PAPER

Impact of Ce–Fe synergism on the catalytic behaviour of Au/CeO₂–FeO_x/Al₂O₃ for pure H₂ production

Cite this: *Catal. Sci. Technol.*, 2013, **3**, 779

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In this work the development of a series of gold catalysts, essentially based on γ -alumina promoted with a small superficial fraction of Ce–Fe mixed oxides, is reported. The catalytic behaviour is evaluated in the water gas shift reaction. The formation of a Ce–Fe solid solution is evidenced by XRD and related to the catalytic activity where the importance of the Ce–Fe interaction is demonstrated. The best catalyst reached CO conversions very close to the equilibrium limit. A long-term stability test is performed and the loss of activity is observed and attributed to reaction intermediates. Almost complete recovery of the initial conversion is achieved after oxidation treatment, suggesting that the problem of stability could be overcome by a suitable change in the reaction parameters thus leading to a highly efficient catalyst for future applications in H₂ production and clean-up.

Received 31st July 2012,
Accepted 21st November 2012

DOI: 10.1039/c2cy20537h

www.rsc.org/catalysis

Introduction

Nowadays, hydrogen is mostly produced from fossil fuels by a multistep process that includes catalytic or autothermal reforming of hydrocarbons, followed by water-gas shift reaction (WGSR). Steam reforming is the most popular mode of generating “water gas” (a mixture of hydrogen and carbon monoxide), especially if the ultimate objective is the generation of pure hydrogen since it provides the highest H₂/CO molar ratio. Generally, the reformat gas is then submitted to WGSR ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$), which has attracted renewed interest in the last decade due to the increasing demands for high-purity hydrogen in conjunction with fuel-cell power generation. A crucial prerequisite for the techno-economic success of fuel cells, especially those that operate either at low temperatures (like the Polymer Electrolyte Membrane Fuel Cells, PEMFC) or in mobile applications (as in automobiles), is the discovery of improved reforming and WGSR catalysts for the generation of hydrogen which are much more active than those used in chemical plants.¹

Common industrial catalysts for WGSR (mixtures of Fe–Cr oxides for high temperature WGSR or Zn–Al–Cu oxides for low

temperature WGSR) are pyrophoric and normally require lengthy and complex activation steps before usage. In response to these needs, noble metal-based WGSR catalysts are under intense development.^{2–6}

Burch summarized recently⁷ the advantages and drawbacks of the gold catalysts for water gas shift reaction. This review shows that well prepared gold catalysts are more active than the corresponding platinum catalysts. However, the activity of the gold catalysts is strongly dependent on the method of preparation and the pre-treatment conditions and especially on the existence of a contact interface between gold and the metal oxide support. In the last decade, CeO₂ has become the most used support for this reaction.^{8,9} The promotion of WGS activity by ceria is due to its ability to undergo fast reduction–oxidation cycles related to its high oxygen storage capacity (OSC) and reducibility.¹⁰ Both could be influenced by the addition of elements with different ionic radii and/or oxidation states thus altering the ceria band structure and decreasing the energy barrier for oxygen migration and exchange.¹¹ It has been reported¹² that the properties and application of the ceria-based solid solutions depend on its defect chemistry, *e.g.* concentrations of oxygen vacancies and reduced cations (Ce³⁺) and on critical parameters of the dopant cation, such as ionic size and valence. Iron is an interesting ceria dopant, especially because it has its own redox behaviour (Fe³⁺/Fe²⁺) and intrinsic activity in WGSR. In the case of Ce–Fe systems, although the solubility of Fe into the CeO₂ network is low, the formation of solid solution has been demonstrated only below a certain

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amount of iron.¹³ Our previous study evidences that a monolayer of Fe₂O₃ over a commercial ceria-alumina support promotes CO abatement ability even without the solid solution formation.¹⁴ However, as mentioned above, the biggest effect on the redox behaviour of ceria and on the WGS activity could be expected when an intimate contact between the components exists, implying the existence of solid solution and controlled deposition of gold nanoparticles.

Despite the large number of gold catalysts studied for the WGS, it is still difficult to find in the literature well performing and economically viable ones. This work is focused on the development of gold catalysts, supported on γ -alumina modified with a small superficial fraction of Ce-Fe mixed oxides as a very efficient system for the WGS.

