A comparative study of oxidation of methanol on $\gamma$-Al$_2$O$_3$ supported group IB metal catalysts

Results are presented concerning the behavior of alumina supported Cu, Ag and Au (M) catalysts and the effect of addition of Li$_2$O and CeO$_x$ on the oxidation of methanol. The $\gamma$-Al$_2$O$_3$ used is able to dehydrogenate methanol to formaldehyde and the addition of a metal to the support increases the CO production. A two-step reaction mechanism is proposed: in the first step, CH$_3$OH is dehydrogenated on alumina to formaldehyde. In the second step, the formaldehyde reacts on M to CO or CO$_2$. Another mechanism is proposed for good oxidizing catalysts: methanol reacts directly on M and is oxidized to CO$_2$. The addition of the co-catalyst CeO$_x$ to the catalysts has a beneficial effect on the oxidation of methanol to CO$_2$ because of its ability to provide oxygen. We suggest that Li$_2$O blocks the adsorption site for methanol on alumina, and hence, decreasing the formation of formaldehyde.
4.1 Introduction

Methanol is used as a precursor for various industrial bulk chemicals, such as formaldehyde and larger hydrocarbons. Its worldwide annual production exceeds 37 million ton [1].

Due to the large demand for formaldehyde for the production of resins and larger base chemicals, an efficient catalytic process to produce formaldehyde is needed. Nowadays, the commercial BASF-process based on silver is still used to produce formaldehyde, although Fe/Mo-based catalysts gain ground. Studies by Lefferts et al. [2] showed that the silver-oxygen interaction is very important in the methanol dehydrogenation and is very sensitive to the silver surface morphology.

Methanol can also be used as a storage medium for hydrogen in cars, because of its relatively high hydrogen content and its fluidity. In principle hydrogen can be stored in various other ways, such as in the form of metal hydrides or as compressed liquefied H$_2$, the existing fueling infrastructure favors the use of methanol and it also introduces less potential safety hazards. Methanol can be oxidized on site to form CO, CO$_2$ and H$_2$ of which the latter can be used in a fuel cell. The formation of CO has to be avoided, because it poisons the catalytic Pt-sites in the PEM fuel cell. So, an extra catalyst that selectively oxidizes CO in the presence of hydrogen is necessary. However a catalyst that is selective to only CO$_2$ and H$_2$ is a better alternative.

In this report the dehydrogenation and oxidation of CH$_3$OH by IB-metals supported on $\gamma$-Al$_2$O$_3$ has been investigated. An earlier study in literature concerning the oxidation of methanol over Au, Ag and Cu on Fe$_2$O$_3$ [3, 4] showed that all these three metals are active in oxidation of methanol and that the choice of the support is very important for the catalytic performance. Sciré et al. [4] stated that the high activity of the investigated catalysts is related to the enhancement of the reducibility of the support by weakening the metal-oxygen bond of the support and, thus, increasing the mobility/reactivity of the surface lattice oxygen.

In addition, the promoting effect of adding Li$_2$O and CeO$_x$ has been investigated. A study by Ross et al. [5, 6] showed that addition of Li$_2$O or CeO$_x$ greatly influences the reaction of methanol on copper based catalysts. A detailed study of Gluhoi et al. [7, 8] on the effects of addition of (earth) alkali metals to an 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. Comparable results have been found for copper and silver based catalysts [9]. Highly dispersed gold on suitable metal oxides exhibits extraordinarily high activity in vari-
ous low-temperature oxidation reactions [10–13]. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al$_2$O$_3$ catalyst in the CO oxidation [13, 14]. It was argued that the active oxygen was supplied by the ceria, rather than from the gas phase. Moreover it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [15].

In literature, methanol oxidation has been studied on various catalysts. The results have been reviewed by Tatibouét [16]. Depending on the catalyst nature and reaction conditions methanol oxidation may result in various products. This property of the methanol oxidation reaction has been used in the reverse process of probing the catalytic surface with this reaction and deducing the nature of the active oxygen. The reaction was found to be structure sensitive and appears to be a good test reaction to study the acidic and oxidation properties of oxide catalysts [16–19]. In contrast to many published studies concerning the total oxidation of methanol [3, 4, 20], in the present comparative study a methanol/O$_2$ ratio of 1 was used. This ratio permits to compare the behavior of Cu, Ag and Au nanoparticles on γ-Al$_2$O$_3$ in both partial oxidation and total oxidation. In addition, we have studied the dehydrogenation of methanol in the absence of O$_2$ in the feed.

