ABSTRACT
The present invention relates to the synthesis and application of gold catalysts supported in mixed CuO/ZnO/Al₂O₃ oxides prepared on the basis of their corresponding solids with a hydrotalcite structure as catalysts in the water-gas shift reaction, for use in fuel processors coupled to fuel cells.
Figure 1
Figure 2
Figure 3

A

GHSV = 4000 h⁻¹
T = 220°C
gas mixture = 30% H₂O + 9% CO + 11% CO₂ + 50% H₂

CO Conversion (%) vs. Time (h)

B

CO Conversion (%) vs. No. of Cycles

0 1 2 3 4
GOLD CATALYST SUPPORTED IN CU/ZNO/A203, PRODUCTION METHOD AND USE THEREOF

FIELD OF THE ART

[0001] The invention relates to the technical field of renewable energies, more specifically to the development of catalysts and their application in the water-gas shift reaction (WGS) for use in fuel processors coupled to fuel cells.

STATE OF THE ART

[0002] Currently, hydrogen-fed PEM-type fuel cells are one of the most attractive energy production devices due to their high-energy efficiency and low levels of pollutant emission, and are earmarked to play a relevant role in the energy system of the future.

[0003] Hydrogen for use as fuel can be generated from fossil fuels (such as coal, hydrocarbons and natural gas) or from other renewable sources, such as biomass. At present, the processes most widely used for such purpose continue to be steam-reforming, autothermal-reforming and partial alcohol and hydrocarbon oxidation processes, although in the near future the use of renewable sources must and will account for the majority. Furthermore, the hydrogen stream produced in the reformer contains not only hydrogen, but also other gases, typically CO₂, H₂O and CO, in varying amounts, depending on the reforming process, operating conditions and fuel used, and may have a content of 15-25% CO₂, 10-30% H₂O and 3-10% CO. Furthermore, PEM fuel cells must be fed with a nearly pure hydrogen stream, since tolerance to certain components is very low. Specifically, the presence of carbon monoxide (CO) in the stream, even at trace levels (typically >10 ppm) is poisonous to the battery anode catalyst (normally based on Pt or Pt—Ru), since it is absorbed thereon, causing cell deactivation. Although physical methods for removing CO from these streams have been studied, catalyst processes have proven more efficient, such as the water-gas shift reaction (WGS, Equation 1) and the Preferential CO Oxidation Reaction in the presence of the H₂/PrOx, Equation 2).

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (\text{Eq. 1})
\]

\[
\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2 \quad (\text{Eq. 2})
\]

[0004] One of the most widely studied aspects is the development of highly efficient, novel catalysts for the water-gas shift reaction (WGS).

[0005] The WGS process constitutes the obligatory catalytic stage (removal) of CO from the hydrogen streams, since quantities of up to 9-11% of CO can reach the WGS unit. Two aspects are relevant in accordance with the characteristics of the reaction and with the integrated nature of the hydrogen production and cleaning process.

[0006] 1) With respect to the reaction itself, it is a reversible and exothermic process (ATr=41.2 kJ/mol). Precisely due to the fact that it is a moderately exothermic process, the WGS reaction is thermodynamically unfavoured at high temperatures. However, from a kinetic viewpoint, the catalytic process is more favourable at high temperatures. Therefore, in order to overcome this thermodynamic limitation, maintaining high reaction speeds, the reaction usually takes place in multiple adiabatic stages; thus, for example, the high temperature shift (HTS) is normally the first stage with high operating temperatures (350°C–600°C), while the low temperature shift (LTS) occurs as a second stage with a temperature range comprised between 150°C and 300°C, inserting an intermediate cooling stage to obtain high global conversion.

[0007] 2) The second aspect to be considered is that the WGS reactor is usually, by far, the largest of the integrated process, since the water-gas shift reaction is favoured at low spatial velocities. To facilitate the implementation of this technology in mobile applications, the reduction in reactor volume is of vital importance. In this regard, the development of catalysts capable of carrying out the WGS reaction at high spatial velocities constitutes one of the greatest challenges in this scientific problem.

[0008] In general, four types of catalysts are identified for the WGS reaction:

[0009] Promoted iron oxide-based catalysts that shift at slightly higher temperatures (350-450°C) and are therefore used in high temperature (HTS) WGS.

