In the study described in this paper we deposited gold, silver and copper on γ-Al₂O₃ as nanoparticles (<4nm) and investigated the behavior of these nanoparticles in the preferential oxidation of CO in presence of H₂. In addition, the effect of addition of CeOₓ and/or Li₂O was investigated. All the three metals show preferential oxidation of CO at low temperatures. The oxides added to Au/γ-Al₂O₃, Ag/γ-Al₂O₃ and Cu/γ-Al₂O₃ improve the catalytic performance of the gold, silver and copper. Interesting and synergistic effects were observed when both the CeOₓ and Li₂O were added. Possible mechanisms are proposed.
2.1 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 $\text{H}_2\text{O}$. 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 $\text{CO}_2$ and $\text{H}_2$. However, in practice the product stream also contains several vol\% $\text{H}_2\text{O}$ and about 1-2 vol\% $\text{CO}$ \([4]\). Especially the presence of $\text{CO}$ in the feed causes major problems as Pt is effectively poisoned by $\text{CO}$ at the operating temperatures of the fuel cell, i.e. 60-100 °C \([5, 6]\). In addition, $\text{H}_2$ oxidation will compete with $\text{CO}$ oxidation in gas streams containing both compounds. Hence, there is an urgent need to find a way to remove $\text{CO}$ selectively from the product stream.

In several papers it is reported that $\text{CO}$ 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 $\text{CO}$ oxidation is rather slow due to inhibition of oxygen adsorption by adsorbed $\text{CO}$. At temperatures above 250 °C the selectivity decreases because thermal desorption of $\text{CO}$ enables $\text{H}_2$ oxidation.

Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in low-temperature $\text{CO}$ oxidation \([10–14]\). In addition, several studies have indicated that the rate of $\text{CO}$ oxidation over supported Au catalysts exceeds that of $\text{H}_2$ oxidation \([15–17]\). Therefore, gold is a promising catalyst for the preferential catalytic oxidation of $\text{CO}$ (PROX) in the presence of $\text{H}_2$ 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 $\text{CO}$ 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 $\text{CO}$ oxidation than for $\text{H}_2$ oxidation. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al$_2$O$_3$ catalyst in $\text{CO}$ 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 3nm 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.

2.2 Experimental

2.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO$_x$) 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 [29]. An appropriate amount of HAuCl$_4$.3aq (99.999% Aldrich chemicals), AgNO$_3$ or CuNO$_3$.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 0.53at% M and resulted in 5wt% for gold, 2.5wt% for silver and 1.5wt% 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$_3$)$_2$]$^+$ 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 200µm for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen.

2.2.2 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 50kV and 40mA. The average particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [30].

### 2.2.3 Activity measurements

Prior to activity experiments the catalysts were reduced with H$_2$ (4 vol% in He) at 400 °C for 2 hours. Activity tests of the catalysts were performed in a micro reactor system. The amount of catalyst used was 200mg for the Au/γ-Al$_2$O$_3$, Ag/γ-Al$_2$O$_3$ and Cu/γ-Al$_2$O$_3$ catalysts. When the catalyst contained CeO$_x$ 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 (4vol% in helium) used were CO+O$_2$ (ratio 1), CO+O$_2$ +H$_2$ (ratio 1:1:5), CO+O$_2$ +H$_2$ (ratio 1:1:50) and CO+O$_2$ +H$_2$ (ratio 1:5:50). Typically a total gas flow of 40ml/min (GHSV ≈ 2500h$^{-1}$) was maintained. The effluent stream was analyzed on-line 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/γ-Al$_2$O$_3$ and Ag/Li$_2$O/γ-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.

### 2.2.4 FTIR measurements

Catalyst powder was pressed into a disc that was mounted in a vacuum cell (base pressure $5 \times 10^{-6}$ mbar) and was reduced in situ by H$_2$ or oxidized by O$_2$ for 1h at 350 °C. Infrared spectra were recorded with a single-beam spectrometer (Mattson Galaxy 2020) operated at a resolution of 4cm$^{-1}$. To reduce the noise/signal ratio 128 scans were taken per spectrum and the applied infrared range was 3000-1000cm$^{-1}$. 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 100mbar. Finally the spectra were corrected for gas phase bands of CO and backgrounds were subtracted.
CHAPTER 2: PREFERENTIAL CO OXIDATION