4.2 Experimental

4.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO$_x$), Li$_2$O with alumina were prepared by pore volume impregnation of γ-Al$_2$O$_3$ (BASF, de Meern) with the corresponding nitrates. After calcination at 350°C these oxides were used as supports 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 [21]. 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 γ-Al$_2$O$_3$ or the mixed oxide. The intended M/Al ratio atomic 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. Because urea and silver atoms can form a soluble Ag[NH$_3$]$_3^+$ complex a large surplus of silver was needed to deposit enough silver on
the Al₂O₃. The catalysts were thoroughly ground to ensure that the macroscopic particle size was around 200\(\mu\)m for all the catalysts used in this study. Prior to the activity measurement all catalysts were reduced at 400°C with hydrogen for 2 hours.

4.2.2 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 aqua regia. 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 an 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 [22].

4.2.3 Activity measurements

The activity and selectivity was determined using a flow reactor system equipped with a HP 5890 series II gas chromatograph. This system contained a set of flow controllers (Brooks) to ensure a steady gas flow, a mixing chamber to mix the gases, a vessel containing liquid methanol through which gases were bubbled and a quartz micro-reactor with oven. 200 mg catalyst was used for activity measurements. The catalyst was pre-treated in a hydrogen-flow and heated up to 300 °C for 2.5 h. After pre-treatment, the catalyst was exposed to a 23.75 mL min\(^{-1}\) flow of 4 vol-% oxygen in He and methanol. The oxygen-helium gas mixture was bubbled through a vessel containing methanol at room temperature, which resulted in an methanol/O\(_2\) ratio of 1:1. The product gas mixture was analyzed using a HP 5890 series II gas chromatograph equipped with a molsieve 13x column (Alltech) for O\(_2\), CO, CO\(_2\) and H\(_2\)O separation and a Hayeseq Q (Alltech) for CH\(_2\)O and CH\(_3\)OH separation. Detection of H\(_2\)-gas was not possible with this system. A TCD-detector was used for analysis. The measurements consisted of at least two heating/cooling cycles from room temperature to 400 °C at a rate of 2 °C min\(^{-1}\).
4.3 Results

4.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction are shown in table 4.1. The catalysts without additives contain small particles of 3-4nm. With CeO$_x$ and Li$_2$O added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [8, 23, 24]. 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 used $\gamma$-Al$_2$O$_3$ support was investated with XRF to determine which impurities are present. Three impurities were found: Na$_2$O(0.05wt%), SiO$_2$(0.1wt%) and Fe$_2$O$_3$(0.05wt%).
4.3.2 Activity of support materials and effect of oxygen

In figs. 4.1 and 4.2 the conversion of methanol by the support oxides is shown. The selectivity is shown as well. The alumina used converts CH$_3$OH above 225 °C selectively to formaldehyde. Maximum conversion is found above 300 °C. Adding CeO$_x$ increases the temperature at which CH$_3$OH starts to decompose to 250 °C. Addition of Li$_2$O decreases maximal conversion to 50 % at 400 °C. When both CeO$_x$ and Li$_2$O are added, behavior intermediate of those of Li$_2$O/Al$_2$O$_3$ and ceria/Al$_2$O$_3$ is observed. CH$_3$OH-conversion starts at 300 °C. The selectivity to formaldehyde decreases to 5 % above 250 °C, while selectivity to CO increases to 55 % and a 40% selectivity toward CO$_2$ is obtained. Addition of Li$_2$O results in a decrease of the selectivity to formaldehyde to 10 %, and the selectivity to CO is increased to 80 %. When both CeO$_x$ and Li$_2$O are added, selectivities resemble those of Li$_2$O/γ-Al$_2$O$_3$ with a higher selectivity to CH$_2$O (30 %). The activity of the used alumina support from BASF with impurities(Na$_2$O, SiO$_2$ and Fe$_2$O$_3$) is compared to a sample of pure Al$_2$O$_3$ (Aldrich) with similar surface area. The results are presented in figure 4.3. The γ-Al$_2$O$_3$ with impurities has a much higher activity compared to the pure alumina. However there is no difference was found in selectivity. Both supports produce mainly formaldehyde. Some CO is formed above 350°C.

