

A comparative study of the effect of addition of CeO_x and Li_2O on $\gamma\text{-Al}_2\text{O}_3$ 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 $\gamma\text{-Al}_2\text{O}_3$ 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_2O was investigated. All the three metals show preferential oxidation of CO at low temperatures. The oxides added to $\text{Au}/\gamma\text{-Al}_2\text{O}_3$, $\text{Ag}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ improve the catalytic performance of the gold, silver and copper. Interesting and synergistic effects were observed when both the CeO_x and Li_2O 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_2O . 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_2O 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 $\text{Au}/\text{Al}_2\text{O}_3$ 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 $\text{Au}/\text{Al}_2\text{O}_3$ 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_2O 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 $\text{Au}/\text{Li}_2\text{O}/\text{CeO}_x/\text{Al}_2\text{O}_3$ 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_x) and Li₂O on alumina were prepared by pore volume impregnation of γ -Al₂O₃ (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 HAuCl₄.3aq (99.999% Aldrich chemicals), AgNO₃ or CuNO₃.3aq was added to a suspension of purified water containing γ -Al₂O₃ or the mixed oxide. The intended M/Al ratio was 1/75 ($M = \text{Cu, Ag or Au}$). This ratio of 1:75 is equal to 0.53at% 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[NH₃] complex is formed. So the silver catalysts were either prepared by homogeneous deposition precipitation using Na₂CO₃ 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 HNO₃ (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 H₂ (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/ γ -Al₂O₃, Ag/ γ -Al₂O₃ and Cu/ γ -Al₂O₃ catalysts. When the catalyst contained CeO_x and/or Li₂O 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 + O₂ (ratio 1), CO + O₂ + H₂ (ratio 1:1:5), CO + O₂ + H₂ (ratio 1:1:50) and CO + O₂ + H₂ (ratio 1:5:50). 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/ γ -Al₂O₃ and Ag/Li₂O/ γ -Al₂O₃ catalyst in CO oxidation in the absence of H₂. 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 5×10^{-1} mbar) and was reduced in situ by H₂ or oxidized by O₂ 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 O₂ (99.998%), H₂ (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 Li₂O 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

Table 1
Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Au/Al ₂ O ₃	4.6 ± 0.1	5.3 ± 0.1
Au/CeO _x /Al ₂ O ₃	4.1 ± 0.1	< 3.0
Au/Li ₂ O/Al ₂ O ₃	4.5 ± 0.1	4.0 ± 0.1
Au/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/CeO _x /Al ₂ O ₃	1.7 ± 0.1	4.1 ± 0.1
Ag/Li ₂ O/Al ₂ O ₃	2.2 ± 0.1	< 3.0
Ag/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/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/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)/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)/CeO _x /Li ₂ O/Al ₂ O ₃	1.7 ± 0.1	8.5 ± 0.1

oxidation) of the silver catalysts prepared with HDP show that the silver particles are converted to Ag₂O. 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 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 and in figures 1 and 2. Gold is the most active catalyst followed by copper and silver. The combined addition of both Li₂O and CeO_x has a very beneficial effect on the activity of the copper and gold catalysts, whereas addition of only CeO_x 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

Table 2

Effect of addition of oxides on the catalytic activity for the CO/O₂ reaction. Temperature of 50% conversion (T_{50%}) and temperature of 95% conversion (T_{95%})

Catalyst	T _{50%} (°C)	T _{95%} (°C)
Au/Al ₂ O ₃	50	100
Au/CeO _x /Al ₂ O ₃	75	150
Au/Li ₂ O/Al ₂ O ₃	50	100
Au/CeO _x /Li ₂ O/Al ₂ O ₃	RT	100
Ag/Al ₂ O ₃	80	160
Ag/CeO _x /Al ₂ O ₃	180	250
Ag/Li ₂ O/Al ₂ O ₃	100	185
Ag/CeO _x /Li ₂ O/Al ₂ O ₃	200	250
Cu/Al ₂ O ₃	160	210
Cu/CeO _x /Al ₂ O ₃	210	250
Cu/Li ₂ O/Al ₂ O ₃	140	190
Cu/CeO _x /Li ₂ O/Al ₂ O ₃	110	150
Ag(LPR)/Al ₂ O ₃	210	250
Ag(LPR)/CeO _x /Al ₂ O ₃	200	250
Ag(LPR)/Li ₂ O/Al ₂ O ₃	210	250
Ag(LPR)/CeO _x /Li ₂ O/Al ₂ O ₃	200	250