2.3 Results

2.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was apparently below 3nm. The results of the characterization of the catalysts after the reaction are shown in table 2.1. The catalysts without additives contain small particles of 3-4nm. When ceria and Li₂O are added the average particle size is lower than the detection limit (3nm) of the XRD machine. The particle size of the silver catalysts prepared with liquid phase reduction was about 8-9nm. The actual metal loading was almost equal to the intended metal loading. The XRD spectra after reaction (CO oxidation) of the all the silver catalysts prepared with HDP show that the silver particles are converted to Ag₂O. The XRD spectra of silver based catalysts prepared by LPR show only peaks of metallic silver after the reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading (wt%)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al₂O₃</td>
<td>4.6±0.1</td>
<td>4.3±0.1</td>
</tr>
<tr>
<td>Au/CeOₓ/Al₂O₃</td>
<td>4.1±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Au/Li₂O/Al₂O₃</td>
<td>4.5±0.3</td>
<td>3.2±0.1</td>
</tr>
<tr>
<td>Au/CeOₓ/Li₂O/Al₂O₃</td>
<td>4.0±0.2</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Ag/Al₂O₃</td>
<td>2.3±0.1</td>
<td>4.5±0.1</td>
</tr>
<tr>
<td>Ag/CeOₓ/Al₂O₃</td>
<td>1.7±0.1</td>
<td>3.3±0.1</td>
</tr>
<tr>
<td>Ag/Li₂O/Al₂O₃</td>
<td>2.2±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Ag/CeOₓ/Li₂O/Al₂O₃</td>
<td>1.6±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Cu/Al₂O₃</td>
<td>1.5±0.1</td>
<td>3.5±0.1</td>
</tr>
<tr>
<td>Cu/CeOₓ/Al₂O₃</td>
<td>1.0±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Cu/Li₂O/Al₂O₃</td>
<td>1.4±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Cu/CeOₓ/Li₂O/Al₂O₃</td>
<td>1.0±0.1</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>Ag(LPR)/Al₂O₃</td>
<td>2.5±0.1</td>
<td>9.2±0.2</td>
</tr>
<tr>
<td>Ag(LPR)/CeOₓ/Al₂O₃</td>
<td>1.7±0.1</td>
<td>8.8±0.2</td>
</tr>
<tr>
<td>Ag(LPR)/Li₂O/Al₂O₃</td>
<td>2.4±0.1</td>
<td>8.7±0.2</td>
</tr>
<tr>
<td>Ag(LPR)/CeOₓ/Li₂O/Al₂O₃</td>
<td>1.7±0.1</td>
<td>8.5±0.1</td>
</tr>
</tbody>
</table>
2.3.2 CO oxidation in the absence of H₂

The behavior of the catalysts in CO oxidation with oxygen in a ratio of 1:1 in the absence of H₂ is illustrated in table 2.2 and in figures 2.1, 2.2, 2.3, 2.4. Gold is the most active catalyst followed by copper and silver. The combined addition of both Li₂O and CeOₓ has a very beneficial effect on the activity of the copper and gold catalysts, whereas addition of only CeOₓ has a negative effect and the addition of only Li₂O a small positive effect on the activity of the catalysts. Addition of Li₂O and/or Li₂O and CeOₓ to the silver catalysts prepared by liquid phase reduction does not affect the catalyst performance, see figure 2.4. The silver catalysts prepared by homogeneous deposition precipitation show a different behavior as is depicted in figures 2.1, 2.2, 2.3. The silver only catalyst shows activity at a much lower temperature than the silver 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 T₅₀% is increased to 180°C. Li₂O addition shows a very small negative effect on these silver catalysts. The effect of addition of both oxides is comparable to addition of CeOₓ only.
Figure 2.2: Effect of additives CeO$_x$ and Li$_2$O on the CO conversion on silver based catalysts in the CO oxidation in the absence of H$_2$

