect the activity and stability of the catalysts. A fine balance between the drying temperature and the pressure (ambient versus reduced pressure) is necessary to ensure high catalytic activity. It is likely that the final gold dispersion and interaction with the support is

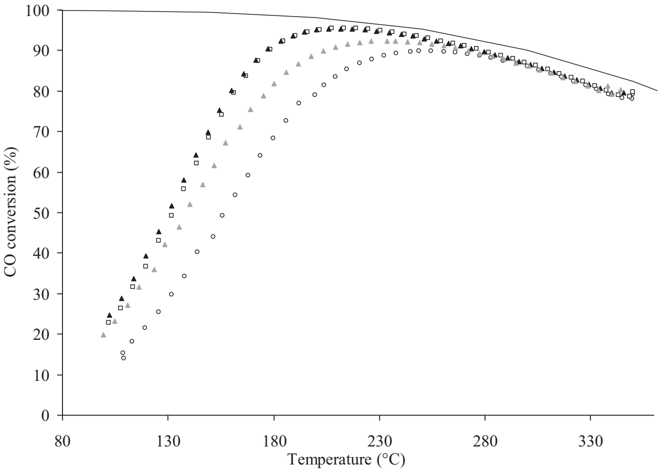

**Fig. 2.** 2 wt% Au/CeZrO$_4$ catalysts prepared by deposition precipitation of the Au, comparing the drying method and temperature on the WGS activity with increasing reaction temperature (feed = 2% CO, 2% CO$_2$, 8.1% H$_2$ and 7.5% H$_2$O) for catalysts after drying in an oven at 70 °C for 6 h (open squares), 100 °C for 6 h (open circle), vacuum drying at 70 °C for 6 h (grey triangles) and at room temperature for 6 h (black triangles). Solid line shows the equilibrium CO conversion with increasing temperature.

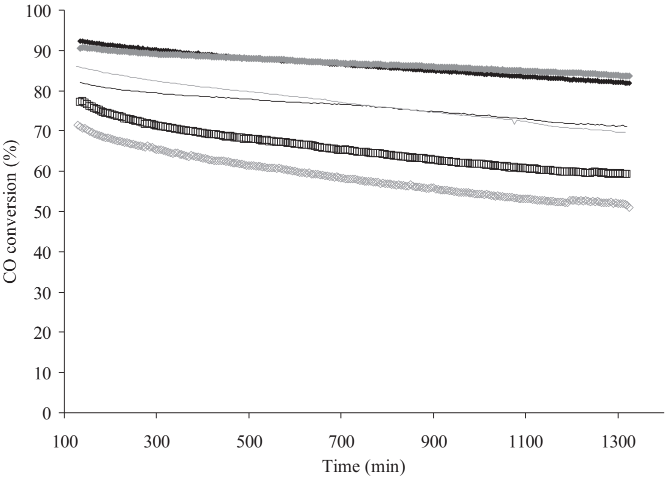

**Fig. 3.** Comparison of % CO conversion with time for the WGS reaction at 200 °C (feed = 2% CO, 2% CO$_2$, 8.1% H$_2$ and 7.5% H$_2$O) for catalysts prepared from AuBr$_3$ (washed with water, thin grey line) and HAuCl$_4$ washed with different washing solvents; no washing (open grey diamonds), water (black diamonds), 0.1 M NH$_4$OH (grey diamonds), 5 M NH$_4$OH (thin black line) and 0.1 M Na$_2$CO$_3$ (open black squares).

conditioned by the rate at which the water is removed and the mobility of gold hydroxide ensembles during the drying step [50]. At 70 °C, the rate of water removal will be quicker during vacuum drying compared with that obtained under ambient pressure, while this will reduce any possible hydrolysis of the gold–support interaction and subsequent gold mobility (expected to be low at this temperature), this will also lead to a rapid precipitation of the gold hydroxide and, therefore, a reduced dispersion of the gold on the support surface. At room temperature the rate of possible hydrolysis of the gold–support interaction will be further reduced and the rate of water removal will be slow enough for the gold to be well dispersed. Under ambient conditions at 70 °C, again hydrolysis will be slow and the rate of water removal lower than that under vacuum leading to a better dispersed gold. At 100 °C, hydrolysis will dominate the process leading to enhanced gold hydroxide mobility and therefore reduced gold dispersion which is detrimental to the catalytic activity [51].