In figure 4.4 the performance of the different supports in the absence of oxygen are presented. On the industrial Al$_2$O$_3$ and CeO$_x$/Al$_2$O$_3$ supports the conversion starts at 200°C and reaches maximum conversion of 75% at 400°C. The Li$_2$O containing supports show only minor methanol conversion at temperature above 300°C with at maximum conversion of 40%. Compared to the measurements with oxygen in figures 4.1 and 4.2 the methanol conversion is dropped, but the selectivity is not significantly affected by oxygen. Formaldehyde is the sole product in the absence of O$_2$. 
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Figure 4.1: Conversion of methanol on different metal supports. CH$_3$OH:O$_2$ ratio of 1:1

Figure 4.2: Product distribution vs temperature during methanol oxidation over Al$_2$O$_3$ (full symbols) and CeO$_x$/Al$_2$O$_3$ (open symbols): S$_{CH_2O}$ (♦), S$_{CO}$ (●), S$_{CO_2}$ (■) CH$_3$OH:O$_2$ ratio of 1:1
Figure 4.3: Conversion of methanol over $\gamma$-$\text{Al}_2\text{O}_3$ and Au/$\text{Al}_2\text{O}_3$ using industrial- and reagent grade $\gamma$-$\text{Al}_2\text{O}_3$ support and on pure $\gamma$-$\text{Al}_2\text{O}_3$ (99.9%). $\text{CH}_3\text{OH}:\text{O}_2$ ratio of 1:1

Figure 4.4: Conversion of methanol in the absence of oxygen on different supports
4.3.3 Effect of Cu, Ag and Au addition using different supports

In figures 4.5, 4.6 and 4.7 the performance of by Cu, Ag and Au on the $\gamma$-Al$_2$O$_3$ in the oxidation of methanol is shown. It can be seen from fig. 4.5 that Au/Al$_2$O$_3$ is the most active catalyst and that CH$_3$OH-oxidation starts at 100 °C. Maximum conversion reaches 100% at 275 °C. On copper the CH$_3$OH conversion starts at 150 °C and reaches 100 % conversion at 300 °C. The CH$_3$OH-oxidation on silver starts at 200 °C and reaches maximum conversion at 350 °C.

Clearly, the effect of addition of Cu and Ag on the methanol conversion is small. However, the effect on the selectivity is huge. Gold is selective to both CH$_2$O (60 %) and CO$_2$ (40 %) at reasonable levels of methanol conversion. Selectivity to CO increases slowly to 40 % above 300 °C. Silver shows equal selectivity to formaldehyde and CO$_2$ (50 %) above 250 °C and shows a slight increase of selectivity to CO above 250 °C. On copper high selectivity to CO$_2$ (up to 100 %) is seen, while selectivity to formaldehyde and CO does not exceed 20 %. Between 200 and 300 °C an increase of selectivity to CH$_2$O (to 20 %) is seen, which is also observed with the copper-catalysts and with some gold-catalysts as well.

![Figure 4.5: Conversion of methanol on different metal catalysts. CH$_3$OH:O$_2$ ratio of 1:1](image-url)
Figure 4.6: Product distribution vs temperature during methanol oxidation over Au/Al₂O₃ (full symbols): S₇CH₂O (♦), S₇CO (●), S₇CO₂ (■) Ag/Al₂O₃ (open symbols): S₇CH₂O (○), S₇CO (○), S₇CO₂ (□) and γ-Al₂O₃: S₇CH₂O (△). CH₃OH:O₂ ratio of 1:1

Figure 4.7: Product distribution vs temperature during methanol oxidation over Cu/Al₂O₃: S₇CH₂O (♦), S₇CO (●), S₇CO₂ (■)
In figures 4.8 and 4.9, the effect of ceria and Li\textsubscript{2}O on the performance of Au/Al\textsubscript{2}O\textsubscript{3} is shown. It can be seen from fig. 4.8 that Au/Al\textsubscript{2}O\textsubscript{3} is active above 100 °C and 100% conversion is obtained above 275 °C. When CeO\textsubscript{x} and/or Li\textsubscript{2}O are added an increase in temperature of 50 °C is needed to obtain the same conversion. However, a large increase in activity is observed compared to the support materials. The supports only show activity above 250 °C, while after the addition of gold, the T50 % lies around 200 °C. The largest increase in performance due to the noble metal is seen for the lithium containing support.