Figure 2.3: Effect of additives CeO$_x$ and Li$_2$O on the CO conversion on gold based catalysts in the CO oxidation in the absence of H$_2$
Table 2.2: Effect of addition of oxides on the catalytic activity for the CO/O\textsubscript{2} reaction. Temperature of 50% conversion (T\textsubscript{50%}) and temperature of 95% conversion (T\textsubscript{95%}).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>T\textsubscript{50%} (°C)</th>
<th>T\textsubscript{95%} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/Al\textsubscript{2}O\textsubscript{3}</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Au/CeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>75</td>
<td>150</td>
</tr>
<tr>
<td>Au/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Au/CeO\textsubscript{x}/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>RT</td>
<td>100</td>
</tr>
<tr>
<td>Ag/Al\textsubscript{2}O\textsubscript{3}</td>
<td>80</td>
<td>160</td>
</tr>
<tr>
<td>Ag/CeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>180</td>
<td>250</td>
</tr>
<tr>
<td>Ag/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>100</td>
<td>185</td>
</tr>
<tr>
<td>Ag/CeO\textsubscript{x}/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>Cu/Al\textsubscript{2}O\textsubscript{3}</td>
<td>160</td>
<td>210</td>
</tr>
<tr>
<td>Cu/CeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>210</td>
<td>250</td>
</tr>
<tr>
<td>Cu/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>140</td>
<td>190</td>
</tr>
<tr>
<td>Cu/CeO\textsubscript{x}/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>110</td>
<td>150</td>
</tr>
<tr>
<td>Ag(LPR)/Al\textsubscript{2}O\textsubscript{3}</td>
<td>210</td>
<td>250</td>
</tr>
<tr>
<td>Ag(LPR)/CeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3}</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>Ag(LPR)/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>210</td>
<td>250</td>
</tr>
<tr>
<td>Ag(LPR)/CeO\textsubscript{x}/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3}</td>
<td>200</td>
<td>250</td>
</tr>
</tbody>
</table>

Figure 2.4: CO conversion over silver catalysts, prepared by liquid phase reduction.
2.3.3 Preferential oxidation of CO in the presence of H\textsubscript{2} (CO:O\textsubscript{2}:H\textsubscript{2} = 1:1:5)

Figures 2.5, 2.6, 2.7 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} conversion starts at 275°C. On Cu/γ-Al\textsubscript{2}O\textsubscript{3} the CO conversion exceeds the H\textsubscript{2} conversion by 125 degrees. The CO conversion starts at 75°C and the H\textsubscript{2} conversion at 200°C. Addition of CeO\textsubscript{x} and/or Li\textsubscript{2}O to the silver catalyst does not effect the performance of the catalyst (not shown). Addition of CeO\textsubscript{x} to copper in the CO oxidation results in a decrease of CO conversion above 200°C shown in figure 2.8. Addition of Li\textsubscript{2}O has a small beneficial effect on the CO conversion, and the combined addition of both Li\textsubscript{2}O and CeO\textsubscript{x} resulted in the best performing Cu-based catalyst, just like in the experiment in the absence of hydrogen presented in section 2.3.2.
Figure 2.6: CO$_2$O$_2$ and H$_2$ conversion over M/Li$_2$O/CeO$_x$/$\gamma$-Al$_2$O$_3$ catalysts M= Au(A), Ag(B) and Cu(C). H$_2$ conversion is normalized to theoretical maximum conversion. CO/O$_2$/H$_2$ = 1:1:5

Figure 2.7: CO$_2$O$_2$ and H$_2$ conversion over M/Li$_2$O/CeO$_x$/$\gamma$-Al$_2$O$_3$ catalysts M= Au(A), Ag(B) and Cu(C). H$_2$ conversion is normalized to theoretical maximum conversion. CO/O$_2$/H$_2$ = 1:1:5
2.3.4 Preferential CO oxidation in a hydrogen rich environment (CO:O\textsubscript{2}:H\textsubscript{2} =1:1:50)

The results of CO oxidation in a hydrogen rich feed are presented in figure 2.9. The Cu/Al\textsubscript{2}O\textsubscript{3} and the Cu/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} catalysts show a sharp maximum in CO conversion at 175°C. Addition of CeO\textsubscript{x} improves the performance of the catalysts. The onset of CO conversion is lowered to 50°C. The catalyst with both Li\textsubscript{2}O and CeO\textsubscript{x} has the same activity as the catalyst with only ceria added. The silver catalyst shows poor performance in CO oxidation with a maximum CO conversion of 20% at 105°C. Addition of Li\textsubscript{2}O shifts the temperature of maximum conversion to 90°C. Addition of CeO\textsubscript{x} increases the maximum conversion to 40% at 130°C. Addition of both Li\textsubscript{2}O and CeO\textsubscript{x} shifts the temperature of maximum conversion to 110°C, compared to the catalyst with ceria. The gold catalysts show a maximum CO conversion at RT. The CO conversion decreases with increasing temperature to about 5% at 300°C. The silver and gold containing catalysts with addition of ceria show an increase of CO conversion above 250°C. This is due to the CeO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} support, which shows a increasing conversion of CO at higher temperatures.