Experimental

Catalyst preparation

Support preparation. In a typical preparation, the desired amounts of Ce(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O (Aldrich) were impregnated on γ -alumina powder (Sasol). The impregnation was carried out in 50 mL of ethanol, evaporated at 50 °C till the dry solid was obtained at reduced pressure in a rotary evaporator. The obtained solid was treated with NH₃ solution (10 mol L⁻¹) for 30 min in order to assure the full conversion of the nitrates to hydroxides. The support was then filtered, dried and calcined at 773 K for 4 hours. The initial precursor quantities (CeO₂, Fe₂O₃ or CeO₂ + Fe₂O₃) are calculated to result in *ca.* 15 wt% of the final solid. The amount of Fe₂O₃ added to promote CeO₂ varies in the range of 0 to 3 wt%. In the adopted nomenclature the oxygen is omitted for simplification and the Fe₂O₃ contents are expressed as the catalysts theoretical loading. For example, the CeFe0.5/Al solid contains 15 wt% CeFe mixed oxide deposited on Al₂O₃, in which the Fe₂O₃ loading is 0.5 wt%.

Gold deposition. The gold was deposited by the direct anionic exchange method, assisted by NH₃ as described elsewhere.¹⁵ A 10⁻⁴ mol L⁻¹ aqueous solution of the gold precursor HAuCl₄ (Alfa Aesar) was used in order to obtain a final Au loading of 2 wt%. The support was sieved and the 100–200 μ m fraction retained. After Au deposition the solid was dried in an oven at 373 K overnight and calcined in air at 573 K for 4 h.

Characterization

The chemical composition of the samples was determined by X-ray microfluorescence spectrometry (XRMF) in an EDAX Eagle III spectrophotometer with a rhodium source of radiation. The textural properties were studied by N₂ adsorption-desorption measurements at liquid nitrogen temperature. The experiments were carried out on a Micromeritics ASAP 2010 instrument. Before analysis, the samples were degassed for 2 h at 150 °C in vacuum.

X-ray diffraction (XRD) analysis was performed on an X'Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu K α radiation (40 mA, 45 kV) over a 2 θ -range of 10 to 80° and a position-sensitive detector using a step size of 0.05° and a step time of 240 s.

The UV-Vis spectra were recorded on a Varian[®] spectrometer model Cary 100, equipped with an integrating sphere and using BaSO₄ as reference. All the spectra were collected in a diffuse reflectance mode and transformed to a magnitude proportional to the extinction coefficient through the Kubelka-Munk function $F(\lambda)$.

High-Resolution Transmission Electron Microscopy (HRTEM) and High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM) images were recorded on a JEOL2010F instrument. The spatial resolution at Scherzer defocus conditions in HRTEM mode is 0.19 nm, while the HAADF-STEM studies were performed using an electron probe of 0.5 nm diameter and a diffraction camera length of 10 cm. It should be pointed that the chemical composition of the sample was studied in STEM mode using an Energy-dispersive X-ray spectrometer (Oxford Instrument, Inca Energy-200). Loose powder samples were supported on a holey carbon-coated copper grid without using any liquid. The excess of sample was removed from the grids using a flow of N₂. This approach allows us to obtain electron transparent thin regions.

The Temperature Programmed Desorption/Oxidation (TPD/TPO) measurements were carried out at atmospheric pressure in a conventional U-shaped quartz reactor connected to a mass spectrometer. The reactive gas stream with a flow rate of 50 mL min⁻¹ was flushed through 50 mg of sample and the temperature rose at 10 K min⁻¹ from room temperature to 900 °C. Helium 99.99% (Air Liquid) was employed in the TPD experiments. TPO tests were carried out with 21% O₂ (Air Liquid) balanced in He.

DRIFTS studies were performed on a Thermo Nicolet Nexus IR spectrometer. Spectra of pure samples were collected at room temperature by co-adding 64 scans at 4 cm⁻¹ resolution in absorbance mode. The spectrum of an aluminum mirror was used as a background.

Catalytic activity

Water-gas shift reaction was performed in a flow reactor at atmospheric pressure in the temperature range of 413 to 623 K. The following conditions were applied: catalyst bed volume 0.5 cm³, space velocity 4000 h⁻¹, partial pressure of water vapour 31.1 kPa and the reactant gas mixture containing 4.494 vol% CO in argon. The CO and CO₂ content was analyzed on “URAS-3G” and “URAS-2T” (Hartmann & Braun AG) gas analyzers and the catalytic activity was expressed as % of CO conversion. Prior to the activity test the samples were treated in air flow at 300 °C for 1 h. Once the WGS performance was evaluated, the best system was submitted to a stability test for 6 days (6 h of reaction per day) at 523 K and a space velocity at 4000 h⁻¹. The reaction flow was stopped during the night.

Results and discussion

Chemical compositions of the prepared supports and gold catalysts are presented in Table 1.