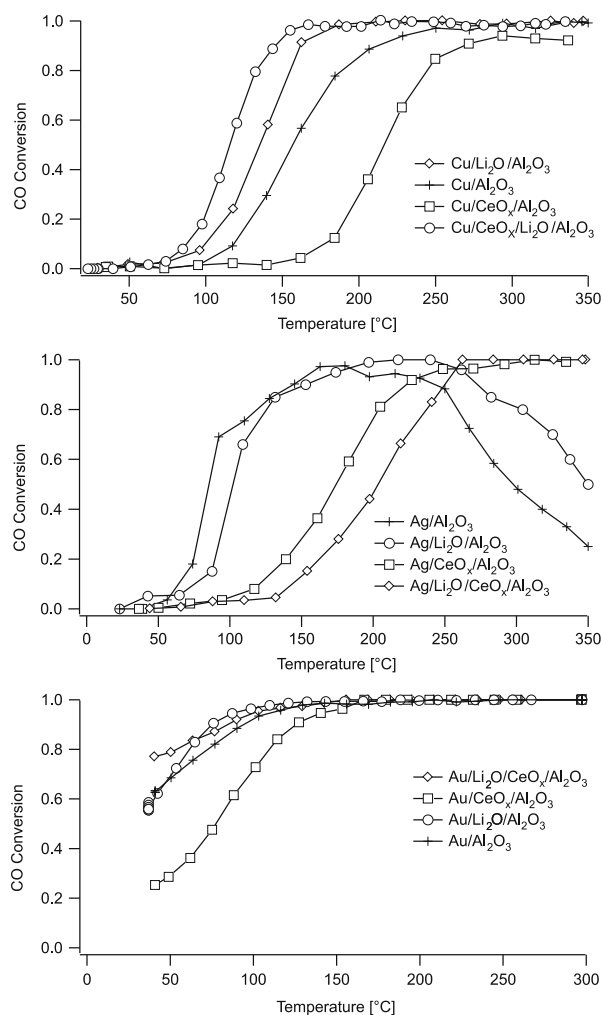


Figure 1. Effect of additives CeO_x and Li₂O on the CO conversion on gold, silver and copper based catalysts in the CO oxidation in the absence of H₂.

and 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

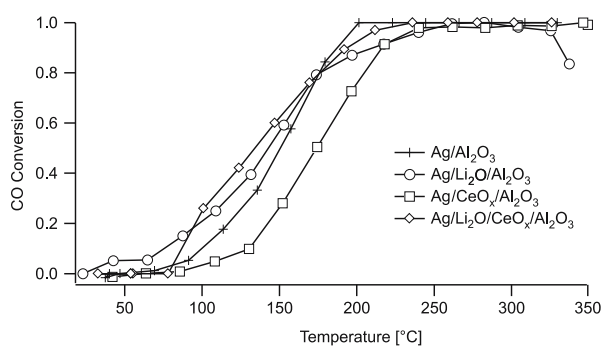


Figure 2. CO conversion over silver catalysts, prepared by liquid phase reduction.

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_2O addition shows a very small negative effect on these silver catalysts. The effect of addition of both oxides is comparable to addition of CeO_x only.