[0010] Copper-zinc mixed oxide catalysts, typically known as low temperature shift catalysts (LTS) because they are used at relatively low temperatures (190-250°C).

[0011] The third type of catalysts use cobalt and molybdenum sulphides as active phases and are resistant to sulphur poisoning.

[0012] Lastly, the fourth type of catalysts consists of those that operate at intermediate temperatures (MTS), usually between the HTS and LTS catalysts.

[0013] They are normally copper-zinc catalysts such as those used in LTS but modified (usually with iron oxide) to operate slightly higher temperatures (275-350°C) than the typical LTS catalysts.

[0014] Given that commercial catalysts for the low-temperature WGS reaction (typically CuO/ZnO mixtures) have a series of drawbacks, such as for example their pyrophoricity, their need for previous activation treatment and, in many cases, their deactivation due to sintering of the metal particles, catalysts based on noble metals (basically Au and Pt) are in fact widely studied as an alternative to the aforementioned commercial catalysts. In particular, catalysts that use gold as the active phase have been studied in detail with promising results in the last decade. Gold-based catalysts offer advantages in the 180-250°C temperature range, where Pt group catalysts are not sufficiently active [Andreeva, D. Andreeva, D., Ivanov, L., Ilieva, J., W. Sobczak, G. B. B. Teer, V. Tabakovka, “Nanosized gold catalysts supported on ceria and ceria-alumina for WGS reaction: Influence of the preparation method”, Appl. Catal. A: Gen., Volume 333, 2007, Page 153-160]. For example, they are not pyrophoric and do not require any type of special treatment prior to use. Recently, [Robbie Burch, “Gold catalysts for pure hydrogen production in the water-gas shift reaction: Activity, structure and reaction mechanism” Phys. Chem. Chem. Phys., 2006, Volume 8, Page 5483-5500] the advantages and drawbacks of gold catalysts for the WGS reaction have been summarised. It is well established that, in the case of gold catalysts, the preparation method and pre-treatment greatly influence the subsequent catalytic activity. The wide disparity in the behaviour of published gold catalysts is attributed essentially to the method for preparing the gold nanoparticles and to the wide diversity of supports used. However, there is general consensus in the literature concerning an active support and, more specifically, CeO₂ as a support for metal nanoparticles for the WGS reaction [Andreeva, D.,...
Ivanov, I., Ilieva, L., Sobzeak, J. W., Avdeev, G., Petrov, K. (2007) “Gold-based catalysts on ceria and ceria-alumina for WGS reaction (WGS Gold catalysts)”: Topics in Catalysis, Volume 44, (1-2), Page 173-182. The main advantage of gold-based catalysts is that they make it possible to operate at low reaction temperatures where the thermodynamic limitation is practically null, making it possible to reach high CO conversions.

[0015] Patent documents disclose the use of CuO—ZnO mixtures as efficient systems in the WGS reaction. For example, a system widely used in the industry is that developed by Larson in the sixties (U.S. Pat. No. 3,797,426 Manufacture of hydrogen). More recently, patents filed by Farraruto and collaborators allude to the use of Pt supported on CuO—CeO2—Al2O3 mixtures (US20020147103 Enhanced stability water-gas shift reaction catalysts and US20020061277 Non-pyrolytic water-gas shift reaction catalysts). In these catalysts, the use of cerium dioxide reduces pyrophoricity and increases stability. This is especially relevant in relation to industrial applications, as proposed in Shore’s patent (U.S. Pat. No. 6,913,739 Platinum group metal-promoted copper oxidation catalysts and methods for carbon monoxide remediation), which places emphasis on the fact that the non-pyrolytic nature of the WGS catalyst is crucial to possible start/stop events. The same inventors designed Pt-based catalysts for WGS with scarce rhodium production (US20030230029 Suppression of methanation activity of platinum group metal water-gas shift catalysts). Catalysts with the formula Fe2O3/Cu2O/ZnO/Al2O3 have been applied very effectively in the WGS reaction at intermediate temperatures, and the preparation and use thereof is included in the patent (U.S. Pat. No. 7,964,114 B2 Iron-based water-gas shift catalysts). The use of Fe—Al—Cu systems with different Fe/Cu ratios is also patented as highly effective catalysts for hydrogen production from WGS (U.S. Pat. No. 7,947,251 B2 Catalyst for hydrogen production from water-gas shift reaction). The conventional CuO/ZnO/Al2O3 system can be enhanced by adding promoters. The patent (U.S. Pat. No. 6,627,572 B1 Water-gas shift catalyst) explains how promoting the aforementioned system with elements chosen from K, Rb, Cs as alkali and metals such as Ti, V, Mn, Mo, Zr, Ru, Ir, Pt, Re, La, Ce, Ba and Rh enhances the catalyst in the WGS process. This strategy of promoting the aforementioned CuO/ZnO system with alkaline elements has been used since the nineties, as disclosed in the patent by Klier and collaborators (U.S. Pat. No. 5,021,233 Water-gas shift reaction alli-doped catalysts).