The measured percentages were close to the targeted chemical compositions. Nevertheless, the gold deposition provokes

Table 1 Chemical composition of the prepared catalysts and supports

Sample	CeO ₂ wt%	Fe ₂ O ₃ wt%	Al ₂ O ₃ wt%	Au wt%
Al ₂ O ₃	—	—	100	—
Au/Al	—	—	98.8	1.16
Ce/Al	11.1	—	88.9	—
Au/CeAl	10.8	—	87.5	1.7
Fe/Al	—	14.7	85.3	—
Au/FeAl	—	13.6	84.5	1.91
CeFe0.5/Al	17.1	0.62	82.2	—
Au/CeFe0.5/Al	14.1	0.44	83.6	1.83
CeFe1/Al	16.8	0.93	82.2	—
Au/CeFe1/Al	16.7	0.85	80.1	2.31
CeFe1.5/Al	15.9	1.34	82.8	—
Au/CeFe1.5/Al	12.9	1.03	84.1	2.09
CeFe2/Al	16.2	2.08	81.7	—
Au/CeFe2/Al	14.9	1.72	81.2	2.17
CeFe3/Al	14.43	2.42	83.2	—
Au/CeFe3/Al	13.73	2.35	81.9	2.03

a small loss of the Ce–Fe oxide component, probably caused by the highly basic conditions during the direct anionic exchange procedure. Experimental values for the gold loadings are close to 2 wt%, the targeted one, except for the Au/Al₂O₃ catalyst where a 40% gold loss is observed. It was reported elsewhere¹⁶ that always 30–32% of gold loss is observed when the direct anionic exchange method assisted by NH₃ is applied for the preparation of Au supported on alumina.

Concerning the textural properties (data not shown), all the samples are mesoporous materials with specific surface area of around $200 \pm 10 \text{ m}^2 \text{ g}^{-1}$ governed by the presence of the primary γ -Al₂O₃ support.

XRD patterns of the prepared supports are shown in Fig. 1A. For every support the XRD pattern shows diffraction lines corresponding to the cubic CeO₂ fluorite type structure (JCPDS# 00-004-0593) and to the γ -Al₂O₃ phase (JCPDS# 00-048-0367). The presence of crystalline iron oxide phases is not observed in any XRD pattern, the formation of mixed oxide phases, a rather high dispersion of the iron phase and/or its amorphous character may account for this absence. All the diffraction peaks of

the cerium oxide fluorite structure shift to higher 2θ on adding iron oxide. This suggests a change of the fluorite cell parameter caused by the formation of the Ce–Fe oxide solid solution.

Fig. 1C presents the shift of the main (111) CeO₂ diffraction line as a function of Fe₂O₃ addition. As most diffraction lines of the CeO₂ fluorite coincide with those of γ -alumina, the formation of a Ce–Fe solid solution, was estimated by the calculation of the ceria lattice parameter through the ceria (111) reflection using the equation:

$$a = \sqrt{h^2 + k^2 + l^2} \left(\frac{\lambda}{2\sin\theta} \right)$$

The results, as a function of the iron oxide loading, are presented in Fig. 1D. All the supports (Fe₂O₃ oxide varying in the range 0.5 to 2 wt%) are composed of a mixed cerium–iron oxide layer well dispersed over the gamma alumina matrix. The addition of iron oxide leads to a noticeable contraction of the cerium oxide fluorite cell. The contraction appears to be linearly dependent on the increase of the iron loading till a certain value (1.5 wt% Fe₂O₃) after which the retrenchment still exists but to a lower extent. Two mechanisms of solid solution formation exist, the *O*-vacancy formation mechanism and the interstitial compensation mechanism.¹² In the first mechanism a direct substitution of some Ce⁴⁺ cations by Fe³⁺ cations causes a contraction of the unit cell because of the smaller size of the Fe³⁺ in comparison to the Ce⁴⁺.¹³ The linearity of this effect agrees with Vegard's law, which establishes that at a constant temperature the cell parameter of a solid solution with complete miscibility changes linearly with the concentration of its constituent elements.¹⁷ However the linearity is achieved till 1.5 wt% Fe₂O₃, and above this value an increase in the fluorite unit cell parameter is observed. The interstitial compensation mechanism was reported as the predominant option for the Ce-rich mixed oxides with the increase of the Fe content.¹⁸ In this mechanism three Ce⁴⁺ are substituted by three Fe³⁺ cations, the neutrality is achieved by placing one additional Fe³⁺ cation in an interstitial site of the fluorite CeO₂ structure. For the iron richest support (CeFe3), the cell parameter is negligibly lower than that of the pure cerium oxide (5.405 vs. 5.407 Å) suggesting the concentration limit for the Ce–Fe oxide solid solution, beyond this limit the interaction between Ce and Fe phases occurs at grain boundaries without direct Ce–Fe interactions.

