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Hakeem, Abrar A.; Rajendran, Jaikishen; Kapteijn, Freek; Makkee, Michiel

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Promotion or additive activity? The role of gold on zirconia supported iron oxide in high temperature water-gas shift

*Abrar A. Hakeem, Jaikishen Rajendran, Freek Kapteijn, and Michiel Makkee**

Catalysis Engineering, Department of Chemical Engineering, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, NL 2628 BL Delft, The Netherlands

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Abstract

Sulfur addition is used to probe the role of gold in Au/Fe₂O₃/ZrO₂ catalyst in the water-gas shift (WGS) at high temperature (623–773 K) and pressure (21 bar). Sulfur poisoning unravels the WGS activity contribution by gold nano-particles and gold promotion of iron oxide in Au/Fe₂O₃/ZrO₂. The active site(s) on gold nano-particles are poisoned by sulfur, which is reflected in a suppressed WGS activity of presulfided Au/ZrO₂. The same holds for the WGS activity contribution of gold nano-particles in Au/Fe₂O₃/ZrO₂, but the promotion by gold of the Fe₂O₃ is still present after presulfidation. The WGS performance of Fe₂O₃/ZrO₂ and Au/ZrO₂ catalysts with and without sulfur pretreatment are also compared with that of Au/Fe₂O₃/ZrO₂.

1. Introduction

In spite of an increasing importance of homogeneous gold catalysis in methodology development [1] and applications in organic synthesis [2], the classical origin of the success of heterogeneous gold catalysis is the ability of low temperature CO oxidation [3, 4]. A review by Hashmi and Hutchings [5] summarizes the different applications of gold as heterogeneous and homogeneous catalysts in a historical perspective. This work is on the application of Au/Fe₂O₃/ZrO₂ for high temperature (623–773 K) water–gas shift (WGS) at high pressure (21 bar). Andreeva *et al.* [6] were the first to report the activity of Au/Fe₂O₃ for low temperature (473–513 K) WGS and claimed it to be higher than that of the commercial low temperature catalyst (CuO/ZnO/Al₂O₃). The high activity of Au/Fe₂O₃ was concluded to be due to the interaction of gold with iron oxide support and higher dispersion of gold [7]. However, Au/Fe₂O₃ is not stable even under low temperature WGS conditions due to the sintering of the iron oxide support [8], resulting in a loss of surface area, and also due to sintering of highly dispersed gold particles [9, 10]. Although in some reports [8, 11] ‘Fe₂O₃ or iron oxide’ is mentioned, it is actually Fe(OH)₃ or FeO(OH) which is not calcined to form Fe₂O₃ and used as a support for the gold nanoparticles. The Au/Fe(OH)₃ initial activity may not be recovered as the phase of Fe(OH)₃ gets transformed easily at high temperature and catalyst changes its morphology. By use of different forms of iron oxide(s)/hydroxide as a catalyst support its stability needs to be interpreted accordingly.

In our previous study a zirconia supported iron oxide catalyst ($\text{Fe}_2\text{O}_3/\text{ZrO}_2$) showed improved stability under atmospheric WGS conditions [12] with iron oxide being highly dispersed on zirconia. In this study gold is deposited on relatively stable $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ to enhance its WGS activity and to study its role in the activity enhancement ($\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$). Gold can have two effects, an additive activity contribution by itself or promoting the activity of the iron oxide. The additive activity contribution from gold nano-particles on a support is due to the associative WGS mechanism, while the contribution from supported iron oxide is considered to be from a redox WGS mechanism [13, 14].

To elucidate the role of gold in $\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$, three catalysts were compared under realistic WGS conditions (10% CO, 20% H_2O , 5% H_2 , 5% CO_2 , $T = 623\text{--}773\text{ K}$, $P = 21\text{ bar}$): zirconia supported iron oxide ($\text{Fe}_2\text{O}_3/\text{ZrO}_2$), zirconia supported gold (Au/ZrO_2), and zirconia supported gold and iron oxide ($\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$). Further, to unravel the activity contribution from gold nanoparticles in $\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$, all of the catalysts were presulfided and tested under WGS conditions. Sulfur poisons irreversibly the active site(s) on gold nano-particles over both presulfided Au/ZrO_2 and $\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$. The sulfur poisoning allows to distinguish the contributions between the gold nano-particles themselves and the promotion effect of gold on iron oxide in $\text{Au}/\text{Fe}_2\text{O}_3/\text{ZrO}_2$.