### 3.1.2. *Effect of the nature of the washing solvent*

Washing the precipitate to remove residual halide has been shown to be critical in determining both the activity and stability of many catalysts. For example, the presence of residual chloride has been reported to cause agglomeration of the Au particles upon heat treatment [52] and also to block the active sites [53]. Oh et al. reported for selective oxidation of CO on Au/Al$_2$O$_3$ catalysts that the activity of the catalyst was increased over 20-fold by removal of chloride prior to calcination of the catalyst with no change in Au particle size.

To investigate the influence of the nature of the washing solution, the precipitate obtained after gold deposition through the DP method was washed using water, an aqueous solution of 5 M NH$_4$OH, an aqueous solution of 0.1 M NH$_4$OH, or an aqueous solution of 0.1 M Na$_2$CO$_3$ before being vacuum dried at room temperature for 6 h. It should be noted that no effect on the final Au loading was observed via ICP as a function of the pretreatment solution (see supplementary information). Fig. 3 compares the activity at 200 °C over a period of ~1200 min for the four catalysts obtained. The results obtained indicated that washing with 0.1 M Na$_2$CO$_3$ or 5 M NH$_4$OH resulted in lower activity compared with the catalyst pretreated with water or a 0.1 M NH$_4$OH solution. In these cases, although pretreatment in water led to a slightly more active catalyst improved catalyst stability was found following washing with 0.1 M NH$_4$OH.

In the case of Au/hydrocalcite CO oxidation catalysts prepared by direct anionic exchange [12,54] it has been observed that the size of the Au particles was found to vary with the solvent used to wash the catalyst, in this case warm water or ammonia solutions. Washing with ammonia solution led to smaller Au particles. As the concentration of ammonia solution was increased smaller Au particles were formed yet this resulted in a catalyst with a CO oxidation activity lower than that achieved following washing with water which gave a catalyst with larger Au particles. It was proposed that ammonia could modify the support and, therefore, the catalyst activity.

The nature of the metal–support interaction is critical in the case of Au/CeZrO$_4$ WGS catalysts [41]. The higher stability of the catalysts washed with the 0.1 M ammonia solution compared with that obtained via the water pretreatment may be due to the increased efficiency of removal of chloride, while the lower activity observed could be due to slight modification of the CeZrO$_4$ support and/or change in the gold dispersion following washing with the ammonia solution. The lower performance observed following washing with the 5 M ammonia solution may be a consequence of a more dramatic modification of the ceria–zirconia support.

In the case of washing with a 0.1 M Na$_2$CO$_3$ solution, the resultant catalyst displayed the worst performance of all the washing pretreatments used. This may be understood by the formation of strongly bound carbonate species on the catalyst support. This is supported by the DRIFT spectra. Although all the fresh catalysts showed carbonate species were present, the spectrum of the catalyst washed with 0.1 M Na$_2$CO$_3$ showed significantly more carbonates than the ones obtained for the samples washed with water or the ammonia solutions (see supplementary information).

The effect of the nature and concentration of washing solution on catalyst activity and stability is a balance between the ability of the solution to remove chloride from the catalyst and modification of the support which could affect the Au dispersion or the ability of the Au nanoparticles to wet the surface reducing the contact/strength of interaction between the Au and support which is key for the high WGS activity. Pretreatment of Au/CeZrO$_4$ catalysts with carbonic acid has been shown previously to have a detrimental effect on catalyst activity and stability and the removal of CO$_2$

**Table 2**
Summary of the BET surface areas of the, $ZrO_2$, $Ce_{0.5}Zr_{1.5}O_4$, $CeZrO_4$, $Ce_{1.5}Zr_{0.5}O_4$ and $CeO_2$ supports together with the 2 wt% Au/$CeZrO_4$ catalyst.