Fig. 1D also shows the ceria crystallite size estimated by the Scherrer equation using the (111) reflection. The average ceria crystallite size varies between 3 and 5 nm. The lattice change in ceria is closely related to the crystal size and the vacancy defect concentration; more vacancies result in lattice expansion, whereas higher crystal size results in lattice contraction.¹⁹ According to this, the decrease of the particle size of ceria for the CeFe2/Al sample together with the increase in the lattice parameter suggests a high density of vacancies.

The electronic defect concentration was studied as well by means of UV-VIS spectroscopy. The diffuse reflectance spectra of the prepared supports are presented in Fig. 2. The Fe/Al sample presents several ligand-to-metal charge transfer absorptions

Fig. 1 (A) XRD patterns of the prepared supports. (B) XRD patterns of the prepared gold catalysts. (C) Shifting of the main ceria diffraction as a function of the iron content. (D) Ceria crystallite size and cell parameter as a function of iron loading of the supports.

Fig. 2 Diffuse reflectance spectra of the prepared supports.

in the UV region attributed to $O \rightarrow Fe^{3+}$ transitions of isolated Fe ions in tetrahedral and octahedral coordination.²⁰ Schwidder *et al.*²¹ assigned the absorption between 300 and 400 nm to oligomeric Fe_xO_y clusters. In the visible region (>450 nm), a broad absorption band characteristic of d-d transitions ${}^6A_{1g} \rightarrow {}^6T_{1g}$ and ${}^6A_{1g} \rightarrow {}^6T_{2g}$ in $\alpha\text{-Fe}_2\text{O}_3$ is detected. A broad band situated at 350 nm in the UV region is observed for all the supports based on Ce/Al. This signal corresponds to the charge transfer transition from the 2p valence band of O^{2-} to the 4f band of Ce^{4+} .²² For the ternary Ce–Fe–Al systems widening and shifting of the absorption edge is observed evidencing Ce–Fe interaction. Table 2 presents the calculated direct and indirect band gap of the solids. The direct band gap for the Ce/Al solid is very close to the one reported in the literature.²³

A progressive decrease of both direct and indirect band gap energies on increasing the iron content is observed for all the Ce–Fe/Al systems, the CeFe2/Al system being the one with the lowest values. This effect was previously observed and attributed to the band tail effect – the fluctuation of potential energy caused by the spatial dependence of the local density of states in doped semiconductors.²⁵ In terms of electronic properties the Fe dopant supplies unoccupied orbitals of lower energy than those of Ce 4f, thus decreasing the energy needed for the $O^{2-} \rightarrow Ce^{4+}$ transitions.²⁶ It should be highlighted that the lowest band gap values were found for the CeFe2/Al sample suggesting a particularly strong effect of Fe in the Ce/Al solid and higher easiness of electron transport.

After gold addition the XRD patterns of the supports remain unaltered (Fig. 1B). The absence of diffraction lines corresponding to metallic gold suggests an Au particle size as small as 5 nm.

Table 2 Band gap energies for the prepared supports estimated through the relationship between the optical absorption coefficients near the absorption edge and the band gap for direct and indirect interband transitions²⁴

Sample	Direct band gap (eV)	Indirect band gap (eV)
Ce/Al	3.04	2.82
CeFe0.5/Al	2.99	2.71
CeFe1/Al	2.98	2.77
CeFe1.5/Al	2.82	2.44
CeFe2/Al	2.67	2.27
CeFe3/Al	2.93	2.66

Fig. 3 (A) Representative HAADF and EDX spectra of selected nanoparticles marked in the HAADF image of the Au/CeFe2/Al sample. (B) Representative HREM (center) and DDP (insets) images of the Au/CeFe2/Al sample (center).

After a TEM study the average particle size of the samples was found to be 4 ± 0.5 nm and considered further in all calculations.

The catalyst showing the strongest Ce–Fe interaction was studied in more detail by high resolution TEM. A typical HAADF image of the Au/CeFe2/Al catalyst is included in Fig. 3A. The white spots correspond to the presence of heavier elements such as Ce, Fe and/or Au supported on alumina. However, it is difficult to determine by Z contrast images the composition of these nanoparticles. In order to elucidate it, energy-dispersive X-ray spectra were recorded in STEM mode, which allow us to locate the focused beam (0.5 nm) on any selected area of the sample. Representative results are included in Fig. 3A, showing that mainly all the particles studied (60) are an agglomeration of gold, ceria and iron. It should be also pointed out that the observed nanoparticles have an average size of 3.4 nm, which is in good concordance with the above reported X-ray results. Moreover, HREM studies show the presence of well-defined ceria nanocrystals of about 2.8–3.3 nm, although no observed spacing corresponds to common iron oxide phases. This result, in combination with EDX and X-ray data, confirms that iron is incorporated in the ceria structure. Fig. 3B is a representative HREM micrograph of the Au/CeFe2/Al catalyst that includes the digital diffraction pattern (DDP) of the selected areas marked in the image. The DDP included in Fig. 3B (left inset) shows four spots that correspond to four families of crystallographic planes, that after in-depth analysis using the Eje-Z software,²⁷ showed *d*-spacings and angles that can be univocally interpreted as ceria structure among the $[0\ 1\ 1]$ axis zone. The other DDP included in Fig. 3B shows spacing corresponding to ceria

(3.1 Å) and another of 2.4 Å that might be attributed to the gold (1 -1 1) family of planes. However, this spacing can also be attributed to different alumina structures.