2. Experimental

2.1. Materials

Zirconium oxide (Alfa Aesar–043815, BET surface area $90\text{ m}^2\text{ g}^{-1}$, pore volume 0.31 ml g^{-1}) 1/8" pellets were crushed to less than $150\text{ }\mu\text{m}$ particle size, alpha alumina (Engelhard, Al–3980 T1/8, surface area $3\text{ m}^2\text{ g}^{-1}$) extrudates crushed to a size fraction of $300\text{--}425\text{ }\mu\text{m}$, quartz wool (Boom B.V., $4\text{--}12\text{ }\mu\text{m}$, 77051065.0100), copper(II) oxide (Alfa Aesar–33307, 99.0%), silicon carbide (Guido Ozinga), iron (III) nitrate nonahydrate (Aldrich–254223, 99.99% trace metals basis), gold(III) chloride hydrate (Aldrich–254169), ammonium hydroxide solution (Fluka–318612, 5 M) diluted to 0.05 M, 1-dodecanethiol (471364–Aldrich, $\geq 98\%$), *n*-octane (74821–Aldrich, $\geq 99\%$), carbon monoxide (Linde, 4.7, 99.997% purity), hydrogen (Linde, 3.0, 99.9 % purity), carbon dioxide (Linde, 2.7, 99.7 % purity), and nitrogen (Linde, 5.0, 99.999 % purity) have been used as received.

2.2. Catalyst Preparation

The composition of the different catalysts prepared and calcination conditions used, are shown in table 1. The Fe-Zr catalyst was prepared by an incipient wetness impregnation (IWI) using crushed ZrO_2 ($< 150\ \mu\text{m}$) and iron nitrate solution equal to the pore volume of ZrO_2 . The catalyst was dried initially at 373 K for 5 h at $1\ \text{K min}^{-1}$ and subsequently calcined at 873 K for 5 h at $2\ \text{K min}^{-1}$ in a static oven. After calcination, gold was added to this catalyst (Fe-Zr) using a deposition precipitation method. A 0.002 M solution (50 ml) of chloroauric acid was used to have a target loading of 1 wt. % Au in this catalyst. The pH of this gold solution was 2.9 and to this solution Fe-Zr catalyst ($<150\ \mu\text{m}$ and 1.98 g) was added at once and the suspension is stirred using a magnetic stirrer in a 250 ml round bottom flask. After the addition of Fe-Zr catalyst the pH of the suspension increased to ~ 3.4 . Next, to this suspension ammonium hydroxide solution (0.01 M) is added at a rate of $1\ \text{ml min}^{-1}$ by using a pump (LabAlliance™ Series I Pump) until pH of 9 is reached and the pH is recorded during this period (Fig. 1). (*Caution:* The direct contact of HAuCl_4 with NH_4OH must be avoided as this could result in the formation of explosive fulminating gold [15, 16]). After reaching pH of 9 the pump is stopped and the suspension is allowed to age for 15 minutes, after which the final pH is noted to have decreased slightly (pH ~ 8.9). The suspension is immediately filtered (Whatman Grade 595 filter paper) and the precipitate is washed using 150–200 ml of demi-water until the filtrate is neutral and to ensure the residual chloride is being removed from the catalyst. The catalyst paste is dried for ~ 30 –40 min in the open air at ambient temperature and then the dried catalyst flakes are recovered from the filter paper. The catalyst was then further dried in static air at $2\ \text{K min}^{-1}$ at 373 K for 2 h and then calcined with at $2\ \text{K min}^{-1}$ to 623 K for 4 h. The calcined catalyst powder was then pelletized at a pressure of ~ 3000 bar for 2 min and crushed again to get a particle size fraction of 150–212 μm to be used in the reactor. Similarly, the Au-Zr catalyst was prepared by deposition precipitation using ZrO_2 as a support and pH profile recorded during its synthesis is shown in Fig. 1. The actual gold loading present in both the catalysts is around ~ 0.65 wt.% (Table 1), measured by ICP-OES analysis. Bulk Fe_2O_3 was also prepared by the direct calcination of iron nitrate. The catalyst after calcination is referred as ‘Fresh catalyst’ and the catalyst used in the WGS testing procedure at 21 bar is referred as ‘Spent catalyst’.