[0016] As regards gold, a small percentage of patents disclose the application of gold-containing systems (WGS) for producing hydrogen. Said patents usually allude to the preparation of the catalysts (for example, Au on zirconium sulphate) for this application (US2007128100 Method for making hydrogen using a gold-containing catalyst [2007]) or even disclose that gold catalysts may have more than one function, for example the application of gold-based catalysts for WGS with the object of obtaining hydrogen and simultaneously the use of the same catalysts in CO oxidation (US2008009823, Method For Making Hydrogen Using A Gold-Containing Water-Gas Shift Catalyst, 2008).

[0017] The deposition of gold in compounds having a pyrochlore structure (US2007269359 Compound having a pyrochlore structure and its use as a catalyst carrier in the water-gas shift reaction, 2007) and in metal oxides (cerium and/or zirconium) wherein at least 40% of the gold is present as Au(III) (WO2005087656 Water-gas shift catalyst, 2005) has also given rise to patents in this field.

[0018] The Japanese National Institute of Advanced Industrial Science and Technology has also filed three patents for the WGS reaction that include gold in the composition of their catalysts. One with a catalyst based on gold and copper oxide (JP20020158816 20020501, Catalyst for water-gas shift reaction, 2003), another with catalysts having an arbitrary composition, where at least one metal oxide of the following elements is present: Mg, Al, Mn, Fe, Co, Ni, Zn, Zr or Ce (JP2004009011 Catalyst for water-gas shift reaction). And in the third patent, a catalyst for WGS is proposed in a proposed gas stream composed of gold and metal oxides whose cations have Pauling electronegativity in the 10-14 range (JP2004066603, Catalyst for water-gas shift reaction of fuel-reformed gas).

[0019] The Korean Institute of Science and Technology has also filed patents alluding to WGS, in this case with catalysts based on Au, Ag, Cu, Ni, Zn, Cr and Al supported on a ceramic. Said ceramic may be cerium, zirconium, bismuth-based perovskite or bismuth oxides (KR20040036106, Catalyst of ceramic supported on metal for water-gas shift reaction and method for preparing the same, 2004).

[0020] However, the scientific articles or patents disclosed do not include references to the use of a combined system based on the CuO/ZnO/Al2O3 and noble metal system. The possible combination of added-value properties of the two types of catalysts would therefore be desirable as an alternative to the requirements for their use in portable energy-producing devices.

[0021] The present invention focuses on the synthesis and application of gold catalysts supported on mixed CuO/ZnO/Al2O3 oxides with different CuO/ZnO ratios and prepared from their corresponding solids with hydroxide structure as highly efficient catalysts in the WGS reaction.

**Explanation of the Invention**

[0022] In a first aspect, an object of the present invention is a gold-containing catalyst supported on CuO/ZnO/Al2O3, comprising between 10% and 80% of Al2O3 and between 90% and 20% of CuO/ZnO.

[0023] In successive embodiments, the CuO/ZnO/Al2O3 support precursor has a hydroxide structure with the following proportions between the compounds:

- 0.24] CuO+ZnO/Al2O3 ratio comprised between 0.5 and 3
- 0.25] CuO/Al2O3 ratio comprised between 1 and 6, and the following percentages by weight:
  - 0.26] from 0.5 to 4% w/w of Au
  - 0.27] from 10 to 90% w/w of CuO/ZnO.