| Support/catalyst | % Au loading | Surface area ($m^2\ g^{-1}$) |
|---|---|---|
| $ZrO_2$ | – | 61.8 |
| $Ce_{0.5}Zr_{1.5}O_4$ | – | 42.2 |
| $CeZrO_4$ | – | 64.7 |
| $Ce_{1.5}Zr_{0.5}O_4$ | – | 84.1 |
| $CeO_2$ | – | 93.5 |
| 2 wt% Au/$CeZrO_4$ | 2.1 | 63.0 |

from the WGS feed following a period of reaction under the full feed has also been shown to improve the stability [43]. Hydrolysis of the adsorbed carbonates/hydrogen carbonates under the WGS feed could be enhancing the rate of restructuring of the Au nanoparticles leading to them becoming detached from the support.

### 3.1.3. *Effect of the nature of the Au precursor*

In order to assess to impact of the nature of the gold precursor on the activity of the Au/$CeZrO_4$, catalysts were prepared with either a chlorine based ($HAuCl_4$) or a bromide based ($AuBr_3$) metal precursor. Fig. 3 reports the activity test for 2 wt% Au/$CeZrO_4$ catalysts prepared from $HAuCl_4$ and $AuBr_3$ by the DP method (washed with water) with vacuum drying at room temperature. The result obtained clearly showed that the catalyst prepared using the $HAuCl_4$ precursor is significantly more active and stable than the catalyst prepared from $AuBr_3$.

As noted previously, the presence of residual chloride can have a detrimental impact on both the activity and stability of the catalysts. Residual bromide is likely to have a similar effect and the decreased activity compared with the catalysts formed via the chloride precursor may be associated with the reduced solubility of bromide, in general, compared with chloride in water leading to less efficient removal.

Bromide has been shown to poison Au/$TiO_2$ catalysts for CO oxidation [55]. Oxford et al. found that the halide prevented the full reduction of the Au by displacing oxyhydroxy ligands and remained bound to the Au even following a low temperature reduction step. They observed that the adsorbed $Br^-$ preferred to be associated with the Au and not the support with no evidence for oxidation of the $Au^0$ (from XANES and CO adsorption studied by FTIR) which likely resulted in active site poisoning. Therefore, given the importance of the formation of $Au^0$ in the case of Au/$CeZrO_4$ WGS catalysts, [42,43] a similar effect may be occurring in the present case.

### 3.1.4. *Effect of support: Ce:Zr ratio and calcination temperature of the support*

Our results have demonstrated that ceria–zirconia mixed oxide based catalysts display significantly higher activity than the corresponding ceria, zircona or titania based catalysts prepared via the DP methods [37]. However, to the best of our knowledge, there have been no significant studies undertaken regarding the impact of the Ce:Zr mole ratio on the Au/$CeZrO_x$ activity. This is despite the fact that this ratio is known to have a significant impact on the reducibility of the support which has been reported as a major factor influence WGS catalytic activity [35].

A series of 2 wt% Au/$CeZrO_x$ ($0 < x < 1$) catalysts were prepared by co-precipitation and gold deposited by the DP method (washed with water) and vacuum dried at room temperature. Table 2 reports the specific surface area of supports used in the study together with the surface area of the 2 wt% Au/$CeZrO_4$ catalyst. The deposition of the gold on the supports only had a marginal effect on the specific surface, with for example a specific surface area of 64.7 $m^2\ g^{-1}$ for the bare $CeZrO_4$ and 63.0 $m^2\ g^{-1}$ after gold deposition. Fig. 4 reports the activity results for all the catalysts prepared and showed the order of activity Au/$CeZrO_4$ > Au/$Ce_{0.5}Zr_{1.5}O_4$ > Au/$CeO_2$ > Au/$Ce_{1.5}Zr_{0.5}O_4$ ≈ Au/$ZrO_2$. On varying the composition of the mixed oxide in this study it was expected that the supports that would give the best performances would have been Au/$CeZrO_4$ and Au/$Ce_{1.5}Zr_{0.5}O_4$ catalysts, i.e. either cerium rich or with the equimolar stoichiometric ratio, since it has been reported that these mixed oxides exhibit enhanced oxygen storage capacity, OSC [38,56,57]. These supports maximise the redox behaviour and stability over extended red/ox cycles which is thought to promote the WGS reaction [37]. However, these catalysts exhibit the highest and lowest WGS activity under the conditions used in this study which suggests that the WGS activity is not solely correlated with the OSC capability of the mixed oxide support. It is also important to note that, as found previously, Au/$CeZrO_4$ catalysts are more active than Au/$ZrO_2$, which is in contrast to the work of Boaro et al. wherein they reported Au/$ZrO_2$ to be more active than Au/$CeZrO_4$. However, they also observed that that the redox properties of the support play a secondary role with the nature of the metal–support interface having a significant influence on the activity [36].

