A comparative study of the effect of addition of CeO$_x$ and Li$_2$O on $\gamma$-Al$_2$O$_3$ supported copper, silver and gold catalysts in the preferential oxidation of CO

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In the study described in this paper we deposited gold, silver and copper on $\gamma$-Al$_2$O$_3$ as nanoparticles ($< 4$ nm) and investigated the behavior of these nanoparticles in the preferential oxidation of CO in presence of H$_2$. In addition, the effect of addition of CeO$_x$ and/or Li$_2$O was investigated. All the three metals show preferential oxidation of CO at low temperatures. The oxides added to Au/$\gamma$-Al$_2$O$_3$, Ag/$\gamma$-Al$_2$O$_3$ and Cu/$\gamma$-Al$_2$O$_3$ improve the catalytic performance of the gold, silver and copper. Interesting and synergistic effects were observed when both the CeO$_x$ and Li$_2$O were added. Possible mechanisms are proposed.

KEY WORDS: gold; silver; copper; ceria; lithium; hydrogen; preferential and total CO oxidation.

1. Introduction

The polymer electrolyte fuel cell (PEMFC) can generate electricity without polluting the environment. In this system hydrogen is oxidized over Pt electrodes and electric energy is generated, with ideally the only reaction product being H$_2$O. The supply of hydrogen needed for operation can be produced from methanol [1,2] or other fuels [2,3], via partial oxidation, steam reforming, and/or water gas shift reactions. In the ideal situation the product stream from these reactions consists of only CO$_2$ and H$_2$. However, in practice the product stream also contains several vol% H$_2$O and about 1–2 vol% CO [4]. Especially the presence of CO in the feed causes major problems as Pt is effectively poisoned by CO at the operating temperatures of the fuel cell, i.e. 60–100 °C [5,6]. In addition, H$_2$ oxidation will compete with CO oxidation in gas streams containing both compounds. Hence, there is an urgent need to find a way to remove CO selectively from the product stream.

In several papers it is reported that CO can be oxidized in the presence of hydrogen on supported noble metal catalysts such as Pt, Ru and Rh report in the temperature range 100–250 °C [7–9]. At lower temperatures the CO oxidation is rather slow due to inhibition of oxygen adsorption by adsorbed CO. At temperatures above 250 °C the selectivity decreases because thermal desorption of CO enables H$_2$ oxidation.

Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in low-temperature CO oxidation [10–14]. In addition, several studies have indicated that the rate of CO oxidation over supported Au catalysts exceeds that of H$_2$ oxidation [15–17]. Therefore, gold is a promising catalyst for the preferential catalytic oxidation of CO (PROX) in the presence of H$_2$ in the temperature range up to 100 °C. By promoting Au catalysts great improvements in activity can be obtained [13,15,16,18] and the temperature range of CO conversion can be enlarged. Recent studies have shown that also CuO mixed with ZnO [19] and CuO mixed with cerium oxide [20–22] are promising PROX catalysts. A DFT study [23] shows that gold and copper have a lower barrier for CO oxidation than for H$_2$ oxidation. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al$_2$O$_3$ catalyst in CO oxidation [13,24]. It was argued that the active oxygen is supplied by the ceria. Moreover, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [25]. A detailed study of Gluhoi et al. [26–28] on the effects of addition of (earth) alkali metals to a Au/Al$_2$O$_3$ catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold nanoparticles i.e. that of a structural promoter in the investigated reactions.

In the present paper a comparative study is described concerning the effect of addition of Li$_2$O and/or CeO$_x$ to copper, silver and gold catalysts on the preferential oxidation of CO in a hydrogen atmosphere. For the activity of gold the particle size is essential. So for a good comparison we also tried to get small metal particles of about 3 nm for the copper and silver catalysts. No literature data has been found for the preferential oxidation of CO on such small particles of copper and silver. The CO PROX reaction over Au/Li$_2$O/CeO$_x$/Al$_2$O$_3$ will be described in more detail in a future paper [29].