Au/Fe₂O₃ was not synthesized as Fe₂O₃ at high temperatures sinters very rapidly and this bulk form of Fe₂O₃ has a very low mechanical strength. Due to rapid sintering of Fe₂O₃ the accessibility to the deposited Au is hindered and can mislead to conclusions regarding activity contribution arising from the Au particles only.

PRESULFIDATION: One gram of fresh calcined catalyst (< 150 μm) was used for the presulfidation in 50 ml of 0.02 M 1-dodecanethiol solution in *n*-octane at room temperature (Table 2). 0.02 M of 50 ml 1-dodecanethiol solution is equivalent to 3 wt. % of sulfur added to one gram of catalyst at 100 % adsorption. The concentration of 1-dodecanethiol was measured in the suspension during the presulfidation (7890 A GC–Agilent Technologies) and its uptake kinetics is illustrated in Fig. 2.

From the adsorption kinetics (Fig. 2) the amount of sulfur present on the catalyst (before heat treatment) after 24 h is calculated (Table 2). All the catalysts (Table 2) were given a heat treatment in N₂ (100 ml_{STP} min⁻¹) at 373 K for 5 h (heating rate 1 K min⁻¹) and then at 623 K for 5 h (heating rate of 2 K min⁻¹). After the heat treatment the sulfur content (Table 2) was estimated by using a LECO CS–225 Carbon/Sulfur Determinator. The sample is combusted (air) in a high-frequency induction furnace (heating up to 1273 K), and the products of combustion are passed through a moisture trap to the sulfur IR cell, where the sulfur is measured as sulfur dioxide. Although this technique may have a limited accuracy to determine the amount of sulfur in an inorganic sample but it provides a rough estimate (not all sulfur present may be combusted to SO₂). The catalysts after the sulfur treatment are referred as ‘Fresh’ catalyst and prefixed by ‘S’ (Table 2).

The amount of sulfur on S-Fe-Zr is 0.22 wt. % and on S-Au-Fe-Zr as 0.20 wt. %. These sulfur amounts observed are mainly adsorbed over iron oxide in these catalysts as the amount of sulfur present over Au is in very low amount to be detected. The presence of low amount of sulfur on Au is supported with no sulfur detection in S-Au-Zr catalyst or low amount of sulfur intake during adsorption (Table 2).

2.3. Characterization

2.3.1 Nitrogen adsorption at 77K

The specific BET surface area and pore volume was determined by using Quantachrome Autosorb-6B unit gas adsorption analyzer. Before the nitrogen adsorption the calcined fresh catalyst samples (~100 mg and particle size < 150 μm) were degassed at 573 K for 16 hours in vacuum (0.05 mbar).

2.3.2. Hydrogen-Temperature Programmed Reduction (TPR)

TPR of the catalysts was carried out in a fixed bed-reactor system in which the hydrogen consumption is measured in a thermal conductivity detector (TCD). A permapure tubular drier is used to remove the water produced during the reduction before the TCD detector. A flow of 30 $\text{ml}_{\text{STP}} \text{min}^{-1}$ gas mixture (10% H_2 in Ar) is used over a packed bed of 100 mg of fresh catalyst (150–212 μm) (in case of bulk iron oxide only 10 mg). The reactor is heated at 10 K min^{-1} to a maximum temperature of 1173 K. The TCD is calibrated by using CuO as a reference. SiC (300–425 μm) is used before (~200 mg) and after (~400 mg) the catalyst bed as an inert for increasing the bed height to have a contact with a thermocouple (K-type), which records the temperature in the packed bed.

2.3.3. Scanning Electron Microscopy (SEM) & Energy-dispersive X-ray (EDX) Analysis

SEM images and EDX mapping of the fresh catalyst samples were taken by using JEOL JSM-6010 LA analytical scanning electron microscope equipped with an integrated EDX (Standard LA Version) with Silicon Drift Detector (SDD). The samples were analyzed at the accelerating voltage of 20 kV with a frame size of 1035 $\times$ 787 pixels.