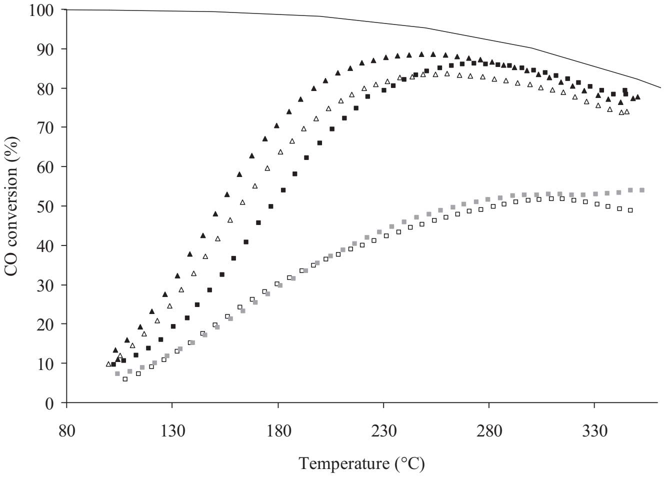

**Fig. 4.** Comparison of WGS activity with increasing reaction temperature (feed = 2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$) for 2 wt% Au/$CeO_2$ (black squares), 2 wt% Au/$ZrO_2$ (open squares) and catalysts with varied $CeO_2$:$ZrO_2$ ratio; 2 wt% Au/$CeZrO_4$ (black triangles), 2 wt% Au/$Ce_{0.5}Zr_{1.5}O_4$ (open triangles) and 2 wt% Au.$Ce_{1.5}Zr_{0.5}O_4$ (grey squares). Solid line shows the equilibrium CO conversion with increasing temperature.

The effect of the support surface area and porosity was also investigated by varying the calcination temperature of the $CeZrO_4$ support prior to gold deposition. When the support was calcined in air at 500 °C, higher WGS activity was obtained compared with calcination of the support at 300 or 400 °C (results not shown). A second calcination step at 600, 800 or 1000 °C following the initial calcination at 500 °C, resulted in a decrease in surface area and an increase in pore diameter (Table 3). The second calcination step did not alter the cubic structure of the support for any of the calcination temperatures explored as shown by powder XRD. No change in WGS activity was observed following the second

**Table 3**
Comparison of Au loading, surface area and average pore diameter for 2 wt% Au/$CeZrO_4$ catalysts calcined at 500 °C and then re-calcined at 600, 800 or 1000 °C.

| Re-calcination temperature (°C) | % Au loading | Surface area ($m^2\ g^{-1}$) | Average pore diameter (nm) |
|---|---|---|---|
| – | 2.1 | 64.7 | 11.1 |
| 600 | 2.1 | 58.4 | 12.3 |
| 800 | 2.2 | 43.9 | 15.5 |
| 1000 | 1.5 | 4.9 | 67.0 |