From figure 4.6 it can be seen that Au/Al\textsubscript{2}O\textsubscript{3} has a high selectivity (60 %) to formaldehyde at temperatures above 200 °C. By adding CeO\textsubscript{x} and/or Li\textsubscript{2}O this selectivity is decreased to under 20 % as shown in figure 4.9. Clearly in the presence of gold the selectivity shifts to total oxidation of methanol. The selectivity to CO is slightly decreased by adding CeO\textsubscript{x} and/or Li\textsubscript{2}O. Notice also the increase in selectivity to formaldehyde at temperature between 180 and 300 °C on Au/Li\textsubscript{2}O/\gamma-Al\textsubscript{2}O\textsubscript{3} and Au/CeO\textsubscript{x}/\gamma-Al\textsubscript{2}O\textsubscript{3}. This behaviour is encountered with copper-catalysts as well. Compared to the support materials, the selectivity to CO\textsubscript{2} increased up to 85 %. The formation of CO above 350 °C is also increased due to Au.
Figure 4.9: Product distribution vs temperature during methanol oxidation over Au/Li$_2$O/Al$_2$O$_3$ (full symbols) and Au/CeO$_x$/Al$_2$O$_3$ (open symbols): S$_{\text{CH}_2\text{O}}$ (♦), S$_{\text{CO}}$ (●), S$_{\text{CO}_2}$ (■) CH$_3$OH:O$_2$ ratio of 1:1

Figure 4.10: Conversion of methanol on Ag based catalysts on different metal supports CH$_3$OH:O$_2$ ratio of 1:1
In figures 4.10 and 4.11 the conversion of methanol over Ag-catalysts on different support oxides is shown. The selectivity to possible products is shown as well. It can be seen from figure 4.6 that Ag/$\gamma$-Al$_2$O$_3$ shows CH$_3$OH-conversion above 200 °C, and reaches maximum conversion (90 %) at 350 °C. After addition of CeO$_x$ or Li$_2$O CH$_3$OH-conversion starts at significantly higher performance of 250 °C. These values are rather similar to the values for the support materials. However a large increase in maximum conversion of the lithium containing support is observed: due to the addition of Ag, the maximum conversion is increased to 100 %. From figures 4.6 and 4.11 it can be seen that Ag/$\gamma$-Al$_2$O$_3$ has an equal selectivity to formaldehyde and CO$_2$ (50 %). By adding CeO$_x$ the selectivity to formaldehyde is lowered slightly to 40 %. It also increases the CO production. Adding Li$_2$O increases selectivity to CO$_2$ to 80 % up to 300 °C and increases the temperature where formaldehyde production (up to 40 %) begins. Compared to the support materials, the silver catalyst show less selectivity to CO.

In figures 4.12, 4.13 the oxidation of methanol over Cu-catalysts on different support oxides is shown. The selectivity of different catalysts to possible products is shown as well. Fig. 4.12 shows that CH$_3$OH-conversion on Cu/$\gamma$-Al$_2$O$_3$ starts at 150 °C, reaching its maximum at 300 °C. Adding CeO$_x$ tends to rise the starting temperature of CH$_3$OH-conversion, but has no effect on maximum conversion. Addition of Li$_2$O decreases the maximum conversion to 50 % at 400 °C. The observed conversions are rather similar to those of the support materials, although the conversion of the Cu/$\gamma$-Al$_2$O$_3$ catalyst starts at lower temperatures. From figs. 4.7 and 4.13 it can be seen that copper-catalysts show a high selectivity (85 %) to CO$_2$. Adding Li$_2$O decreases the CO-formation at high temperatures (up to 30 %). Notice the increase in selectivity to formaldehyde between 200 and 300 °C. This behaviour is encountered for all copper catalysts and some gold catalysts. Copper increases the selectivity to CO$_2$ to 95 % compared to the support materials.
Figure 4.11: Product distribution vs temperature during methanol oxidation over Ag/Li$_2$O/Al$_2$O$_3$ (full symbols) and Ag/CeO$_x$/Al$_2$O$_3$ (open symbols): $S_{CH_2O}$ (♦), $S_{CO}$ (●), $S_{CO_2}$ (■) CH$_3$OH:O$_2$ ratio of 1:1

Figure 4.12: Conversion of methanol on Cu based catalysts on different metal supports CH$_3$OH:O$_2$ ratio of 1:1
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Figure 4.13: Product distribution vs temperature during methanol oxidation over Cu/Li$_2$O/Al$_2$O$_3$ (full symbols) and Cu/CeO$_x$/Al$_2$O$_3$ (open symbols): $S_{\text{CH}_2\text{O}}$ (♦), $S_{\text{CO}}$ (●), $S_{\text{CO}_2}$ (■) CH$_3$OH:O$_2$ ratio of 1:1