3.3. Preferential oxidation of CO in the presence of H_2 ($\text{CO}:\text{O}_2:\text{H}_2 = 1:1:5$)

Figure 3 shows that when CeO_x and Li_2O are added to the Au, Ag, Cu based catalysts, the CO oxidation precedes the H_2 oxidation on all three metals when a ratio of $\text{CO}:\text{O}_2:\text{H}_2$ (1:1:5) is used. At temperatures below 100 °C Au/ $\gamma\text{-Al}_2\text{O}_3$ 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_2 conversion increases. The CO oxidation on silver starts at 150 °C and reaches a maximum at 250 °C, and the H_2 conver-

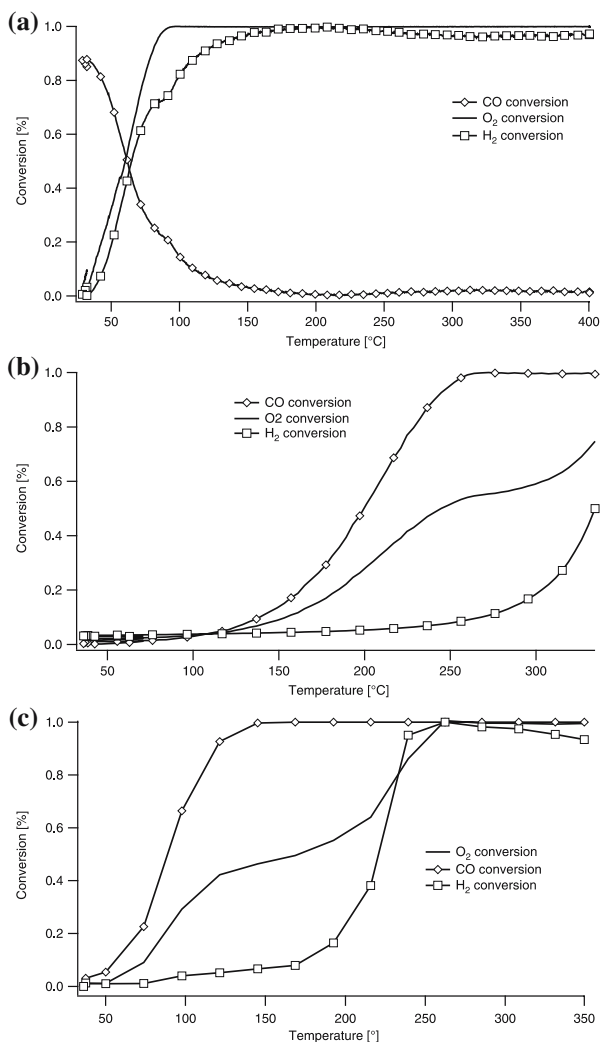


Figure 3. CO , O_2 and H_2 conversion over $\text{M}/\text{Li}_2\text{O}/\text{CeO}_x/\text{Al}_2\text{O}_3$ catalysts $M = \text{Au}$ (A), Ag (B) and Cu (C). H_2 conversion is normalized to theoretical maximum conversion. $\text{CO}/\text{O}_2/\text{H}_2 = 1:1:5$.

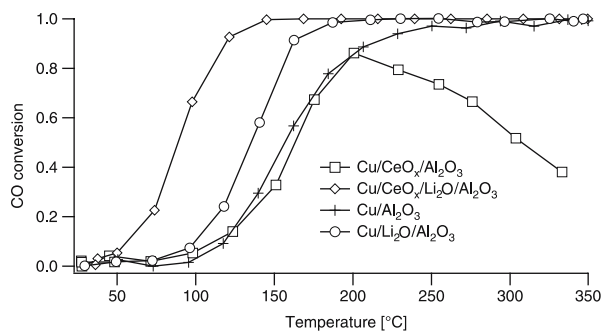


Figure 4. Effect of additives CeO_x and Li_2O on the CO conversion on Cu catalysts.