Water-gas shift behavior

Fig. 4 shows the CO conversion as a function of temperature for the studied gold systems. As expected the CO conversion increases on raising the temperature but the shape of the conversion vs. temperature curve is affected by the catalyst nature reflecting the influence of the catalysts composition on their kinetic parameters. In general, the iron-promoted Au/CeAl catalysts with the iron content in the range of 0.5 to 2 wt% show higher catalytic activities than Au/CeAl and Au/FeAl ones suggesting a synergic effect of cerium and iron in the solid solution. Above 2 wt% iron oxide the gold catalyst is hardly active showing performances close to that of the Au/Al catalyst.

The specific reaction rates at 453 K and the measured turnover frequency (TOF) using gold dispersion are presented in Table 3. Table 3 presents the gold particle size together with the Au dispersion, evaluated on the basis of the hemispherical ball model.²⁸ These reaction rates expressed as $\text{mol}_{\text{CO converted}} \text{g}_{\text{Au}}^{-1} \text{s}^{-1}$ and TOF in s^{-1} are compared to literature data for different catalysts measured in the same WGSR conditions. Compared to industrial FeCr high temperature shift catalysts the AuCeFe2/Al presents a similar reaction rate at a temperature of 623 K ($1.36 \times 10^{-5} \text{ mol CO g}^{-1} \text{s}^{-1}$ vs. $1.04 \times 10^{-5} \text{ mol CO g}^{-1} \text{cat s}^{-1}$).²⁹

As can be seen in Table 3 the gold-supported γ -alumina catalyst demonstrates poor activity in the WGSR. The addition of CeO_2 clearly enhances the reaction rate and gold TOF; however, Fe_2O_3 addition only slightly improves the catalytic performance of the bare Au/ Al_2O_3 catalyst. These catalysts have performances slightly superior to the previously reported bare Au/ CeO_2 systems^{30,31} and clearly improved compared to the Au/ CeO_2 - Al_2O_3 catalysts.³¹ In fact, only the Au/mesoporous

Table 3 WGSR reaction rates (r) in $\text{mol}_{\text{CO conv.}} \text{g}_{\text{Au}}^{-1} \text{s}^{-1} \times 10^5$, TOF in $\text{s}^{-1} \times 10^2$ measured at 453 K, gold particle size (d) in nm and dispersion (%) for the prepared gold catalysts together with literature data

Catalysts	r	TOF	d	%
Au/Al	1.36	0.8	4	32
Au/Ce/Al	3.27	1.9	4	32
Au/Fe/Al	1.56	0.96	4	32
Au/CeFe0.5/Al	2.63	1.5	4	32
Au/CeFe1/Al	3.59	2.2	4	32
Au/CeFe1.5/Al	4.56	2.7	4	32
Au/CeFe2/Al	5.01	2.97	4	32
Au/CeFe3/Al	1.09	0.7	4	32
Au/Ce ³⁰	3.10	2.3	5	26
Au/Ce75Fe25 ³⁰	0.43	0.32	5	26
Au/Ce50Fe50 ³⁰	0.62	1.2	1.5	70
Au/Ce25Fe75 ³⁰	0.32	0.6	14.2	10
Au/Fe ³⁰	0.28	0.9	25.3	6
Au/CeM ³²	4.6	4	6	22
Au/Ce ^{30b}	2.9	2	4.5	29
Au/Ce ³¹	3.2	2.3	5	26
Au/CeAl10 ³¹	0.79	0.8	7	19
Au/CeAl20 ³¹	0.37	0.4	7	19

CeO_2 ³² showed better activity than the catalysts presented in this study at 473 K.