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2. Experimental

2.1. Catalyst preparation

Mixed oxides of ceria (denoted as CeO$_2$) and Li$_2$O on alumina were prepared by pore volume impregnation of $\gamma$-Al$_2$O$_3$ (Engelhard) with the corresponding nitrates. After calcination at 350 °C these oxides were used as support for the catalysts. The prepared mixed oxides have an intended Ce/Al and Li/Al ratio of 1/15. The copper and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [30]. An appropriate amount of HAuCl$_4$·3aq (99.999% Aldrich chemicals), AgNO$_3$ or Cu(NO$_3$)$_2$·3aq was added to a suspension of purified water containing $\gamma$-Al$_2$O$_3$ or the mixed oxide. The intended M/Al ratio was 1/75 ($M = Cu, Ag$ or Au). This ratio of 1:75 is equal to 0.53 at% M and resulted in 5 wt% for gold, 2.5 wt% for silver and 1.5 wt% for copper. The temperature was kept at 80 °C allowing urea (p.a., Acros) to decompose ensuring a slow increase of pH. When a pH of around 8–8.5 was reached the slurry was filtrated and washed thoroughly with water and dried overnight at 80 °C. Silver catalysts could not be prepared with urea, because a soluble Ag[NH$_3$] complex is formed. So the silver catalysts were either prepared by homogeneous deposition precipitation using Na$_2$CO$_3$ as precipitating agent or by liquid phase reduction (LPR) using glucose as reducing agent. With the latter method it is possible to deposit metallic silver particles on the supporting oxide. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200 μm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400 °C with hydrogen.

2.2. Catalyst characterization

The metal loading was verified by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Varian Vista-MPX. For that purpose, a small fraction of the catalyst was dissolved in diluted HNO$_3$ (copper and silver) or aqua regia (gold). X-ray diffraction measurements were done using a Philips Goniometer PW 1050/25 diffractometer equipped with a PW Cu 2103/00 X-ray tube operating at 50 kV and 40 mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [31].

2.3. Activity measurements

Prior to activity experiments the catalysts were reduced with H$_2$ (4 vol% in He) at 400 °C for 2 h. Activity tests of the catalysts were performed in a micro reactor system. The amount of catalyst used was 200 mg for the Au/$\gamma$-Al$_2$O$_3$, Ag/$\gamma$-Al$_2$O$_3$ and Cu/$\gamma$-Al$_2$O$_3$ catalysts. When the catalyst contained CeO$_2$ and/or Li$_2$O the amount of catalyst was adjusted in such a way that the amount of metal (Au, Ag or Cu) was similar for all the catalysts with and without additives. Gas mixtures (4 vol% in helium) used were CO + O$_2$ (ratio 1), CO + O$_2$ + H$_2$ (ratio 1:1:5), CO + O$_2$ + H$_2$ (ratio 1:1:5) and CO + O$_2$ + H$_2$ (ratio 1:5:5). Typically a total gas flow of 40 ml/min (GHSV $\approx$ 2500 h$^{-1}$) was maintained. The effluent stream was analyzed online by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture and an activated molecular sieve. The experiments were carried out at a pressure of 1 bar. Each measurement consists of four temperature programmed cycles of heating and cooling, with a rate of 4 °C/min. No deactivation of the catalysts was observed except for the Ag/$\gamma$-Al$_2$O$_3$ and Ag/Li$_2$O/$\gamma$-Al$_2$O$_3$ catalyst in CO oxidation in the absence of H$_2$. Unless otherwise stated the results of the second cooling stage are depicted in the figures.

2.4. FTIR measurements

Catalyst powder was pressed into a disc that was mounted in a vacuum cell (base pressure $5 \times 10^{-1}$ mbar) and was reduced in situ by H$_2$ or oxidized by O$_2$ for 1 h at 350 °C. Infrared spectra were recorded with a single-beam spectrometer (Mattson Galaxy 2020) operated at a resolution of 4 cm$^{-1}$. To reduce the noise/signal ratio 128 scans were taken per spectrum and the applied infrared range was 3000–1000 cm$^{-1}$. Background spectra were recorded before admitting reaction mixtures. Reactant gases used were O$_2$ (99.998%), H$_2$ (99.999%) and CO (99.997%, Messer Griesheim), and were admitted up to a pressure between 1 and 100 mbar. Finally the spectra were corrected for gas phase bands of CO and backgrounds were subtracted.

3. Results

3.1. Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was apparently below 3 nm. The results of the characterization of the catalysts after the reaction are shown in table 1. The catalysts without additives contain small particles of 4–5 nm. When ceria and Li$_2$O are added the average particle size is lower than the detection limit (3 nm) of the XRD machine. HRTEM data of comparable catalysts have been published in earlier papers of our group [26,27]. The particle size of the silver catalysts prepared with liquid phase reduction was about 8–9 nm. The actual metal loading was almost equal to the intended metal loading. In addition, we have checked the catalysts for the Li and Ce contents with ICP-OES. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts. The XRD diagram after reaction (CO
oxidation) of the silver catalysts prepared with HDP show that the silver particles are converted to \( \text{Ag}_2\text{O} \). The XRD diagram of silver based catalysts prepared by LPR show only peaks of metallic silver after the reaction.