sion starts at 275 °C. On $\text{Cu}/\gamma\text{-Al}_2\text{O}_3$ the CO conversion exceeds the H_2 conversion by 125 degrees. The CO conversion starts at 75 °C and the H_2 conversion at 200 °C. Addition of CeO_x and/or Li_2O to the silver catalyst does not effect the performance of the catalyst (not shown). The effect of the additives on the performance of $\text{Au}/\text{Al}_2\text{O}_3$ will be described in detail in a future paper [29]. Addition of CeO_x to copper in the CO oxidation results in a decrease of CO conversion above 200 °C shown in figure 4. Addition of Li_2O has a small beneficial effect on the CO conversion, and the combined addition of both Li_2O and CeO_x resulted in the best performing Cu-based catalyst, just like in the experiment in the absence of hydrogen presented in section 3.2.

3.4. Preferential CO oxidation in a hydrogen rich environment $\text{CO}:\text{O}_2:\text{H}_2 = 1:1:50$

The results of CO oxidation in a hydrogen rich feed are presented in figure 5. The $\text{Cu}/\text{Al}_2\text{O}_3$ and the $\text{Cu}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ catalysts show a sharp maximum in CO conversion at 175 °C. Addition of CeO_x improves the performance of the catalysts. The onset of CO conversion is lowered to 50 °C. The catalyst with both Li_2O and CeO_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_2O shifts the temperature of maximum conversion to 90 °C. Addition of CeO_x increases the maximum conversion to 40% at 130 °C. Addition of both Li_2O and CeO_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 $\text{CeO}_x/\text{Al}_2\text{O}_3$ 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_2 in the gas stream. The ratio used was $\text{CO}:\text{O}_2:\text{H}_2 = 1:5:50$. The results are presented in figure 6 and figure 7. Under

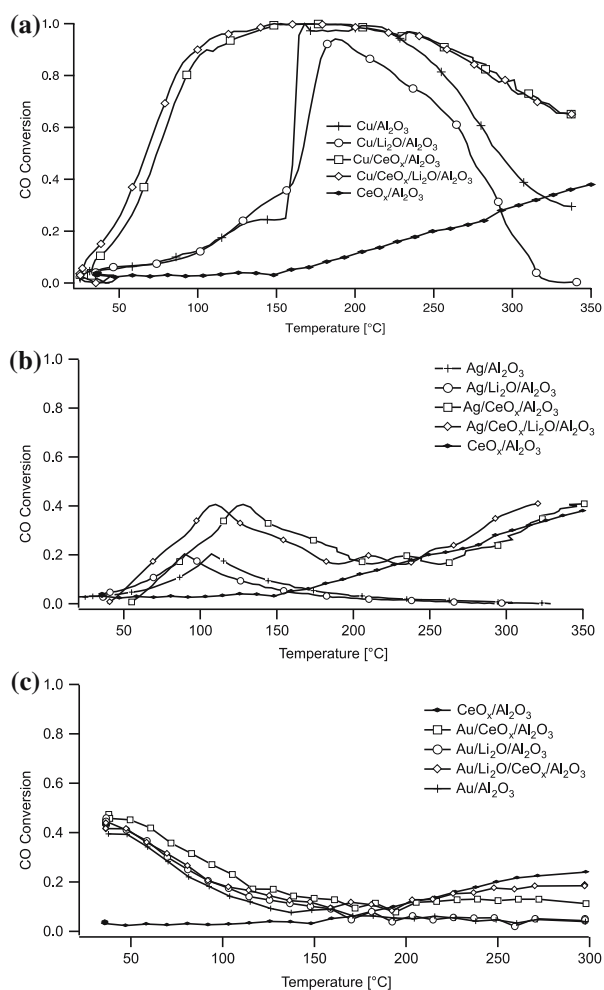


Figure 5. Effect of additives CeO_x and Li_2O on gold, silver and copper based catalysts in the CO conversion in a hydrogen rich environment. $\text{CO}/\text{O}_2/\text{H}_2 = 1:1:50$.

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_2O and CeO_x results in a wider temperature range at which CO is converted to CO_2 .