2.3.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed on a K-alpha Thermo Fisher Scientific spectrometer using mono-chromated Al $K\alpha$ X-ray source. The measurements were done by using a line scan of four points with each point having a spot size of 300 μm at ambient temperature and chamber pressure of about 10^{-7} mbar. A flood gun is always used for a charge compensation. All the spectra measured were corrected by setting the reference binding energy of carbon (1s) at 285 ± 0.025 eV. The electron energy analyzer was operated with a pass energy of 50 eV and each high resolution

spectrum is scanned for ten times. The spectra were analyzed and processed using Thermo Advantage v5.903 software (Thermo Fisher Scientific). The peaks were fitted using a fixed Lorentzian–Gaussian product function. Smart background (derived from the Shirley background) was used over the peak width. The binding energies reported are within ± 0.1 eV. XPS was performed on fresh and spent catalyst samples (that had been only exposed to air at room temperature).

2.3.5. Transmission Electron Microscopy (TEM) and Energy–dispersive X-ray (EDX) analysis

TEM was performed using an FEI Tecnai 20 equipped with a FEG operated at 200 kV. EDX was performed using an Oxford Instruments analyzer. Samples were prepared for analysis by suspending them in ethanol and then placing droplets on copper grids with a carbon film support.

2.4. Catalyst Performance

The catalysts were tested at 21 bar with a feed composition of 10% CO, 20% H₂O, 5% H₂, 5% CO₂, and balance N₂ having a H₂/CO ratio equal to 0.5 typically present in the dry synthesis gas obtained from a coal gasification [17]. The total space velocities used was 240,000 ml_{STP} g_{cat}⁻¹ h⁻¹. The temperature is programmed to increase in steps of 50 K from 623 to 773 K and then decreasing back in steps of 50 K to the starting temperature (*i.e.* 623 K). The catalysts are tested at each temperature for 15 h. The amount of catalyst used was 40 $\pm$ 0.5 mg with the catalyst particle size used was 150–212 μ m. The details of the experimental unit can be found elsewhere [12].

3. Results

3.1. BET surface area

The BET specific surface area and pore volume of catalysts (Table 3) are calculated from the nitrogen adsorption data. The gold is deposited on ZrO₂ and Fe-Zr having similar surface area (Table 3). No appreciable change in the surface area is observed after calcination of Fe-Zr at 873 K compared that with ZrO₂. A decrease in the pore volume of Fe-Zr and Au-Fe-Zr is expected due to the pores of ZrO₂ filled by 3.57 wt.% Fe₂O₃ (equivalent to 2.5 wt. % of Fe).

3.2. Temperature Programmed Reduction (TPR)

As observed from the TPR results, the bulk ZrO_2 is not reducible (Fig. 3). The reduction of bulk iron oxide takes place in its characteristic two stages [18]: (1) Fe_2O_3 to Fe_3O_4 (around 656 K) and (2) Fe_3O_4 to Fe (around 805 K).

In case of Fe-Zr the reduction also takes place in two steps, but the peaks do correspond with a hydrogen consumption for the reduction steps (1) and (2) of Fe_2O_3 . Moreover, the complete reduction of the iron oxide in Fe-Zr to metallic iron does not take place as per the total hydrogen consumption (Table 4). The iron oxide in Fe-Zr catalyst is only reduced to about 60% based on the stoichiometry of the overall reduction reaction (3).

This is can be explained due to the strong interaction of highly dispersed iron oxide with zirconia. Further, the presence of Au in Fe-Zr shifts the Fe_2O_3 reduction temperature to lower temperature (395 K), which is attributed to hydrogen spill-over from metallic Au [19-21] and keeping the reduction level of 60 %, similar to that of Fe-Zr (Table 4).

3.3. Scanning Electron Microscopy (SEM) & Energy-dispersive X-ray (EDX) Analysis

Typical SEM-EDX mapping of fresh and spent Au-Fe-Zr catalyst shows a homogeneous distribution of iron oxide present in the catalysts (Fig. 4). The color code on the left edge (Fig. 4(b) and 4(c)) represent the intensities that increases from black to red. The intensities for zirconium are high as it is present as the support. Gold was not detected by this analysis due to the low amount of Au (~ 0.65 wt.%) present in the catalysts. No change in the morphology is observed in the spent catalyst.