### 3.2. CO oxidation in the absence of \( \text{H}_2 \)

The behavior of the catalysts in CO oxidation with oxygen in a ratio of 1:1 in the absence of \( \text{H}_2 \) is illustrated in table 2 and in figures 1 and 2. Gold is the most active catalyst followed by copper and silver. The combined addition of both \( \text{Li}_2\text{O} \) and \( \text{CeO}_x \) has a very beneficial effect on the activity of the copper and gold catalysts, whereas addition of only \( \text{CeO}_x \) has a negative effect and the addition of only \( \text{Li}_2\text{O} \) a small positive effect on the activity of the catalysts. Addition of \( \text{Li}_2\text{O} \) and/or \( \text{Li}_2\text{O} \) and \( \text{CeO}_x \) to the silver catalysts prepared by liquid phase reduction does not affect the catalyst performance, see figure 2. The silver catalysts prepared by homogeneous deposition precipitation show a different behavior as is depicted in figure 1. The silver only catalyst shows activity at a much lower temperature than the silver

| Catalyst                  | Metal loading (wt%) | Average particle size (nm) |
|---------------------------|--------------------|---------------------------|
| Au/Al\(_2\)O\(_3\)        | 4.6 ± 0.1          | 5.3 ± 0.1                 |
| Au/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 4.1 ± 0.1          | <3.0                      |
| Au/Li/O/Al\(_2\)O\(_3\)    | 4.5 ± 0.1          | 4.0 ± 0.1                 |
| Au/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 4.0 ± 0.2          | <3.0                      |
| Ag/Al\(_2\)O\(_3\)        | 2.3 ± 0.1          | 5.6 ± 0.1                 |
| Ag/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 1.7 ± 0.1          | 4.1 ± 0.1                 |
| Ag/Li/O/Al\(_2\)O\(_3\)    | 2.2 ± 0.1          | <3.0                      |
| Ag/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 1.6 ± 0.1          | <3.0                      |
| Cu/Al\(_2\)O\(_3\)        | 1.5 ± 0.1          | 4.4 ± 0.1                 |
| Cu/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 1.0 ± 0.1          | <3.0                      |
| Cu/Li\(_2\)O/Al\(_2\)O\(_3\) | 1.4 ± 0.1          | <3.0                      |
| Cu/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 1.0 ± 0.1          | <3.0                      |
| Ag(LPR)/Al\(_2\)O\(_3\)   | 2.5 ± 0.1          | 9.2 ± 0.2                 |
| Ag(LPR)/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 1.7 ± 0.1          | 8.8 ± 0.2                 |
| Ag(LPR)/Li\(_2\)O/Al\(_2\)O\(_3\) | 2.4 ± 0.1          | 8.7 ± 0.2                 |
| Ag(LPR)/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 1.7 ± 0.1          | 8.5 ± 0.1                 |

| Catalyst                  | \(T_{50\%}\) (°C) | \(T_{95\%}\) (°C) |
|---------------------------|-------------------|-------------------|
| Au/Al\(_2\)O\(_3\)        | 50                | 100               |
| Au/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 75                | 150               |
| Au/Li/O/Al\(_2\)O\(_3\)    | 50                | 100               |
| Au/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | RT                | 100               |
| Ag/Al\(_2\)O\(_3\)        | 80                | 160               |
| Ag/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 180               | 250               |
| Ag/Li\(_2\)O/Al\(_2\)O\(_3\) | 100               | 185               |
| Ag/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 200               | 250               |
| Cu/Al\(_2\)O\(_3\)        | 160               | 210               |
| Cu/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 210               | 250               |
| Cu/Li\(_2\)O/Al\(_2\)O\(_3\) | 140               | 190               |
| Cu/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 110               | 150               |
| Ag(LPR)/Al\(_2\)O\(_3\)   | 210               | 250               |
| Ag(LPR)/\(\text{CeO}_x\)/Al\(_2\)O\(_3\) | 200               | 250               |
| Ag(LPR)/Li\(_2\)O/Al\(_2\)O\(_3\) | 210               | 250               |
| Ag(LPR)/\(\text{CeO}_x\)/Li\(_2\)O/Al\(_2\)O\(_3\) | 200               | 250               |
catalyst prepared by LPR, but deactivates already in the first heating stage above 250 °C, in the following stages the deactivation continues. Addition of ceria stabilizes the silver catalyst but the T_{50%} is increased to 180 °C. Li_{2}O addition shows a very small negative effect on these silver catalysts. The effect of addition of both oxides is comparable to addition of CeO\textsubscript{x} only.