The Au/CeFe/Al quaternary solids present noticeably higher catalytic activities than gold-supported on mixed Ce-Fe oxide catalysts earlier reported in the literature.³⁰ Considering that the gold particle size is similar for all the systems (ternary or quaternary), it may be argued that a synergic effect between cerium and iron is responsible for the enhanced WGS activity observed in this study. An increase in the activity as a function of the Fe loading is observed, showing clearly the relationship between the CO conversion and the Ce/Fe molar ratio but for the highest iron loading. For the catalytic oxidation of CO over these catalysts it has been demonstrated that the support indirectly influences the activity either by increasing the number of low coordinated Au atoms³³ or by the presence of the Ce-O-Fe surface bonds generated upon solid solution formation that results in lower energy barriers for oxygen migration.²⁶ Fig. 5 plots the gold TOF vs. the iron content of the catalysts, the catalysts having iron oxide contents that are in the range of 0.5 to 2 wt% show TOF values clearly above those of the Au/CeAl or Au/FeAl catalysts. Considering that together cerium and iron oxide loading is approximately constant and that gold loading and dispersion remains constant the higher TOF values, whatever the WGSR temperature, account for a synergic effect between cerium and iron in the mixed oxide forming solid solution.

The decrease of the band gap energies of all iron doped solids (Table 2), no matter the iron concentration, with respect to the ceria-alumina un-promoted support suggests the presence of Fe dopant unoccupied orbitals of lower energy facilitating the electron transport and easiness of $\text{O}^{2-} \rightarrow \text{Ce}^{4+}$ transitions. This enhancement in terms of electron transfer and of course the successful formation of Ce-Fe solid solution influences positively the reaction rate. However, the catalytic activity of the Au/CeFe3/Al sample for which the limit value of the solid solution is obtained is well below that of the un-promoted catalyst in the temperature range studied suggesting

Fig. 4 Catalytic activity of the gold systems as a function of temperature.

Fig. 5 Gold TOF values for the all Ce–Fe oxide solid solution catalysts prepared compared to the gold-supported ceria–alumina and gold-supported iron oxide catalysts.

that not only the increase in the number of oxygen vacancies is responsible for the observed synergic effect.

The key step in the preparation of highly efficient gold-based catalysts for the WGS is the presence of an adequate support able to overcome the rate limiting step – water activation. Computational studies pointed to a very high energetic barrier for the dissociation of water on gold nanoparticles.³⁴ The latter could explain the poor activity of Au/Al₂O₃ in which gold nanoparticles are considered to be the only active species. However, the introduction of any oxide that facilitates the adsorption and dissociation of water should result in very promising systems. Ceria and iron oxide may not be simple spectators in the reaction. The Au/FeO_x activity in WGS is related to an associative mechanism involving the formation of formate and/or carbonate species as reaction intermediates through the interaction between a CO molecule and an OH group of the oxide surface.² A redox mechanism consisting of the reduction of Ce⁴⁺ to Ce³⁺ by CO adsorbed on gold particles is accepted for the Au/CeO₂ catalyst. This reduction produces CO₂ leaving behind an oxygen vacancy that is replenished by H₂O producing H₂.³⁵

However, when discussing the quaternary solids Au/CeFe/Al, several points must be taken into consideration. First of all, the activity of these systems in terms of TOF is superior to the activity of the ternary Au/Fe/Al and Au/Ce/Al systems when the iron oxide content is in the range of 0.5 to 2 wt%. As specified above, the activity improvement cannot be due only to the dispersion of the gold nanoparticles or to the increase in the number of oxygen vacancies, but more to the synergic effect between the two doping oxides and their cooperative role in the water activation mechanism. Preparation of a solid solution by the O vacancy formation mechanism should promote the redox WGS mechanism, and when the interstitial compensation mechanism occurs the water splitting takes place probably by two mechanisms simultaneously: associative mechanism (due to iron in interstitial position) and redox mechanism

(due to isomorphic iron to cerium oxide promotion). This co-operative effect may explain why the Au/CeFe₂/Al catalyst presents the highest catalytic activity reaching CO conversion very close to the thermodynamic limit.

When the limit value of the solid solution formation is attained, as for the Au/CeFe₃/Al catalyst, the activity dramatically falls confirming that the formation of the CeO₂–Fe₂O₃ solid solution is the critical point for this type of catalysts.