[0028] In a second aspect, another object of the present invention is the method for preparing the above-referenced catalyst, comprising the following stages:

- 0.29] synthesis of hydroxalates as CuO/ZnO/Al2O3 mixed oxide precursors,
- 0.30] deposition of gold on the CuO/ZnO/Al2O3 substrate,
- 0.31] in a preferred embodiment, the synthesis of hydroxaltes takes place by means of co-precipitation at low oversaturation of Cu, Zn and Al salts at a pH comprised between 7 and 10 and temperatures comprised between 20°C and 80°C. Preferably, the salts used as precursors are Cu(NO3)2·2H2O, Zn(NO3)2·6H2O and Al(NO3)3·9H2O and
1M Na₂CO₃ is used as a precipitation agent, maintaining the precipitation for a period of 48 hours. After the precipitation, it is dried at a temperature comprised between the ambient temperature and 100°C, followed by subsequent calcination at 300°C for 4 hours with a ramp of 10°C/min. In another preferred embodiment of the method of the invention, Au deposition is performed by means of direct anionic exchange assisted by NH₃, using an aqueous HAuCl₄ solution to which the support is added. Another way of performing Au deposition is by means of deposition-precipitation, wherein Au is deposited in the form of auric hydroxide on the oxide layers under agitation at a constant pH.

[0032] In a third aspect, another object of the present invention is the use of the catalyst in the water-gas shift reaction. In a preferred embodiment, the reaction occurs in reactive streams with a composition comprising:

- between 4.5% and 9% of CO
- between 0% and 11% of CO₂
- between 30% and 50% of H₂O

wherein the reaction takes place at a temperature comprised between 140 and 350°C and a spatial velocity of between 4,000 and 8,000 h⁻¹.

**BRIEF DESCRIPTION OF THE FIGURES**

- [0036] FIG. 1 — X-Ray diffraction patterns
- [0038] B) X-Ray diffraction patterns of the calcined sample.
- [0039] C) Comparison of the diffraction patterns of a pre-reaction calcined sample with the same sample after use thereof in WGS.
- [0040] D) Comparison of a calcined mixed oxide with its corresponding gold-containing catalyst.

**FIG. 2** — Results of catalytic activity in WGS of the systems where M⁺⁺M⁺⁺⁺⁺ remained constant at 1 and the gold was deposited by means of the assisted anionic exchange method.

- [0042] A) Comparison of the activity of the mixed oxides with those of their corresponding gold catalysts supported under ideal conditions (mixture of the described model).
- [0043] B) Comparison of the activity of the mixed oxides with those of their corresponding gold catalysts supported under the described industrial conditions.

**FIG. 3** — Au/HIT_2 catalyst
- [0044] A) Continuous stability under real operating conditions.
- [0046] B) Start/stop cycles under industrial mixture.

**DETAILED DESCRIPTION OF THE INVENTION**

[0047] The present invention relates to the synthesis and application of gold catalysts supported on mixed CuO/ZnO/Al₂O₃ oxides prepared from their corresponding solids with a hydroxalate structure as catalysts in the WGS reaction.

[0048] Firstly, the invention describes the synthesis of mixed copper zinc and alumina oxides (CuO/ZnO/Al₂O₃) in an extraordinarily controlled manner through the use of a defined hydroxalate-type structure as a precursor thereof. As a result, these solids are stable with respect to the significant sintering, which is reflected in a constant and long-lasting catalytic activity.

[0049] The addition of a minimum quantity of gold gives rise to a maximum increase (maximum permitted by the thermodynamics in the temperature window of 140-250°C) of the activity, to which other advantages are added such as the omission of the catalyst pre-conditioning stage, reduction of its deactivation, increase in its durability and significant stability in the event of changes in flow or temperature or start/stop cycles.

**Synthesis of Hydroxalates as a CuO/ZnO/Al₂O₃ Precursor**

[0050] The synthesis of hydroxalates as CuO/ZnO/Al₂O₃ mixed oxide precursors takes place by means of co-precipitation under oversaturation, where the salts and alkaline solution are slowly added, ensuring that the pH and temperature remain constant. The most widely used conditions are: between 10-80% in w/w of Al₂O₃ and 90-20% in w/w of CuO/ZnO; pH between 7 and 10 (pH at which most hydroxides precipitate); temperatures between 20° and 80°C; under concentrations and slow flows of reagents; washing after filtration with hot water, to fully remove the sodium ions; and drying at low temperatures (maximum 120°C).