3.3. Preferential oxidation of CO in the presence of H\textsubscript{2} (CO:O\textsubscript{2}:H\textsubscript{2} = 1:1:5)

Figure 3 shows that when CeO\textsubscript{x} and Li\textsubscript{2}O are added to the Au, Ag, Cu based catalysts, the CO oxidation precedes the H\textsubscript{2} oxidation on all three metals when a ratio of CO:O\textsubscript{2}:H\textsubscript{2} (1:1:5) is used. At temperatures below 100 °C Au/γ-Al\textsubscript{2}O\textsubscript{3} is the most active catalyst. It shows a maximum CO conversion at room temperature (RT) which decreases to 5% at 350 °C as the H\textsubscript{2} conversion increases. The CO oxidation on silver starts at 150 °C and reaches a maximum at 250 °C, and the H\textsubscript{2} convers-
these conditions maximum CO conversion can also be reached for the multicomponent gold and silver catalysts. For gold this was reached at RT and for silver at 95°C. The results of the copper catalyst were comparable to the results with less oxygen as shown in figure 5. Under these conditions the combined addition of Li$_2$O and CeO$_x$ results in a wider temperature range at which CO is converted to CO$_2$.

3.5. FTIR

The effect of addition of Li$_2$O on the CO adsorption on the metal particles has been investigated with FTIR. The results are presented in figure 8. On Ag/Al$_2$O$_3$ and Ag/Li$_2$O/Al$_2$O$_3$ no CO absorption band was found at pressures up to 100 mbar. A band at 2165 cm$^{-1}$ was found when the silver catalyst was oxidized at 300°C with oxygen. This band can be assigned to CO on oxidic silver [32]. Addition of Li$_2$O to the copper catalysts shifts the CO absorption band from 2125 cm$^{-1}$ to 2106 cm$^{-1}$. On the gold catalyst there is a shift from 2113 cm$^{-1}$ to 2104 cm$^{-1}$. Besides the frequency shift the absorption bands become narrower and more symmetrical. The frequency of the CO absorption bands on gold and copper can be assigned to CO adsorbed on metallic particles [13].

4. Discussion

4.1. Particle size

The catalytic activity of gold is very dependent on the gold particle size [11]. In this paper it is shown that also
copper and silver, when deposited as nano particles on \( \gamma-Al_2O_3 \) are active in low-temperature CO oxidation. In an attempt to prepare catalysts with small metallic silver particles two preparation methods were used. With LPR it is possible to directly deposit metallic silver on the support [32] and using HDP with Na\(_2\)CO\(_3\) as precipitating agent small silver particles can be deposited, but these particles have to be reduced to become metallic. These silver catalysts show different behavior. The silver catalysts prepared by LPR show activity at 200 °C whereas the silver catalysts prepared by homogeneous deposition precipitation already show activity at 100 °C. These two catalysts differ in the particle size of the silver particles. The catalyst prepared by LPR contains big particles of about 8–9 nm, compared to silver particles of < 3 nm for the silver catalysts prepared by HDP. The catalyst with the smaller particles is the most active one. However the metallic silver particles smaller than 3 nm are not stable in an oxidizing environment, whereas the bigger silver particles of 8–9 nm are stable. Addition of CeO\(_x\) or Li\(_2\)O to the silver catalysts results in an increase in CO conversion for the small silver particles and has no effect for the bigger silver particles. This suggests that the chemistry on these catalysts may be different. Probably CO adsorbed on 8–9 nm silver particles combines with O\(_{ad}\) on large metallic silver particles to CO\(_2\) in a Langmuir–Hinshelwood type mechanism. This will explain why addition of CeO\(_x\) and Li\(_2\)O does not have any effect on the activity. The influence of addition of CeO\(_x\) and Li\(_2\)O to the < 3 nm silver particles suggests a different mechanism for the CO oxidation. It is proposed that the CO oxidation on silver is analogous to a mechanism for gold in the presence of transition metal oxides [16]. The CO binds onto the silver and reacts on the interface of the silver with oxygen supplied by the cerium oxide support. CeO\(_x\) also stabilizes the small silver particles.