3.4. X-Ray Photoelectron Spectroscopy (XPS)

XPS spectra indicate the presence of metallic gold in the fresh as well as spent catalysts with a binding energy of $Au4f_{7/2}$ close to 84 eV (Fig. 5). No significant change in the binding energy (~ 0.3 eV) is observed after sulfur adsorption and heat treatment (N_2) in $Au4f_{7/2}$ binding energy for the fresh S-Au-Fe-Zr compared with that of the fresh Au-Fe-Zr catalyst. Sulfur was detected to be in the form of sulfites over the fresh S-Fe-Zr and S-Au-Fe-Zr with the same binding energy of $S2p_{3/2} \sim 168$ eV on S-Fe-Zr and S-Au-Fe-Zr (Fig. 5). No sulfur was detected by XPS on S-Au-Zr catalyst. This also corresponds to the amount of sulfur present in S-Au-Zr catalyst (Table 2). Sulfites detected on S-Au-Fe-Zr catalyst is due to the presence of iron sulfite as is the case with S-Fe-Zr.

The oxidation state of sulfur present on the gold particles cannot be determined for the low amount of sulfur present. A small peak around 94 eV is the binding energy of $Fe3s$ which overlaps in the region of binding energy of $Au4f$ and also observed elsewhere [22].

No sulfur compounds could not be detected on the spent S-Au-Fe-Zr and S-Fe-Zr catalysts used in WGS at 21 bar, which indicate to the removal of most of the sulfur in WGS conditions over iron oxide (reversible nature to the sulfur presence). A small amount of sulfur (ppm levels) is required to poison irreversibly the gold nanoparticles almost completely under WGS conditions (Fig. 6b). Further, a low signal to noise ratio in the XPS spectra due to the low amount of gold (~ 0.65 wt. %) does not allow to make a statement on any higher other oxidation state of gold present in the catalysts. In literature, the oxidation state of the gold present over CeO_2 have been determined by FT-IR using CO as probe molecule [23]. However, CO being a strong reducing agent and might also induce some changes to the oxidation state of Au in a heterogeneous catalyst.

3.5. Catalyst Testing

Sulfur Free Catalysts

Au-Fe-Zr is more active than the Fe-Zr and Au-Zr catalysts at different temperatures (Fig. 6a). This higher activity of Au-Fe-Zr can be due to a combined activity of gold particles supported on iron oxide and iron oxide on zirconia and/or due to the

promotion of iron oxide by gold and some activity contribution of the Au particles themselves on iron oxide. No appreciable activity (<5% CO conversion at 773 K) is observed over the ZrO₂ support under these WGS conditions. The activity of Au-Fe-Zr is slightly higher than the algebraic sum of the activities of Fe-Zr and Au-Zr at temperatures above 623 K. At 623 K the WGS activity observed is due to only gold nano-particles dispersed on support ZrO₂ and Fe-Zr with no significant activity contribution from either of the supports (Fig. 6a). Comparing the CO conversion in the heating and cooling stage at 723 K Au-Fe-Zr, Au-Zr, and Fe-Zr undergo deactivation.

Presulfided Catalysts

The pre-sulfided gold catalyst (S-Au-Zr) has an activity similar to that of a bare S-ZrO₂ or ZrO₂, indicating that the active sites on gold nano-particles are poisoned by the presulfidation with sulfur (Fig. 6b). S-Fe-Zr has a similar activity as that of Fe-Zr at different temperatures except at 773 K, where the CO conversion over Fe-Zr is ~11% higher than that over S-Fe-Zr (Fig. 6b). This indicates that iron oxide is mostly resistant to the presulfidation. The activity of S-Au-Fe-Zr is lower than the activity of Au-Fe-Zr, but higher than the activity of Fe-Zr (Fig. 6b and 6c). This indicates that a promotion effect due to 'Au-S' on iron oxide is still present at higher temperatures (>623 K) in S-Au-Fe-Zr, since the activity contribution from the gold nanoparticles on zirconia is less likely to contribute due to its easy poisoning as it is in the case with S-Au-Zr. At 623 K in the heating stage the activity of S-Au-Fe-Zr and S-Au-Zr are similar (Fig. 6b), which indicates a similar poisoning of the gold nano-particles in both these catalysts as the activity contribution of Fe-Zr or S-Fe-Zr at this temperature is equal to that of the bare ZrO₂ (Fig. 6b and 6a). A small amount of sulfur (Table 2) is required to poison irreversibly the gold nanoparticles almost completely under WGS conditions.