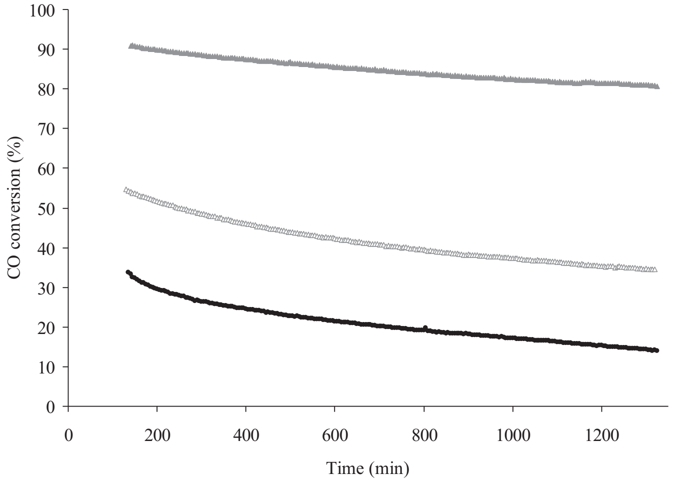

**Fig. 5.** Comparison of WGS activity with time for Au supported on $CeZrO_4$ (grey triangles) and sulfated $CeZrO_4$ catalysts; Au/CZS-I (black circles) and Au/CZS-II (open triangles), under the WGS feed at 200 °C (feed = 2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$).

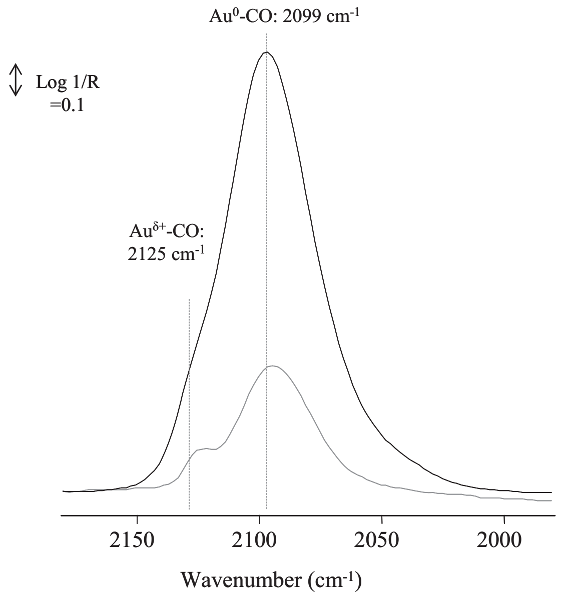

**Fig. 6.** DRIFT spectra of room temperature adsorption of 2% CO/Ar over 2 wt% Au/$CeZrO_4$ catalyst (black line) compared to the Au–CO bands obtained over a 2 wt% Au/$CeZrO_4$ under the WGS feed (2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$; grey line) at 150 °C.

calcination at 600 or 800 °C compared with that of the catalyst prepared with a support calcined once at 500 °C. However, following the calcination at 1000 °C, the activity of the catalyst was significantly reduced (Table 2). This latter result is easily understood from the observation that the calcination at 1000 °C led to a dramatic drop of the support surface area from 65 $m^2 g^{-1}$ to 5 $m^2 g^{-1}$. Moreover, this decrease in surface area also altered the amount of gold that could be deposited on the support since the gold loading achieved was only 1.5 wt% compared to 2.1 wt% for all supports calcined at lower temperatures (see supplementary information). This decreased gold capacity is likely due to a lowering in the number of defects on the support which can influence the number of sites onto which the deposited gold can anchor following high temperature treatment.

### *3.1.5. Effect of support: sulfation of Ce:Zr*

Sulfation of the $CeZrO_4$ support, prior to addition of Au by the deposition precipitation method, was carried out by two different methods; one based on the patent of Kuperman and Moir [33] (Au/CZS-I) and another where all the reagents were added together in a one pot synthesis (Au/CZS-II). Fig. 5 reports the activity for the 2 wt% Au supported on $CeZrO_4$ and sulfated $CeZrO_4$ catalysts under WGS reaction conditions at 200 °C over a period of 1200 min. For both sulfation methods, the catalysts prepared with the sulphated $CeZrO_4$ support exhibited lower activity compared with the non-sulfated support with Au/CSZ-II showing the lowest activity. Unlike reports for Au/$ZrO_2$ catalysts [33,35], no improvement in activity was observed on sulfating $CeZrO_4$ supports.

