



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



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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.

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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 (Fe₂O₃/ZrO₂) 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 Fe₂O₃/ZrO₂ to enhance its WGS activity and to study its role in the activity enhancement (Au/Fe₂O₃/ZrO₂). 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 nanoparticles 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 Au/Fe₂O₃/ZrO₂, three catalysts were compared under realistic WGS conditions (10% CO, 20% H₂O, 5% H₂, 5% CO₂, T=623–773 K, P=21 bar): zirconia supported iron oxide (Fe₂O₃/ZrO₂), zirconia supported gold (Au/ZrO₂), and zirconia supported gold and iron oxide (Au/Fe₂O₃/ZrO₂). Further, to unravel the activity contribution from gold nanoparticles in Au/Fe₂O₃/ZrO₂, 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/ZrO₂ and Au/Fe₂O₃/ZrO₂. The sulfur poisoning allows to distinguish the contributions between the gold nano-particles themselves and the promotion effect of gold on iron oxide in Au/Fe₂O₃/ZrO₂.

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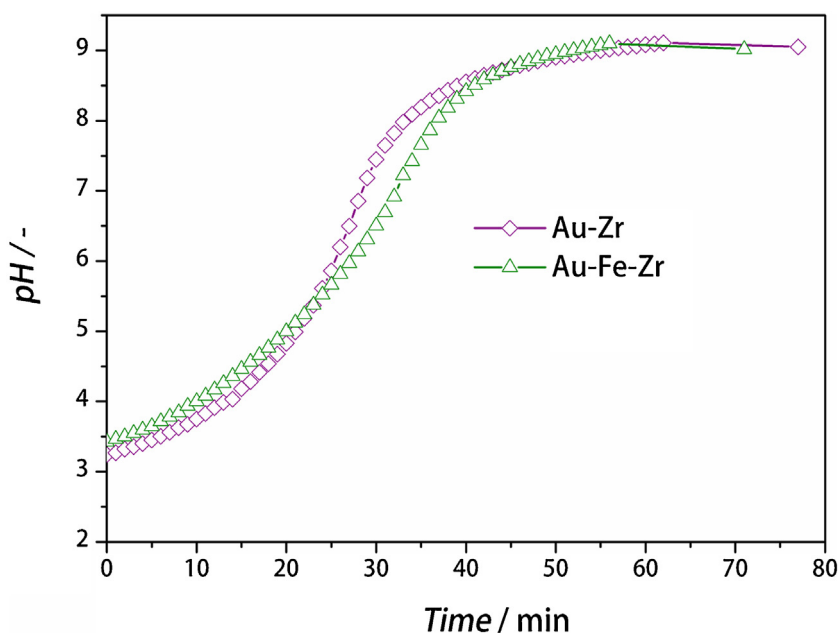


Fig. 1. pH profile recorded during deposition precipitation synthesis of gold catalysts using 0.01 M NH_4OH solution at a flow rate of 1 ml min^{-1} : Au-Fe-Zr (Δ) and Au-Zr (\diamond).

Table 1
Overview of the catalysts prepared.

Catalyst nomenclature	Au wt.%	Fe_2O_3 wt.%	ZrO_2 wt.%	Calcination T/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_2O_3	–	100	–	873	Static oven

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 $150 \mu\text{m}$ 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 $300\text{--}425 \mu\text{m}$, quartz wool (Boom B.V., $4\text{--}12 \mu\text{m}$, 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 K min^{-1} and subsequently calcined at 873 K for 5 h at 2 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 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 min, 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 $\sim 30\text{--}40 \text{ min}$ 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 K min^{-1} at 373 K for 2 h and then calcined with at 2 K min^{-1} to 623 K for 4 h. The calcined catalyst powder was then pelletized at a pressure of $\sim 3000 \text{ bar}$ for 2 min and crushed again to get a particle size fraction of $150\text{--}212 \mu\text{m}$ 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 $\sim 0.65 \text{ wt.}\%$ (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'.

$\text{Au/Fe}_2\text{O}_3$ was not synthesized as Fe_2O_3 at high temperatures sinters very rapidly and this bulk form of Fe_2O_3 has a very low mechanical strength. Due to rapid sintering of Fe_2O_3 the accessibil-

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