[0051] First, an aqueous Na₂CO₃ solution with a concentration of 1 M is prepared as a precipitation agent. Next, the necessary quantity of each of the precursors is added in a 1L beaker. In all cases, the precursors used were the nitrates of said metals, Cu(NO₃)₂, 2H₂O, Zn(NO₃)₂, 6H₂O, Al(NO₃)₃, 9H₂O, since it does not generate solid residue and makes it possible to obtain cleaner hydroxalite. These were dissolved in a volume of 0.8 L of distilled water and magnetically agitated throughout the precipitation phase. The resulting colour of the dissolution is sky blue, characteristic of copper hydroxalites. The precipitation of the hydroxides is maintained for a period of 48 hours. Next, it is left to dry at a temperature below 100°C, to which end a heater may be used, or left to dry at room temperature for a couple of days. Lastly, after the drying phase, the sample is calcined. Lastly, the samples were calcined at a temperature of 300°C and a heating ramp of 10°C/min for a period of 4 hours.

[0052] This process has two major advantages: on the one hand, it makes it possible to integrate a large group of anions and cations in the structure and, on the other, the large-scale preparation thereof is less complex.

**Gold Deposition Method**

[0053] Two different gold impregnation methods were used. In both gold deposition methods, loads of 0.5%-4% (w/w) of gold were swept.


[0055] Said method consists of taking an aqueous solution of H₂AuCl₄, with concentrations of 10⁻⁴ M, which is heated to a temperature of approximately 70°C. Once said temperature is reached, the support is added to the solution and the mixture is left in agitation for 20 minutes. After said period of time has elapsed, the solution is cooled to approximately 40°C and 20 mL of NH₃ 30% (v/v) are added. It is agitated again for 20 minutes, filtered and the solid collected. Lastly, it is rinsed and calcined at 300°C for 4 hours.

alpha-Fe₂O₃ catalyst for water-gas shift reaction prepared by
deposition-precipitation™ Applied Catalysis A—General

[0057] Precipitation was performed by means of an
automated system (Contalab) that makes it possible to
control all the precipitation parameters (pH, temperature,
agitation speed, reagent feed flow, etc.). The gold is
deposited in the form of Auric Hydroxide, Au(OH)₃,
on the oxide layers, under vigorous agitation, main-
taining a constant pH of 7. After filtration and thorough
washing, the precursors were vacuum-dried and calcined
in air at 400°C for 2 hours.

Embodying the Invention

[0058] By way of example, following is a description of the
most representative results of a series of gold catalysts
supported on mixed CuO/ZnO/Al₂O₃ oxides, which are not
intended to be representative of their scope.

Chemical Composition

[0059] The elemental analysis was performed using
X-Ray micro fluorescence spectrometry (XRMFS) in an
EDAX Eagle III spectrometer with a rhodium source of
radiation.

[0060] In order to synthesize a series of precursor hydro-
talcites of the CuO/ZnO/Al₂O₃ mixed oxides, M⁴⁺/M⁺⁺
ratios from 1 to 6 were swept. Additionally, for each one of
these M⁴⁺/M⁺⁺ ratios, the M⁴⁺/M⁺⁺ ratio was varied between
1 and 6.

[0061] Table 1 includes the ratios of some of the represen-
tative M⁴⁺/M⁺⁺ ratios.

<table>
<thead>
<tr>
<th>TABLE 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁴⁺/M⁺⁺ ratios for the synthesis of hydrotalcites</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(Cu + Zn)/Al Molar Ratio</th>
<th>0.5</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
</table>

[0062] As with the M⁴⁺/M⁺⁺ ratio, some of the different
Cu²⁺/Zn²⁺ molar ratios that were prepared are exemplified in
Table 2.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁴⁺/M⁺⁺ ratios for the synthesis of hydrotalcites</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cu/Zn Molar Ratio</th>
<th>1.4</th>
<th>2.8</th>
<th>5.6</th>
</tr>
</thead>
</table>

[0063] The objective pursued is to perform a representa-
tive sweep of the ratios in order to find or at least come as
close as possible to the ideal M(II)/M(III) ratio. Table 3
shows the composition of some of the solids prepared (1T)
maintaining the M⁴⁺/M⁺⁺ ratio constant at 1, where M⁺⁺ is
Al³⁺ and M⁺⁺ is a mixture of Cu²⁺/Zn²⁺ whose Cu²⁺/Zn²⁺
ratio varies between 1.4 and 5.6.