Figure 4.14: Conversion of methanol in the absence of oxygen on Au-catalysts on different supports CH$_3$OH:O$_2$ ratio of 1:1
4.3.4 The effect of oxygen on supported gold catalysts

In figures 4.14, 4.15 and 4.16 are shown the results of the measurements of the methanol only flow over the gold based catalysts. Upon comparison to figure 4.4 which depict the results of the different supports, it is clear that the addition of gold has a significant contribution to the activity of the catalysts. A striking effect is found for Li$_2$O, a maximum conversion of 50% is found in the presence of Li$_2$O, whereas in the absence of Li$_2$O a conversion of almost 100% is found. As can be seen from figs. 4.15 and 4.16, Au/γ-Al$_2$O$_3$ and Au/CeO$_x$/γ-Al$_2$O$_3$ have a high selectivity (90%) to formaldehyde at temperatures below 300 °C. Above this temperature the selectivity decreases to 40% on gold with an increase in the selectivity towards CO. Addition of CeO$_x$ results in formation of CO$_2$ with a selectivity up to 60% above 300 °C. All catalysts show an increased selectivity (up to 60%) to CO at temperatures above 300 °C. Adding both CeO$_x$ and Li$_2$O decreases the selectivity to formaldehyde to 60%, with an increase of selectivity to CO$_2$. For the Au/γ-Al$_2$O$_3$ support also a long during experiment was done for 65h at 300 °C with methanol in the absence of oxygen. This resulted in a stable 88% conversion and a selectivity to CH$_2$O of 90%, without apparent coke forming.

Figure 4.15: Product distribution vs temperature during methanol dehydrogenation over Au/Al$_2$O$_3$ (full symbols) and Au/CeO$_x$/Al$_2$O$_3$ (open symbols): $S_{\text{CH}_2\text{O}}$ (●), $S_{\text{CO}}$ (●), $S_{\text{CO}_2}$ (▲) and the $S_{\text{CH}_2\text{O}}$ over Al$_2$O$_3$: △ CH$_3$OH:O$_2$ ratio of 1:1
4.4 Discussion

4.4.1 Activity of the bare supports and effect of oxygen

The most active support in this study is the acidic $\gamma$-Al$_2$O$_3$ that is able to produce formaldehyde, with high selectivity. The presence or absence of O$_2$ does not seem to have a big influence on this selectivity. A part of the activity of the commercially $\gamma$-Al$_2$O$_3$ support used, might be attributed to the presence of impurities, as very pure $\gamma$-Al$_2$O$_3$ exhibits a much lower activity in the reaction with methanol. It is not clear whether the activity is caused by the intrinsic catalytic activity of the impurities or by the influence of the impurities on the $\gamma$-Al$_2$O$_3$. Cariati et al. [20] found CO to be the principal product on Al$_2$O$_3$. They used a flow of 20% O$_2$ and 5.5% CH$_3$OH, which is a much higher oxygen content than we used. So the high selectivity to formaldehyde found in our studies is probably related to the small or absent oxygen content in the reaction flow. The rate determining step of formaldehyde formation was found to be the C-H bond breaking of the adsorbed methoxy species [16]. The ability to break
a C-H bond will depend on the basic or nucleophilic character of oxygen species in proximity of the methoxy group [16]. The desorption of reaction products will be favored by weak acid sites [25]. For CH$_2$O formation both weak acid and weak basic sites are needed to limit the H abstraction and prevent strong adsorption. This is clearly the case for the Al$_2$O$_3$ support. When Li$_2$O, which has a basic character, is added the methanol conversion is greatly decreased and the selectivity to CH$_2$O goes to zero. Instead CO and CO$_2$ are formed. This indicates further oxidation of formaldehyde to HCOOH due to the increased basic character [16]. This HCOOH is dehydrated to CO or further oxidized to CO$_2$ with oxygen. Addition of CeO$_x$ to Al$_2$O$_3$ results in a small decrease in methanol conversion. This catalyst shows selectivity to CO and CO$_2$ at the expense of CH$_2$O, which is further oxidized. This can be attributed to the oxygen atoms of the ceria available for the oxidation reaction. Although oxygen is not needed for the CH$_2$O formation it seems to increase the methanol conversion and so increases the formaldehyde production. Possibly, small amounts of oxygen can prevent deactivation of the catalytic surface.