3.6. Transmission Electron Microscopy (TEM) and Energy-dispersive X-ray (EDX) analysis

Typical TEM-EDX analyses of the spent samples indicates the presence of Au nanoparticles in vicinity of iron oxide in Au-Fe-Zr. At different spots (A and B) the presence of intensities from Au and Fe is clear from the micrographs (Fig. 7). The copper signal is due to the grid support material used in this measurement. The

average particle size of Au particles in the spent catalyst is calculated to be around 5.5 nm, assuming spherical gold particles. In case of the fresh Au-Fe-Zr the gold particles were not easy to detect by bright field TEM analysis, most likely due to very high dispersion of gold particles, although XPS clearly indicates the presence of gold in the fresh catalyst (using spot size of 300 μm). ZrO_2 and 3.57 wt. % $\text{Fe}_2\text{O}_3/\text{ZrO}_2$ have been used to deposit the gold using a uniform and controlled deposition precipitation method (similar pH profile-Fig. 1) and both of these supports having similar surface area $\sim 100 \text{ m}^2 \text{ g}^{-1}$. A similar yield of gold is obtained $\sim 0.65 \text{ wt. \%}$ (Table 1), reflecting to the similar conditions of the preparation used. A similar dispersion of Au is expected under these similar preparation conditions. Further, similar activities of Au-Zr and Au-Fe-Zr at 623 K (Fig. 6b) reflect similar dispersion of Au, as the activity at 623 K is only due to the gold particles.

4. Discussion

A similar amount of gold (Table 1) in almost equal surface area catalysts Au-Fe-Zr and Au-Zr is obtained which is very essential to compare the performance of these catalysts to elucidate the role of gold. Also a similar pH curve obtained in the synthesis of these catalysts (Au-Fe-Zr and Au-Zr) further supported similar amount ($\sim 0.65 \text{ wt. \%}$) of gold present in the catalysts (Fig. 1). Further, XPS analysis of these catalysts (Au-Fe-Zr and Au-Zr) calcined at similar conditions indicated similar oxidation state of the gold in both Au-Zr and Au-Fe-Zr. Hence the small amount of iron oxide (3.57 wt. %) present in the Fe-Zr which was used for the synthesis of Au-Fe-Zr did not create any significant changes in the gold loading, surface area of the catalyst, pH curve during the synthesis and the oxidation state of the Au species in the catalyst. This further indicated we have a similar dispersion of Au particles present in Au-Zr and Au-Fe-Zr, which is good in order to have a comparison of activity between the catalysts and role played by gold in the catalyst.

The catalyst performance of the sulfur free and presulfided Au-Fe-Zr, Au-Zr, and Fe-Zr catalysts have provided insight into the role of gold in Au-Fe-Zr. The WGS activity over Au-Fe-Zr is the combination of activity due to gold promoted iron oxide and active site(s) present on the gold nano-particles themselves. The gold promotion of iron oxide on zirconia only appears at temperatures above 623 K *i.e.* above the light-

off temperature for Fe-Zr. At the low temperature WGS reaction conditions (< 623 K), bare ZrO_2 and Fe_2O_3 used as a support for gold nanoparticles do not show any significant activity [8]. The WGS activity at these low temperature conditions observed over $\text{Au/Fe}_2\text{O}_3$ and Au/ZrO_2 is due to the presence of gold nano-particles dispersed on these supports. However, at the high temperature WGS conditions iron oxide itself is an active catalyst [12] and the addition of the gold to it can further enhance the WGS activity with a possible promotion effect and/or additive activity.

The independent contribution to the WGS activity by the gold nano-particles in Au-Fe-Zr can be observed below or equal to 623 K, at which the activity of Fe-Zr is insignificant (equal to bare ZrO_2). Au-Zr and Au-Fe-Zr have equal activity (Fig. 6a) in the cooling stage at 623 K in the case of the sulfur free catalysts although in the heating stage at same temperature Au-Zr catalyst even has slightly higher activity than Au-Fe-Zr. This indicates that the WGS activity contribution from gold nanoparticles is more or less independent of the type of support used iron oxide or zirconia.