For Au/Fe₂O₃ catalysts working in the WGS at 473 K Silberova *et al.*³⁶ have proposed that linearly adsorbed CO on metallic Au particles react with OH groups to form hydroxyl-carbonyl species that further reacts with oxygen atoms at the Au–support interface resulting in adsorbed bicarbonates. These species decompose to CO₂ removing oxygen atoms from the support mainly at the Au–Fe₂O₃ interface, which leads to reduction of the support. If this scheme is assumed for our ceria–iron oxide mixed systems, once the Fe³⁺ species are reduced two possibilities may be envisaged: (i) the resulting divalent iron species is stabilized in the hematite matrix leading to the formation of the iron spinel (magnetite) or (ii) the divalent species undergoes a further redox reaction with CeO₂ that reoxidizes the iron species and reduces Ce⁴⁺ to Ce³⁺ in a mechanism similar to that previously proposed for CeO₂–MO_x systems by Laguna *et al.*^{11b,37} The formation of a Fe₃O₄ spinel has been demonstrated by *in situ* XRD and XANES experiments for Au/Fe/CeAl catalysts constituted by a segregated hematite phase supported on a ceria–alumina support during the WGS, while an increase in Ce³⁺ concentration and the absence of divalent iron species is observed for catalysts constituted by gold-supported on ceria–iron oxide solid solutions prepared on alumina.³⁸ The formation of a solid solution enhances oxygen transfer reaction and alters the electron density of anions and cations of the support surface favoring water dissociation and therefore the catalytic activity in the WGS. Once the solubility limit for the formation of the solid solution is reached the segregated iron oxide particles enhance the oxygen transfer rate but this enhancement should be proportional to the length of the ceria–iron oxide interface.

The influence of the space velocity and water partial pressure on the activity of the catalysts forming ceria–iron oxide solid solutions is shown in Fig. 6. On increasing the space velocity the CO conversion steadily decreases, the iron oxide loading having no influence on the general trend (Fig. 6A). Fig. 6B plots the catalytic activity data at six different H₂O/CO ratios for the catalysts forming ceria–iron oxide solid solutions. No serious changes in CO conversion were observed in the whole range of studied water vapor pressures. The Au/CeFe₂/Al sample maintains high CO conversion even at rather low H₂O/CO ratios. The catalytic activity slightly decreases at high H₂O/CO ratios 30 kPa being the optimum water partial pressure.

It is well known that the stability of a catalyst is even more important than activity, especially, in terms of possible industrial applications. In this way, the stability under WGS conditions for the most active catalyst within the series (Au/CeFe₂/Al) was followed (Fig. 7). The stability experiment lasted one week and the data were collected for six hours every day.

Fig. 6 Experimental variables: (A) influence of the space velocity on CO conversion at constant temperature (523 K) and water vapour pressure (30 kPa) for the series of catalysts forming ceria-iron oxide solid solutions. (B) Influence of the water vapor partial pressure on CO conversion at constant temperature (523 K) and space velocity (4000 h^{-1}).

However, during the night the catalyst was kept at room temperature in a CO-rich atmosphere – the reactant gas mixture from which water vapour is eliminated. The stability test is thus carried out by continuously alternating WGS and CO atmospheres.

Fig. 7 Evolution of the CO conversion with time during the stability test of the Au/CeFe2/Al catalyst.

For the stability test the temperature was fixed at 523 K to ensure a CO conversion close to 80%. CO conversion progressively decreases at this temperature revealing the deactivation of the gold catalysts. Several factors could be responsible for this deactivation. First, gold nanoparticles are not kinetically stable and they tend to agglomerate at high temperatures thus reducing the number of active sites and hence the catalytic activity. However, the XRD pattern of the spent catalyst (not shown) does not reveal any change in gold particle size suggesting that gold sintering hardly occurs. The accumulation of adsorbed intermediate or spectator species like formate, carboxylate or carbonate may result in a significant loss of activity by blocking active sites for water dissociation. It has been demonstrated for Au/CeO₂ catalysts that adsorbed water dissociates on ceria oxygen vacancies reoxidizing Ce³⁺ species left behind upon interaction of ceria with CO.³⁹ Typically those adsorbed species tend to join cerium atoms in a chelating or bridged conformation with desorption temperatures up to 625 K.⁴⁰ Furthermore, adsorbed formate species may evolve at the reaction temperatures to carbonate species reducing the ceria surface, the thermal stability of these Ce(III) carbonates, well above the WGS temperatures, irreversibly blocks surface sites for water dissociation.³⁹ If the surface is deactivated by the existence of such a species, an oxidation treatment should regenerate the activity of the catalyst. Indeed, activation with air at 473 K for 1 h restored almost entirely the initial CO conversion after a one-week test, as shown in Fig. 7. The cyclic WGS/CO-rich treatments to which the catalyst was submitted for the stability test, allow suggesting the existence of adsorbed formate and/or carbonate species, either intermediates or spectators of the WGS, together with the reduction of the ceria surface. The reduction of the surface during the reaction and during the night (under CO without water) promotes the formation of the carbonaceous deposits on the catalyst surface. However, the regeneration of the activity after an oxidative post-reaction treatment suggests that the loss of stability could be solved by a suitable change in the reaction parameters.