<table>
<thead>
<tr>
<th>TABLE 3</th>
</tr>
</thead>
</table>
| Chemical composi-
| tion of some of the
<p>| solids prepared, |
| maintaining M⁴⁺/M⁺⁺ constant. |
|-----------------|-----------|-----------|-----------|-----------|-----------|</p>
<table>
<thead>
<tr>
<th>Sample</th>
<th>CuO (%)</th>
<th>ZnO (%)</th>
<th>Al₂O₃ (%)</th>
<th>Cu/Zn ratio</th>
<th>Cu/Zn Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>JHT 1.4</td>
<td>35.82</td>
<td>25.97</td>
<td>38.21</td>
<td>1.4</td>
<td>1.38</td>
</tr>
<tr>
<td>JHT 2.8</td>
<td>17.40</td>
<td>47.73</td>
<td>34.87</td>
<td>2.8</td>
<td>2.74</td>
</tr>
<tr>
<td>JHT 5.6</td>
<td>51.95</td>
<td>10.34</td>
<td>37.71</td>
<td>5.6</td>
<td>5.02</td>
</tr>
</tbody>
</table>

[0064] In all cases, a Cu/Zn ratio close to the targeted ratio
in the synthesis was achieved.

[0065] The X-Ray diffraction analysis (XRD) was perfo-
med on an X’Pert Pro PANalytical X-Ray diffractometer.
The diffraction patterns were recorded using the Kα1 radia-
tion of Cu (40 mA, 45 kV) in a range of 20 comprised
between 3° and 80° and a sensitive detector position using
a sieve size of 0.05μm and a passage time of 240 s. The XRD
patterns of the synthesized solids are shown in FIG. 1.

[0066] FIG. 1A shows the X-Ray diffraction patterns of
the non-calcined samples. In all cases the typical hydro-
talcite signals are obtained and a certain proportion of mal-
achite phase appears. After calcining the sample, FIG. 1B, the
CuO—ZnO—Al₂O₃ mixed oxide is obtained, as shown by the
reflections of the diffractogram. FIG. 1C shows a com-
parison between the diffraction patterns of a pre-reaction
calcined sample and the same sample after its use in WGS.
It can be clearly observed how the copper oxide is reduced
to metal copper during the reaction. The latter is the active
species in the water-gas shift. Lastly, FIG. 1D shows a com-
parison between a calcined mixed oxide and its corre-
sponding gold-containing catalyst. Typical reflections of
metal gold and of any other gold species were not observed,
which indicates that the gold nanoparticles are small (they
are smaller than 5 nm in size, which is the detection limit of
the diffractometer) and are well dispersed on the CuO—
ZnO—Al₂O₃ mixed oxide.

[0067] The WGS reaction was carried out in a proprietary
design diffractometer. The typical gas mixtures used for
the water-gas shift reaction were:

Model Mixture:

| [0068] 4.5% CO in Ar (Abelló Linde); 30% H₂O (0.024
| ml/min H₂O (l)). |

Industrial Conditions (Imitating the Outlet of an Ethanol
Reformer):

| [0069] 9% CO (Abelló Linde); 11% CO₂ (Abelló Linde);
| 50% H₂ (Abelló Linde); 30% H₂O (0.024 ml/min H₂O (l)). |

[0070] FIG. 2 shows the results of catalytic activity of the
systems where M⁴⁺/M⁺⁺ remained fixed at 1 and the gold
was deposited by means of the assisted anionic exchange
method. FIG. 2A shows a comparison of the activity of the
mixed oxides with that of their corresponding gold catalysts
supported under ideal conditions (previously described
model mixture). Within the mixed oxides, CuO/ZnO≈2.8
and 5.6 seem to be the optimum ratios, reaching equilibrium
conversions of 330°C. The activity of the gold systems is
very superior to that of their corresponding supports.
Equilibrium reductions are achieved practically from the start
of the reaction, making these systems very promising and
superior catalysts to the current low-temperature water-gas
shift industrial systems. In FIG. 2B, the supported gold
systems are tested under realistic operating conditions (previously described industrial conditions). The solids with Cu/Zn ratios of 1.4 and 2.8 reached equilibrium at 270°C and the Au-HT 2.8 system was the most active in the entire temperature range studied.