The contribution to the WGS by the promotion of gold nano-particles on iron oxide in Au-Fe-Zr can be observed at temperatures above 623 K. This can be only evident when the WGS activity due to the gold nano-particles is completely suppressed in Au-Fe-Zr. This is done by poisoning the active site(s) on the gold nanoparticles with sulfur. A very small amount of sulfur (Table 2) is required to completely poison all active sites present on the gold nano-particles in S-Au-Zr. This is based on the observation of the difference in the activity of S-Au-Zr and Au-Zr as can be seen in Fig. 6b. No detection of sulfur by the XPS analysis in S-Au-Zr also indicates that a low amount of sulfur is present (Fig. 6b). The poisoning of active site(s) on the gold nano-particles in Au-Zr (S-Au-Zr) indicates the sensitive nature of gold towards sulfur. In case of S-Au-Fe-Zr the poisoning of the gold particles can similarly be accomplished even with a higher sulfur uptake due to the iron oxide (Fig. 2). This is supported by the fact that at 623 K the WGS activity of S-Au-Zr and S-Au-Fe-Zr is similar to the WGS activity of Fe-Zr or S-Fe-Zr at this temperature equal to that of bare ZrO_2 . Any part of the gold is not sulfur free in S-Au-Fe-Zr as the activity of S-Au-Fe-Zr is similar to that of Fe-Zr/S-Fe-Zr at 350°C (623 K) in the cooling stages (no activity contribution from the gold). At temperatures above 625 K the WGS activity of S-Au-Fe-Zr is still higher than that of Fe-Zr even after complete suppression of the WGS activity contribution from gold nano-particles (associative

type). This indicates the promotion role of 'Au-S' on iron oxide (redox type) present that can enhance the activity of S-Au-Fe-Zr at temperature above 625 K.

It is speculated that the promotion of the redox mechanism of iron oxide by the gold nano-particles even after their presulfidation is due to an electronic effect of 'Au-S' particles on iron oxide. In the literature the rate limiting elementary step for iron oxide based catalysts used in WGS is claimed to be typically the dissociation of H₂O [24, 25] and it can be further argued that the presence of 'Au-S' can still promote this elementary step which results in a higher activity of S-Au-Fe-Zr than compared that of both Fe-Zr and S-Fe-Zr. The nature of sulfur present under the WGS conditions (*in-situ*) needs further investigation.

5. Conclusions

Gold promotes iron oxide in Au/Fe₂O₃/ZrO₂ catalyst at temperatures above 623 K and also contributes to the WGS activity by being active itself at all investigated temperatures via the associative mechanism. Sulfur presulfidation made it possible to distinguish the activity contributions due to the gold nano-particles and the promotion of iron oxide by the gold in Au/Fe₂O₃/ZrO₂. The WGS activity contribution over the active site(s) on the gold nano-particles are poisoned in Au/Fe₂O₃/ZrO₂ by the presence of sulfur, whereas the promotional role of the gold at higher temperatures (> 623 K) is still operational on the iron oxide catalyst even after the presulfidation.

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Tables

Table 1. Overview of the catalysts prepared.

Catalyst nomenclature	Au wt. %	Fe ₂ O ₃ wt. %	ZrO ₂ wt. %	Calcination <i>T</i> / K	Conditions
Fe-Zr	–	3.57	balance	873	Static oven
Au-Fe-Zr	0.66	3.57	balance	623	Static oven
Au-Zr	0.64	–	balance	623	Static oven
Fe ₂ O ₃	–	100	–	873	Static oven

Table 2. Adsorption of 1-dodecanethiol during presulfidation at room temperature for different catalysts.

Catalyst Tag	[†] Sulfur before heat treatment wt. %	Sulfur after heat treatment (N ₂) wt. %
S-Fe-Zr	2.8 ± 0.1	0.22
S-Au-Fe-Zr	2.8 ± 0.1	0.20
S-Au-Zr	0.7 ± 0.1	bdl
S-ZrO ₂	0.4 ± 0.1	bdl

[†] Calculated from 1-dodecanethiol adsorption after 24 h (Fig. 2); bdl = below detection limit

Table 3. Texture properties of fresh catalysts.