4.2. Selective CO oxidation

The results presented in figure 3 show that Au/\( \gamma-Al_2O_3 \), Ag/\( \gamma-Al_2O_3 \) and Cu/\( \gamma-Al_2O_3 \) oxidize CO at lower temperatures than hydrogen. On silver and copper based catalysts maximum CO conversion is maintained at higher temperatures whereas on Au/\( \gamma-Al_2O_3 \) the start of hydrogen oxidation at 50 °C lowers the CO conversion to 0 at 150 °C. The copper catalysts are able to oxidize CO even if the hydrogen content is increased. Only at temperatures above 200 °C there is a slight decrease in CO conversion. For silver and gold maximum conversion can only be reached at higher oxygen content. Gold is the most active catalyst at low temperature. But the optimal conversion of CO is probably at temperatures lower than was used in this study. Silver shows little activity in preferential CO oxidation with a maximum conversion of 40% if CeO\(_x\) and Li\(_2\)O are added. Probably the concentration of adsorbed CO on silver is too low.

4.3. Addition of Li\(_2\)O

Addition of Li\(_2\)O has a small positive effect on the activity of the copper and gold catalyst and the silver catalyst prepared by HDP in preferential CO oxidation. Figure 8 shows that addition of Li\(_2\)O to the catalysts results in a shift of the CO absorption band to lower wave numbers, which implies a stronger adsorption of the CO on the metal particles. The more symmetrical shape of the CO band suggests that the Li\(_2\)O has an effect on the morphology of the nanoparticles. These results are in agreement with Gluhoi et al. [26,27] that Li\(_2\)O can act as a structural promoter. The absence of CO adsorption on a reduced silver catalyst suggests a very low CO coverage at room temperature. This is in line with literature data [32] and suggests that the silver particles are in the metallic state after reduction. Apparently, the presence of Li\(_2\)O does not result in a sufficient increase in CO coverage.

4.4. Addition of CeO\(_x\)

Ceria has only on the gold catalysts a positive effect on the CO conversion. Addition of CeO\(_x\) to the silver catalysts with < 3 nm particles stabilizes the silver particles, but increases the T\(_{50\%}\) to 180°C. Addition of CeO\(_x\) to the copper catalyst also has a negative effect in the CO oxidation with a small amount of H\(_2\) present. Figure 4 shows that the CO conversion drops above 200°C. This is also reported by Avgouropoulos on a CuO-CeO\(_x\) catalyst [20]. With a large amount of hydrogen present CeO\(_x\) has a positive effect on the CO conversion on all three metals. Clearly, the CeO\(_x\) has an important role in the catalysis of the selective CO oxidation especially on copper. The proposed role is that CeO\(_x\) under strongly reducing conditions can provide the oxygen for the oxidation of CO to CO\(_2\), but can also facilitate the oxidation of the silver and copper particles in a more oxidative environment.

4.5. Addition of CeO\(_x\) and Li\(_2\)O

Addition of both oxides provides the best performing catalysts under all conditions. The positive effect of addition of both oxides is greater than the contribution of both oxides separately. This synergistic effect has been reported before [28] but it is not completely understood. Probably the Li\(_2\)O prevents the oxidation of the metal particles under oxidizing conditions and stabilizes them, while CeO\(_x\) addition may result in another route of O supply needed for CO oxidation.

5. Conclusions

This study shows that all three IB metals are active in low temperature preferential CO oxidation provided that the metal particles are small (< 3 nm). Measurements showed that when the particle size of the silver is
increased the CO oxidation is not affected by the additives and the CO oxidation is probably a reaction of adsorbed CO and O on the metal particle. CeO$_x$ positively contributes to the gold catalyst in increasing its performance by supplying oxygen [33]. On silver and copper it has a negative effect. The role of Li$_2$O can be attributed to strengthening of the CO adsorption and stabilizing the small metallic particles. Addition of both CeO$_x$ and Li$_2$O provides the best performing catalysts in selective CO oxidation. All three metals preferentially oxidize CO over H$_2$ at low temperatures in agreement with the DFT study of Kandoi [23]. Gold is the most active catalyst in CO oxidation with hydrogen present at low temperatures. Copper shows the highest selectivity toward CO at temperatures above 100 °C and silver is the least active metal with low CO selectivity and activity. The Cu/CeO$_x$/Li$_2$O/Al$_2$O$_3$ shows the best activity in the selective oxidation in the temperature range in which the PEMFC is operating (100°C).

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