TPD/TPO (Fig. 8) experiments of the reacted Au/CeFe2/Al catalyst were carried out to elucidate the surface oxidation state and the nature of the adsorbed species responsible for the catalyst deactivation/regeneration process. The TPD under He flow is shown in Fig. 8A. Two desorption zones can be clearly observed, in the first one, below 473 K, adsorbed water was totally removed as well as some weakly adsorbed CO and CO₂ species. Above 650 K, the second desorption zone of the TPD profile hydrogen and CO evolves simultaneously accounting for the presence of hydrogen-carbonaceous intermediate removal (most probably formate or carboxylate). CO₂ evolution follows an independent profile showing two high-temperatures desorption peaks with maximum desorption rates at 723 and 953 K that may correspond to the decomposition of carbonate species as suggested by the independent CO and CO₂ profiles. After the TPD test the sample was submitted to TPO conditions. Fig. 8B shows the corresponding CO, CO₂ and H₂ profiles, the previous TPD experiment prevents water evolution. Hydrogen evolution may mean that some of the intermediates formed

Fig. 8 (A)TPD-He experiment of a post reaction Au/CeFe₂/Al sample. (B) TPO after (A). (C) TPO experiment of Au/CeFe₂/Al holding the temperature at 200 °C for 1 h like in the stability test. (D) DRIFTS spectra of Au/CeFe₂/Al.

during WGS were not removed from the catalyst surface during TPD. In an oxidizing environment after TPD the evolution of carbon oxides, mainly CO₂ since the profile of the *m/z* signals at 28 and 44 are parallel, together with the presence of hydrogen may account for the decomposition of formate species un-stabilized by the presence of oxygen that allows Ce³⁺ oxidation and decreases the decomposition temperature of adsorbed formates.

Finally, a TPO was carried out on the reacted Au/CeFe₂/Al catalyst, reproducing the performed reaction oxidative treatment (Fig. 8C). Evolution of gaseous CO, CO₂ and H₂ species occurs in two well-differentiated temperature regions. A sharp and intense desorption at low temperatures, 395 K, and broad signals starting at 623 K in the high temperature region are observed. From this experiment it is clear that the oxidation treatment at 473 K removes partially adsorbed species, either intermediates or spectators, nevertheless a fraction of the adsorbed species remains adsorbed and starts decomposing at temperatures above the maximum reaction temperature in the WGS. This explains why the catalyst did not completely recover its activity after the oxidation treatment at 473 K. Again hydrogen and carbon monoxide reasonably follow the carbon dioxide profile allowing us to speculate that the intermediates are hydrogen-carbonaceous species most probably formates.

To confirm this statement several DRIFTS spectra of the Au/CeFe₂/Al catalyst were recorded. Fig. 8D presents the C–O stretching region characteristic of carbonate/formate species for the catalyst after the WGS and the IR spectrum of this catalyst after reactivation. The broad and complex IR patterns prevent univocally assigning all the observed absorptions of definite adsorbed species. However, in both cases the presence of bands at 1590 cm^{−1} (asymmetric OCO stretching vibration) and 1375 cm^{−1} (symmetric OCO stretching vibration) is clearly evidenced indicating the presence of adsorbed formate species.⁴¹ Bands at 1459 cm^{−1} and 1738 cm^{−1} characteristic of monodentate and bridged carbonates, respectively, are also observed.

Therefore, DRIFTS experiments confirm that after the WGS and the reoxidation treatment adsorbed formates remain adsorbed on the catalyst surface while the more labile monodentate carbonate species are eliminated during the re-activation process.

Conclusions

A series of Au/CeFe/Al catalysts have been prepared and compared to Au/Ce/Al, Au/Fe/Al and Au/Al in the WGS. The quaternary systems showed superior catalytic activity to the bare γ -alumina or ternary supported gold catalyst. The WGS activity is governed not only by the presence of gold and particle size but also by the formation of a ceria–iron solid solution. The activity enhancement is related to a Ce–Fe synergic effect that favors water activation, either by the redox or associative mechanism. A deactivation of the gold catalysts was observed and attributed principally to the formation of carbonate and formate species that were identified by DRIFT, which limit the accessibility of the support active sites for the activation of water. Nevertheless after oxidative treatment the catalyst rapidly almost recovers its initial conversion, pointing that the problem of stability could be overcome by a suitable change in the reaction parameters.

It is important to underline that these very efficient catalysts are mostly composed of alumina (80%), which contributes to their economic viability in case of major scale applications.

Acknowledgements

Financial support for this work has been obtained from the Spanish Ministerio de Ciencia e Innovación (ENE2009-14522-C05-01) and from Junta de Andalucía (P09-TEP-5454). These projects are partially supported by FEDER funds from the European Union. S. Ivanova acknowledges MEC for her contract Ramon y Cajal and Tomás Ramírez acknowledges CSIC for his JAE-Predoc fellowship. The authors are also grateful for the financial support offered by the CSIC-BAS project 2009B60024.

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