For the Au/CZS-I, XRD of the catalyst showed the same cubic structure of a ceria–zirconia solid solution as found for the non-sulfated catalyst indicating that the effect is mainly surface related (see supplementary information). However, for Au/CZS-II, where all the reagents were added together, the cubic structure was clearly modified leading to a disrupted support structure which may explain the significant decrease in the activity of the catalyst.

## *3.2. CO adsorption as a probe of catalyst activity*

The infrared spectra of CO adsorption have been used to characterise the state of gold on the support. Fig. 6 shows a comparison of the adsorption of CO at room temperature on a 2 wt% Au/$CeZrO_4$ catalyst (calcined at 500 °C, DP method used to deposit the Au, washed with water and vacuum dried at room temperature) with that obtained under WGS conditions at 150 °C. In both cases, bands in similar positions were observed. Under WGS reaction conditions (150 °C with feed of 2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$) CO adsorbs on Au with a main feature at 2098 $cm^{-1}$ assigned to CO adsorbed on metallic gold. A shoulder at higher wavenumber (2125 $cm^{-1}$) is also observed which has been assigned to $Au^{\delta+}$–CO species. $Au^{\delta+}$ species have been proposed to be very active for the WGS reaction [28]. However, these $Au^{\delta+}$ species have been observed to be unstable over Au/ceria–zirconia catalysts and are rapidly reduced to zero valent gold when in contact with the WGS feed [43].

Following room temperature CO adsorption, the position of the $Au^0$–CO band occurs at 2099 $cm^{-1}$ for catalysts prepared from different Au precursors and for the sulphated supported catalysts (supplementary information). However, for the catalyst washed with $Na_2CO_3$ the $Au^0$–CO band is red-shifted slightly to 2091 $cm^{-1}$. DRIFT spectra of the 0.1 M $Na_2CO_3$ catalysts showed that prior to adsorption of CO there were more carbonates on the support than for all the other catalysts irrespective of the method of preparation. The increased surface carbonate present may imply the presence of small amounts of sodium on the catalyst which, therefore, could be the reason for the change in the Au–CO band position observed.

A general trend was observed between the catalytic activity at 100 °C (% CO conversion $\leq$30% for the catalysts to ensure comparison of rates of the forward WGS reaction away from the equilibrium) and the Au–CO band area with the most active catalysts having the more intense Au–CO bands (Fig. 7). The data shown in Fig. 7 is for catalysts supported on $CeZrO_4$ with a range of gold loadings, prepared using different washing solutions and from different gold precursors. These latter results suggest that the activity of the various catalysts may be correlated with CO chemisorption on Au species and, moreover, that the concentration of such species is affected by the method used to prepare the catalysts. The nature of the interaction between the active fraction of the gold and the support is likely to be of a similar kind as that reported in [41–43]. This interaction conditions the adsorptive properties of the gold with respect to CO and the main difference between catalysts exhibiting different activities correspond to the relative fraction of the gold exhibiting the necessary intimate interaction with the support. Linear trends were observed