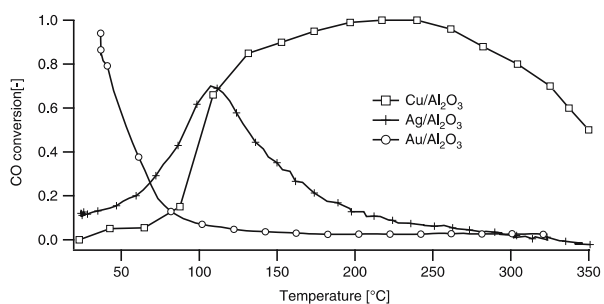


Figure 6. CO conversion in a hydrogen rich environment ($\text{CO}:\text{O}_2:\text{H}_2 = 1:1:50$) over $\text{Cu}/\text{Al}_2\text{O}_3$, $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Au}/\text{Al}_2\text{O}_3$.

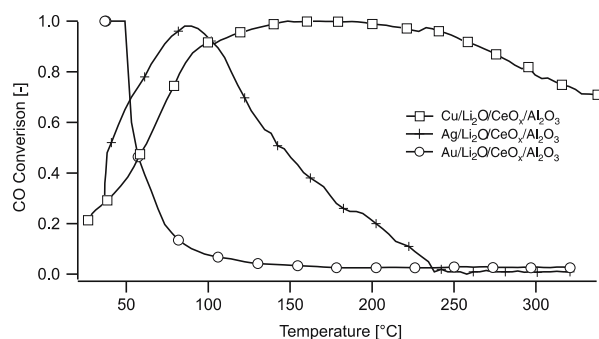


Figure 7. CO conversion in a hydrogen rich environment over $\text{M}/\text{CeO}_x/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ $\text{M} = \text{Au}, \text{Ag}, \text{Cu}$ ($\text{CO}:\text{O}_2:\text{H}_2 = 1:1:50$).

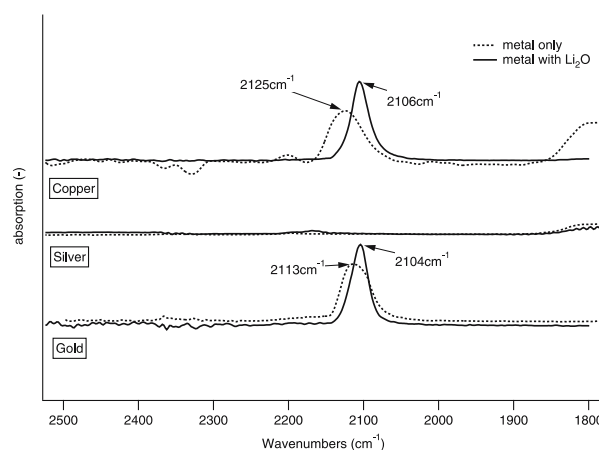


Figure 8. Effect of addition of Li_2O on the CO absorption band for copper, silver and gold-based catalysts at RT. CO pressure is 30 mbar for copper and gold. CO pressure for silver based catalysts is 100 mbar.

3.5. FTIR

The effect of addition of Li_2O on the CO adsorption on the metal particles has been investigated with FTIR. The results are presented in figure 8. On $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ 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_2O 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_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 °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_2O 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_2O does not have any effect on the activity. The influence of addition of CeO_x and Li_2O 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_2O are added. Probably the concentration of adsorbed CO on silver is too low.

4.3. Addition of Li_2O

Addition of Li_2O 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_2O 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_2O has an effect on the morphology of the nanoparticles. These results are in agreement with Gluhoi *et al.* [26,27] that Li_2O 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_2O 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_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.

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 Li₂O can be attributed to strengthening of the CO adsorption and stabilizing the small metallic particles. Addition of both CeO_x and Li₂O provides the best performing catalysts in selective CO oxidation. All three metals preferentially oxidize CO over H₂ 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/Li₂O/Al₂O₃ shows the best activity in the selective oxidation in the temperature range in which the PEMFC is operating (100°C).

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