### 4.4.2 Gold catalysts

Addition of gold to all used supports results in an enhanced methanol conversion. The effect is most pronounced for the Li$_2$O/Al$_2$O$_3$ support where the onset temperature is lowered from 250°C to 150°C. The smallest effect is for the ceria containing catalysts, where also the selectivity is hardly affected by the gold. In contrast Scirè et al. found a great improvement by adding gold to ceria in total oxidation of methanol [4]. They claimed that gold weakens the Ce-O bond and thus increases the mobility/activity of the surface lattice oxygen. In our measurements no evidence is found for such an effect. However, it should be emphasized that we did not use pure CeO$_x$ as support but CeO$_x$/Al$_2$O$_3$. It might be that in our system the Ce-O bond is already weakened by the γ-Al$_2$O$_3$ support or that the ceria is more reduced into Ce$^{3+}$ in our oxygen lean conditions. Scirè et al. used an excess of oxygen with a methanol to oxygen ratio of 0.7:10. In our opinion methanol is converted to formaldehyde on the support and further oxidized on the metallic gold particles to CO and CO$_2$. The selectivity to formaldehyde of the gold catalyst is comparable to that of the γ-Al$_2$O$_3$-support (fig. 4.2). Addition of gold affects the T50 % temperature - and therefore the activity - positively. It can be seen that adding gold does not change the selectivity of oxidation of methanol to formaldehyde by alumina below 350 °C. Adding gold does increase the selectivity to CO above this temperature. Only above this temperature CO is
formed. This effect is caused by gold particles, because this increase is not observed using pure alumina. These observations suggest a possible mechanism of CH\textsubscript{3}OH oxidation: methanol is first decomposed to formaldehyde on the alumina support at low temperatures. When the temperature increases formaldehyde is oxidized on gold to CO. This suggests that gold is not active in formaldehyde formation below 350 °C. While no increase of CO\textsubscript{2} production is observed above 350 °C, gold does not oxidise CO further to CO\textsubscript{2}, possibly this is caused by the lack of oxygen. An increase of selectivity to CO\textsubscript{2} in the whole temperature region is observed when gold is added. Probably another mechanism than the one described above takes place at the same time. CH\textsubscript{3}OH is adsorbed directly on the gold, and oxidised fully to CO\textsubscript{2}. This suggestion is supported by literature data [26], where O-H bond breaking was observed for methanol on the Au(310) surface.

When CeO\textsubscript{x} is added to the catalyst, the selectivity to formaldehyde drops completely, while the selectivity to CO and CO\textsubscript{2} is increased to over 80 % (figs. 4.8, 4.9). Above 300 °C the formaldehyde is further oxidised to CO and CO\textsubscript{2} probably by the gold particles, assisted by the ceria, which can provide the oxygen necessary for complete oxidation and can act as a co-catalyst [23]. The results of the non-oxidative dehydrogenation of methanol show the same trend as the results with O\textsubscript{2}. The Au/Al\textsubscript{2}O\textsubscript{3} catalyst produces mainly CH\textsubscript{2}O at temperatures up to 350 °C. Above this temperature the formaldehyde, which is probably formed on the support is further oxidized to CO by the gold particles. Measurements in the presence of oxygen showed a higher selectivity toward CO and CO\textsubscript{2}. With the addition of metal oxides more CO and CO\textsubscript{2} are formed. This indicates further oxidation of the formed formaldehyde by the same reasons as mentioned above. The results on the Au/Al\textsubscript{2}O\textsubscript{3} catalysts with O\textsubscript{2} produce more CO\textsubscript{2}, so it is likely that oxygen is needed for the crucial step for the oxidation of formaldehyde to CO\textsubscript{2} on the metal particles.