[0071] Frequently, from the industrial viewpoint, the stability of the catalyst is more important than the catalytic activity itself and this stability under operating conditions is a determining factor when selecting a catalyst. FIG. 3A shows the stability of one of the Au/CuO-ZnO/Al₂O₃ systems synthesized by means of the deposition–precipitation method under industrial conditions. Specifically, it is a system with a (Cu+Zn)/Al ratio of 2 and a Cu/Zn ratio of 5.6, called Au-HT/2.

[0072] The catalyst slightly loses activity in the first 14 hours of operation (from 70% to 65% of CO conversion). After said period has elapsed, the stationary state is reached and CO reduction remains high and stable. It should be noted that the temperature of the stability test is very low (220°C) and, therefore, the performance of this catalyst, considering the high activity and good stability shown at such a low temperature, is excellent and exceeds that of the CuO/ZnO-based catalysts currently used in the industry for the low temperature water-gas shift reaction.

[0073] In addition to continuous stability, it is of vital importance to verify catalyst resistance in start/stop cycles. Start/stop cycles imply lowering the temperature of the reaction mixture to room temperature (approximately 30°C) and maintaining said situation for 40 minutes (always with the gases and water flowing through the catalytic bed). After said period, the system is heated again up to the stability test temperature (220°C). This implies that the catalyst will come into contact with liquid water. The selected catalyst was capable of successfully tolerating up to four start/stop cycles without showing any deactivation. This result is quite promising and makes the catalysts studied very adequate for WGS processes in both stationary and portable applications.

[0074] It should be noted that in all the catalytic tests the reaction mixture, once stabilised, is free to flow directly over the catalyst. In other words, no treatment is performed prior to activation. The catalysts are activated directly in the reaction mixture, which implies an additional advantage with regard to possible applications in fuel processors that work in continuous mode.

[0075] The overall activity and stability results are quite satisfactory taking into account the characteristics offered by the catalysts currently available in the market, making these systems promising candidates for direct application thereof in real hydrogen stream purification processes.

1. A catalyst comprising gold supported on CuO/ZnO/Al₂O₃ wherein the catalyst comprises between 10% and 80% of Al₂O₃ and between 90% and 20% of CuO/ZnO.

2. The catalyst, according to claim 1, wherein the CuO/ZnO support precursor has a hydrotalcite structure.

3. The catalyst, according to claim 1, wherein the Cu/Zn/Al ratio is comprised between 0.5 and 3.

4. The catalyst, according to claim 1, wherein the Cu/Zn ratio is comprised between 1 and 6.

5. The catalyst, according to claim 1, wherein the catalyst comprises:
   - between 0.5% and 4% w/w of Au
   - between 10% and 90% w/w of CuO/ZnO

6. A method for preparing a catalyst, as defined in claim 1, comprising the following operations:
   - synthesis of hydrotalcites as CuO/ZnO/Al₂O₃ mixed oxide precursors, and
   - deposition of gold on the CuO/ZnO/Al₂O₃ substrate.

7. The method, according to claim 6, wherein the synthesis of hydrotalcites takes place by means of co-precipitation at a low supersaturation of Cu, Zn and Al salts at a pH comprised between 7 and 10 and temperatures comprised between 20°C and 80°C.

8. The method, according to claim 7, wherein Cu(NO₃)₂·2H₂O, Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O are used as precursors and Na₂CO₃ 1M as a precipitation agent, said precipitation being maintained for a period of 48 hours.

9. The method, according to claim 7, wherein precipitation is followed by drying at a temperature comprised between room temperature and 100°C, followed by subsequent calcination at 300°C for 4 hours with a ramp of 10°C/min.

10. The method, according to claim 7, wherein the deposition of Au is performed by means of direct anionic exchange assisted by NH₃.

11. The method, according to claim 10, wherein it is based on an aqueous H₂AuCl₄ solution to which the support is added.

12. The method, according to claim 7, wherein the deposition of Au is performed by means of deposition-precipitation.

13. The method, according to claim 12, wherein Au is deposited in the form of auric hydroxide on the oxide layers under agitation at a constant pH.

14. A process for a water-gas shift reaction comprising the use of a catalyst, as defined in claim 1.

15. The process, according to claim 14, wherein the reaction takes place in reactive streams having a composition comprising:
   - between 4.5% and 9% of CO,
   - between 0% and 11% of CO₂, and
   - between 30% and 50% of H₂O.

16. The process, according to claim 14, wherein the reaction takes place at a temperature comprised between 140 and 350°C and at a spatial velocity between 4,000 and 8,000 h⁻¹.