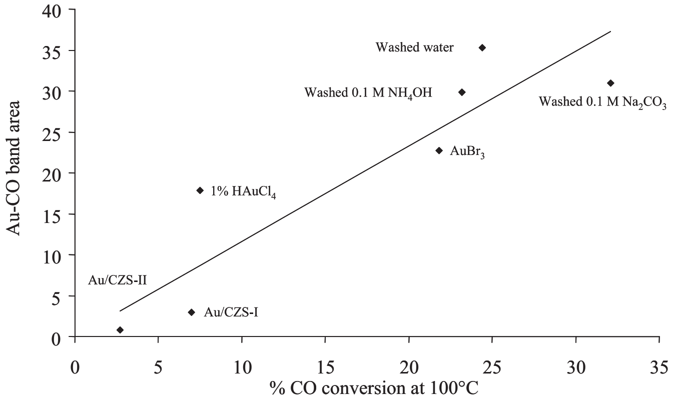

**Fig. 7.** % CO conversion at 100 °C for catalysts under WGS feed (2% CO, 2% $CO_2$, 8.1% $H_2$ and 7.5% $H_2O$) against Au–CO band area for room temperature adsorption of 2% CO/Ar on 2% Au/$CeZrO_4$ (prepared from $HAuCl_4$) washed with water, 0.1 M $NH_4OH$ and 0.1 M $Na_2CO_3$, 2% Au/$CeZrO_4$ prepared from $AuBr_3$ washed with water, 1% Au/$CeZrO_4$ prepared from $HAuCl_4$ and washed with water and sulphated Au/$CeZrO_4$ catalysts (Au/CZS-I and Au/CZS-II).

for both $Au^{\delta+}$ and $Au^0$ species; however, less than 5% of the Au was in the oxidised form. This trend is consistent with the recent report that a linear relationship between Au dispersion (from pulse-flow CO chemisorption at 157 K) and WGS activity was observed for Au/$ZrO_2$ (and sulphated Au/$ZrO_2$) catalysts for the low temperature WGS reaction [62].

It was notable that the Au–CO adsorption bands were very weak for the catalysts prepared with sulfated supports compared with that obtained for catalysts with similar Au loadings on unsulfated supports (see supplementary information). This notable difference is likely to be related to the size and/or shape of the Au nanoparticles due to the preparation method altering the nature of the Au species formed on the catalyst with more Au being in an inactive form and unable to adsorb CO. This hypothesis is consistent with the well acknowledged observation that CO does not adsorb on Au terrace sites and will only significantly bind to low co-ordination sites, e.g. those with a coordination number (CN) $\leq$7 and defects even at low temperatures [58,59]. We conclude that CO adsorption may be an indicator of activity in the WGS reaction and for a series of similar catalysts (as is the case with our non-sulfated catalysts prepared in different ways) the quantity of CO adsorbed is likely to be only proportional to the true number of active sites. For example, if the CO is only adsorbed at sites with a CN $\leq$7 it may be that the CO measures all such sites but only those which are located at the gold/support interface are actually important for the WGS reaction. This would certainly explain the great importance of the support in the WGS reaction but it would differ from the recent proposal [60] that CO only adsorbs on corner sites and that these are the active sites for WGS even if they are far away from the gold/support interface.

Cíes et al. [59] and Calvino and co-workers [61] recently reported a detailed volumetric adsorption, FTIR, computer modelling and HAADF-STEM of Au/$CeZrO_x$ catalysts with different dispersions which provided an insight into the mechanism by which CO adsorbed on these catalysts can be transferred from the metal centre to the support by a spillover mechanism. Therein, the amount of CO adsorbed at 308 K on the support of 2.5 wt% Au/$Ce_{0.62}Zr_{0.38}O_2$ catalysts was significantly increased by the presence of Au compared with that over the bare support [59]. The amount of CO, adsorbed irreversibly as carbonates on the support, was found to increase with the Au dispersion. It was estimated that the total surface area of the support that became covered with spilt-over CO was 57% and 23% for the high (68%) and medium (49%) gold dispersion catalysts, respectively. It is also interesting to note that for catalysts prepared by the DP method with the same support and Au loading, but only changing the precipitating agent from sodium carbonate to urea, significant changes in the Au dispersion was observed leading to high and medium dispersions, respectively. This demonstrates the importance of the surface composition in determining the wetting ability of the Au on the oxide and how small changes can significantly affect the catalyst structure and thus the activity.

## 4. Conclusions

A range of preparation methods were examined for the formation of active low temperature gold based water gas shift catalysts. The drying procedure was found to be particularly important as was the choice of gold precursor. In addition, the maximum activity was observed for equimolar Ce:Zr ratios in the mixed oxide support. Importantly, unlike in the case of zirconia supported materials, sulfation only lead to lower activity and stability of the catalysts. Over the range of catalysts prepared, a correlation of their activity with the surface concentration of adsorbed CO on the gold was observed showing that this may be used as a measure of the relative number of available active sites for the water gas shift reaction.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.04.053.

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