### 4.4.3 Silver catalysts

The Ag/Al\textsubscript{2}O\textsubscript{3} catalyst is more selective to CO\textsubscript{2} than γ-Al\textsubscript{2}O\textsubscript{3}, and it is equally active. While almost no increase in the production of CO is seen, it is suggested that silver is able to either oxidize formaldehyde that is formed on the alumina directly to CO\textsubscript{2} or oxidize methanol fully to CO\textsubscript{2}. In order to do this, the oxidizing capabilities of the Ag-catalyst have to be better than that of Au-catalyst, which is normally not the case. Above 350 °C slightly more CO is formed compared to the alumina support, due to the addition of Ag. This increase is smaller than the increase that is seen with the
Au/Al$_2$O$_3$ catalyst. At these temperatures the selectivity to formaldehyde drops, while the selectivity to CO$_2$ remains the same. This suggests that formaldehyde is oxidized to CO, instead of CO$_2$. It also shows that two mechanisms take place at the same time: In the first mechanism CH$_3$OH is activated on the Ag-particles and oxidized directly to CO$_2$ at temperatures above 200 °C. In the second mechanism CH$_3$OH is activated on the alumina and converted to formaldehyde. The produced formaldehyde is then converted to CO on the silver, at temperatures above 350 °C.

The addition of silver to the Li$_2$O/Al$_2$O$_3$ support causes the formation of CH$_2$O at temperatures above 300°C. As the support only does not convert methanol into formaldehyde, the formation can be attributed to the silver particles. Addition of CeO$_x$ to the Ag-catalysts leads to an increased selectivity to CO$_2$ (fig. 4.11), but still 40% selectivity to formaldehyde is observed. Because CeO$_x$ is known for its oxygen storage capacity, it is suggested that the oxygen supplied by ceria is used for full oxidation of methanol to CO$_2$. The high selectivity to formaldehyde might be explained by the worse oxidising capabilities of silver compared to gold. Above 350 °C the selectivity to CO increases, while the selectivity to formaldehyde drops. Formaldehyde formed on the alumina will be oxidized to CO on silver. This reaction is enhanced in comparison to the silver-only catalyst by the addition of ceria.

### 4.4.4 Copper catalysts

While addition of gold and silver do not alter the selectivity to formaldehyde very much compared to γ-Al$_2$O$_3$, addition of copper leads to 85% selectivity to CO$_2$ (figure 4.7). Almost no formaldehyde is formed. This illustrates that Cu is more active in complete oxidation of CH$_3$OH than the other metals. At high temperatures not sufficient O$_2$ in the feed is available for complete oxidation to CO$_2$ and CO is formed. Addition of CeO$_x$ does not affect the activity and the selectivity of the catalyst (fig. 4.13), because Cu/Al$_2$O$_3$ is already very efficient in total oxidation of methanol. When Li$_2$O is added to the Cu/Al$_2$O$_3$ catalyst, the conversion drops to 65% at 400°C, while the selectivity to CO$_2$ remains 85% (figure 4.13). Almost no CO is formed at high temperatures. As pure alumina shows a much higher conversion of methanol, it is suggested that the addition of Li$_2$O deactivates the catalytic activity of the support. This implies that the suggested mechanism plays a major role: if no formaldehyde can be formed on the support, it cannot be oxidised to CO$_2$ on copper.
4.4.5 Comparison of the copper, silver and gold catalysts

On all the three $\gamma$-$\text{Al}_2\text{O}_3$ supported Cu, Ag and Au catalysts the same mechanism can explain the results. Methanol is dehydrogenated on the support to formaldehyde and is further oxidized on the metal particles. Copper is most active in total oxidation and shows the highest selectivity to CO$_2$. The gold and silver based catalyst show similar behavior when $\gamma$-$\text{Al}_2\text{O}_3$ is used as support. The addition of Li$_2$O to Al$_2$O$_3$ results in a drastic decrease in formaldehyde formation. On the silver containing catalyst there is some selectivity to CH$_2$O at temperature above 300 °C, which is not observed for the gold containing catalyst, demonstrating that gold is better in total oxidation of methanol.

4.5 Conclusions

In the dehydrogenation and oxidation of methanol the support and additives play a major role in the activity and selectivity. It is suggested that the first step in the oxidation is the dehydrogenation of methanol into CH$_2$O on the acidic support: $\gamma$-$\text{Al}_2\text{O}_3$. Addition of Li$_2$O to the support diminishes this reaction. When Cu, Ag and Au particles are added oxidation of the formed formaldehyde is observed, leading to complete oxidation on Cu/$\text{Al}_2\text{O}_3$. The results of the Ag/Li$_2$O/$\text{Al}_2\text{O}_3$ catalyst suggest that silver particles are capable to oxidize methanol partially into formaldehyde. Addition of CeO$_x$ results in an increased selectivity to CO and CO$_2$ and acts as a co-catalyst next to the deposited metal particles. In the absence of oxygen the presence of gold particles enhances the catalytic activity.

References