Catalyst	<i>S</i> _{BET}	<i>V</i> _p	Pore size
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Tag	(m ² g ⁻¹)	Pore volume (ml g ⁻¹)	range (nm)
ZrO ₂	102	0.31	3–50
Fe-Zr	94	0.23	3–50
Au-Fe-Zr	96	0.23	3–50

Table 4. Hydrogen consumption by the fresh catalysts in temperature programmed reduction.

Catalyst	Weight (mg)	H ₂ consumption Theoretical mmol	H ₂ consumption Observed mmol	Reduction ^a %
Fe ₂ O ₃	10	0.188	0.195	104
Fe-Zr	100	0.067	0.041	61
Au-Fe-Zr	100	0.067	0.039	58

^aIn all cases the calculations are made for the reduction reaction $\text{Fe}_2\text{O}_3 + 3 \text{H}_2 \rightleftharpoons 2 \text{Fe} + 3 \text{H}_2\text{O}$ (3). The error in calculating total hydrogen consumption is within $\pm 5\%$.

Captions

Fig. 1. pH profile recorded during deposition precipitation synthesis of gold catalysts using 0.01 M NH_4OH solution at a flow rate of 1 ml min^{-1} : Au-Fe-Zr (Δ) and Au-Zr ($\diamond$).

Fig. 2. Adsorption of 1-dodecanethiol during presulfidation for the different catalysts at room temperature: S-Fe-Zr ($\bullet$), S-Au-Fe-Zr ($\blacktriangle$), S-Au-Zr ($\blacklozenge$), and S-ZrO₂ ($\blacksquare$).

Fig. 3. Hydrogen–Temperature Programmed Reduction of several fresh catalysts using 10% H_2 in Ar gas mixture at a total flow rate of $30 \text{ ml}_{\text{STP}} \text{ min}^{-1}$.

Fig. 4. Typical SEM–EDX analysis of fresh and spent Au-Fe-Zr catalyst (scale of 0.1 mm at bottom). (a) SEM image; (b) EDX mapping of Zr; and (c) EDX mapping of Fe.

Fig. 5. XPS spectra of fresh and spent catalysts after air exposure at room temperature. (a) $\text{Au}4f$ of fresh Au-Fe-Zr, fresh S-Au-Fe-Zr, fresh S-Au-Zr, spent Au-Fe-Zr, and spent S-Au-Fe-Zr; (b) $\text{S}2p$ of fresh S-Fe-Zr, fresh S-Au-Fe-Zr, and spent S-Au-Fe-Zr.

Fig. 6. CO conversion in WGS at different temperatures for several catalysts: (a) Au-Fe-Zr (Δ), Fe-Zr ($\circ$), Au-Zr ($\diamond$), and ZrO₂ ($\triangleright$); (b) Au-Fe-Zr (Δ), Au-Zr ($\diamond$), S-Au-Fe-Zr ($\blacktriangle$), S-Au-Zr ($\blacklozenge$), and S-ZrO₂ ($\blacktriangleleft$); (c) S-Au-Fe-Zr ($\blacktriangle$), Fe-Zr ($\circ$), and S-Fe-Zr ($\bullet$). Solid black line represents equilibrium conversion levels (X_e) and red line the temperature (T). Inlet gas compositions are 10% CO, 20% H_2O , 5% H_2 , 5% CO_2 , 60% N_2 , $P = 21 \text{ bar}$, and space velocity (SV) of $240,000 \text{ ml}_{\text{STP}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ($1.07 \text{ mol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$).

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Fig. 6. CO conversion in WGS at different temperatures for several catalysts:

(a) Au-Fe-Zr (Δ), Fe-Zr ($\circ$), Au-Zr ($\diamond$), and ZrO_2 ($\triangleright$); (b) Au-Fe-Zr (Δ), Au-Zr ($\diamond$), S-Au-Fe-Zr ($\blacktriangle$), S-Au-Zr ($\blacklozenge$), and S- ZrO_2 ($\blacktriangleright$); (c) S-Au-Fe-Zr ($\blacktriangle$), Fe-Zr ($\circ$), and S-Fe-Zr ($\bullet$). Solid black line represents equilibrium conversion levels (X_e) and red line the temperature (T). Inlet gas compositions are 10% CO, 20% H_2O , 5% H_2 , 5% CO_2 , 60% N_2 , $P = 21$ bar, and space velocity (SV) of $240,000 \text{ ml}_{\text{STP}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ($1.07 \text{ mol}_{\text{CO}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$).

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