In an attempt to get maximum CO conversion we also performed measurements with more O\textsubscript{2} in the gas stream. The ratio used was CO:O\textsubscript{2}:H\textsubscript{2} =1:5:50. The results
Figure 2.9: Effect of additives CeO$_x$ and Li$_2$O on gold, silver and copper based catalysts in the CO conversion in a hydrogen rich environment. CO/O$_2$/H$_2$ = 1:1:50
Figure 2.10: CO conversion in a hydrogen rich environment (CO:O\textsubscript{2}:H\textsubscript{2} = 1:5:50) over Cu/Al\textsubscript{2}O\textsubscript{3}, Ag/Al\textsubscript{2}O\textsubscript{3} and Au/Al\textsubscript{2}O\textsubscript{3}

are presented in figure 2.10 and figure 2.11. Under 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 2.9. Under these conditions the combined addition of Li\textsubscript{2}O and CeO\textsubscript{x} results in a wider temperature range at which CO is converted to CO\textsubscript{2}.

2.3.5 FTIR

The effect of addition of Li\textsubscript{2}O on the CO adsorption on the metal particles has been investigated with FTIR. The results are presented in figure 2.12. On Ag/Al\textsubscript{2}O\textsubscript{3} and Ag/Li\textsubscript{2}O/Al\textsubscript{2}O\textsubscript{3} no CO absorption band was found at pressures up to 100mbar. A band at 2165cm\textsuperscript{-1} was found when the silver catalyst was oxidized at 300°C with oxygen. This band can be assigned to CO on oxidic silver [31]. Addition of Li\textsubscript{2}O to the copper catalysts shifts the CO absorption band from 2125cm\textsuperscript{-1} to 2106cm\textsuperscript{-1}. On the gold catalyst there is a shift from 2113cm\textsuperscript{-1} to 2104cm\textsuperscript{-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].
Figure 2.11: CO conversion in a hydrogen rich environment over M/CeO$_x$/Li$_2$O/Al$_2$O$_3$ M= Au, Ag, Cu (CO:O$_2$:H$_2$ =1:5:50)

Figure 2.12: Effect of addition of Li$_2$O on the CO absorption band for copper, silver and gold based catalysts at RT. CO pressure is 30mbar for copper and gold. CO pressure for silver based catalysts is 100mbar
2.4 Discussion

2.4.1 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 [31] and using HDP with \( Na_2CO_3 \) 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\(^\circ\)C whereas the silver catalysts prepared by homogeneous deposition precipitation already show activity at 100\(^\circ\)C. These two catalysts differ in the particle size of the silver particles. The catalyst prepared by LPR contains big particles of about 8-9nm, compared to silver particles of <3nm 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 3nm are not stable in an oxidizing environment, whereas the bigger silver particles of 8-9nm 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 8-9nm 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 <3nm 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.

2.4.2 Selective CO oxidation

The results presented in figures 2.5, 2.6, 2.7 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\(^\circ\)C lowers the CO conversion to 0 at 150\(^\circ\)C. The copper catalysts are able to oxidize CO even if the hydro-
gen 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.

2.4.3 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 2.12 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 [31] 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.

2.4.4 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 <3nm 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 2.8 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.
2.4.5 Addition of CeO_x and Li_2O

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_2O 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.

2.5 Conclusions

This study shows that all three IB metals are active in low temperature preferential CO oxidation provided that the metal particles are small (<3nm). 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 [32]. On silver and copper it has a negative effect. The role of Li_2O can be attributed to strengthening of the CO adsorption and stabilizing the small metallic particles. Addition of both CeO_x and Li_2O 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_2O/Al_2O_3 shows the best activity in the selective oxidation in the temperature range in which the PEMFC is operating (100°C).

References


