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A comparative study of oxidation of methanol on γ-Al_2O_3 supported group IB metal catalysts

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ABSTRACT

Results are presented concerning the behavior of alumina supported Cu, Ag and Au (M) catalysts and the effect of addition of Li_2O and CeO_xon the dehydrogenation and oxidation of methanol. The γ-Al_2O_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_3OH 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_2O blocks the adsorption site for methanol on alumina, and hence, decreasing the formation of formaldehyde.

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. Although 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. Hence, 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_3OH by IB metals supported on γ-Al_2O_3 has been investigated. Scirè et al. [3,4] studied the oxidation of methanol over Au, Ag and Cu on Fe_2O_3 and 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. Scirè 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_2O and CeO_x has been investigated. A study by Ross et al. [5,6] showed that addition of Li_2O 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_2O_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 various low-temperature oxidation reactions [10–13]. Previously reported results show that ceria has a promoting effect on the activity of the Au/Al_2O_3catalyst 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

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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 Tatibouët [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 [3,4,24], in this 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_2O_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.

2. Experimental

2.1. Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x), Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_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, silver and gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent [20]. 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_2O_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 0.53 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. Because urea and silver atoms can form a soluble $Ag[NH_3]^+$ complex, a large surplus of silver was needed to deposit enough silver on the Al_2O_3. 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 for 2 h.

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 50 kV and 40 mA. The average M particle size of the IB metals was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [21].

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 13× column (*Alltech*) for O_2, CO, CO_2 and H_2O separation and a Hayesep Q (*Alltech*) for CH_2O and CH_3OH 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}.

3. Results

3.1. Characterization

The average M particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3 nm. The results of the characterization of the catalysts after the reaction are shown in Table 1. The catalysts without additives contain small M particles of 3–4 nm. With CeO_x and Li_2O added the average particle size is lower than the detection limit (3 nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [8,22,23]. 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 after deposition of the IB metals. These measurements showed that the appropriate amount of Li and/or Ce was deposited on the catalysts. The used γ-Al_2O_3 support was investated with XRF to determine which impurities are present. Three impurities were found: Na_2O (0.05 wt%), SiO_2 (0.1 wt%) and Fe_2O_3 (0.05 wt%).

Table 1
Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Metal loading (at.%)	Average particle size (nm)
Au/Al_2O_3	4.8 ± 0.1	0.51	4.5 ± 0.1
$Au/CeO_x/Al_2O_3$	4.0 ± 0.2	0.42	3.3 ± 0.3
$Au/Li_2O/Al_2O_3$	4.5 ± 0.3	0.48	<3.0
$Au/CeO_x/Li_2O/Al_2O_3$	4.0 ± 0.2	0.42	<3.0
Ag/Al_2O_3	2.2 ± 0.1	0.47	4.9 ± 0.2
$Ag/CeO_x/Al_2O_3$	1.8 ± 0.1	0.39	3.9 ± 0.2
$Ag/Li_2O/Al_2O_3$	2.2 ± 0.1	0.47	<3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6 ± 0.1	0.34	<3.0
Cu/Al_2O_3	1.3 ± 0.1	0.46	3.6 ± 0.3
$Cu/CeO_x/Al_2O_3$	1.0 ± 0.1	0.35	<3.0
$Cu/Li_2O/Al_2O_3$	1.4 ± 0.1	0.49	<3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0 ± 0.1	0.35	<3.0

3.2. Activity of support materials and effect of oxygen

In Fig. 1 the conversion of methanol by the support oxides is shown using the methanol/O_2 ratio of unity. Hence, the O_2 concentration in the feed is too low for complete oxidation of CH_3OH to H_2O and CO_2. The selectivity is shown in Table 2. The alumina used converts CH_3OH above 225 ° C selectively to formaldehyde. Maximum conversion is reached above 300 °C. Adding CeO_xincreases the temperature at which CH_3OH starts to decompose to 250 °C. The selectivity to formaldehyde decreases to 5% at 400 °C, while selectivity to CO increases to 55% and a 40% selectivity toward $CO_2$is obtained. Addition of Li_2O decreases maximal conversion to 50% at 400 °C. The selectivity to formaldehyde drops to 10%, and the selectivity to CO and CO_2 is increased. When both CeO_x and Li_2O are added, a behavior intermediate of those of Li_2O/Al_2O_3 and ceria/Al_2O_3 is observed. CH_3OH-conversion starts at 300 °C. Selectivities resemble those of Li_2O/γ-Al_2O_3 with a higher selectivity to CH_2O (30%).

The activity of the used alumina support from BASF with impurities (Na_2O, SiO_2 and Fe_2O_3) is compared to a sample of pure Al_2O_3(Aldrich) with similar surface area. The results are also presented in Fig. 1. The γ-$Al_2O_3$with impurities has a much higher activity compared to the pure alumina. However there no difference was found in selectivity. Both supports produce mainly formaldehyde.

In Fig. 2 the performance of the different supports in the absence of oxygen is presented. On the industrial Al_2O_3 and CeO_x/Al_2O_3 supports, the conversion starts at 200 ° C and reaches maximum conversion of 75% at 400 °C. The Li_2O containing supports show only minor methanol conversion at temperature above 300 ° C with at maximum conversion of 40%. Compared to the measurements in the presence of O_2 shown in Fig. 1 the methanol conversion is dropped, but the selectivity is not significantly affected by oxygen. On γ-Al_2O_3 formaldehyde is the sole product in both the presence and the absence of O_2.

3.3. Cu, Ag and Au on γ-Al_2O_3

In Fig. 3 and Table 3 the performance of Cu, Ag and Au on the γ-Al_2O_3 in the oxidation of methanol is shown. It can be seen from Fig. 3 that Au/Al_2O_3 is the most active catalyst and that CH_3OH-oxidation starts at 100 °C. Maximum conversion reaches 100% at 275 °C. On copper the CH_3OH conversion starts at 150 ° C and reaches 100% conversion at 300 °C. The CH_3OH-conversion 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, as the selectivity towards CH_2O is greatly decreased.

Table 2
Selectivity of the support oxides $S_1 = CH_2O$, $S_2 = CO$, $S_3 = CO_2$

Catalyst	Temperature	S_1	S_2	S_3
Al_2O_3	250	100	0	0
	300	100	0	0
	400	95	5	0
CeO_x/Al_2O_3	250	–	–	–
	300	30	37	33
	400	5	55	40
Li_2O/Al_2O_3	250	–	–	–
	300	–	–	–
	400	10	40	50
$CeO_x/Li_2O/Al_2O_3$	250	–	–	–
	300	–	–	–
	400	30	10	60

Gold is selective to both CH_2O (60%) and CO_2 (40%) at reasonable levels of methanol conversion. Selectivity to CO increases slowly to 40% at 400 °C. Silver shows equal selectivity to formaldehyde and CO_2 (50%) above 250 ° C and shows a slight increase of selectivity to CO of 20% at 400 °C. On copper high selectivity to CO_2 (up to 90%) is seen, while selectivity to formaldehyde and CO does not exceed 20%.

3.4. Effect of Li_2O and CeO_x additive

In Fig. 4 the effect of CeO_x and Li_2O on the performance of Au/Al_2O_3 is shown. It can be seen from Fig. 4 that Au/Al_2O_3 is active above 100 ° C and 100% conversion is obtained above 275 °C. When CeO_x and/or Li_2O 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, when gold particles are added as can be seen upon comparison of Figs. 1 and 4. The supports without gold deposited show only activity above 250 °C, whereas after the addition of gold, the conversion onset lies below 200 °C. The largest increase in performance due to addition of gold is seen for the lithium containing support.

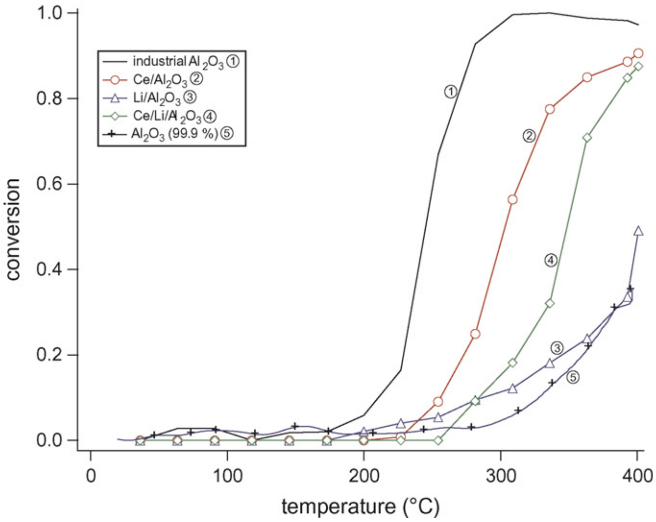

Fig. 1. Conversion of methanol on different supports. $CH_3OH:O_2$ ratio of 1:1.

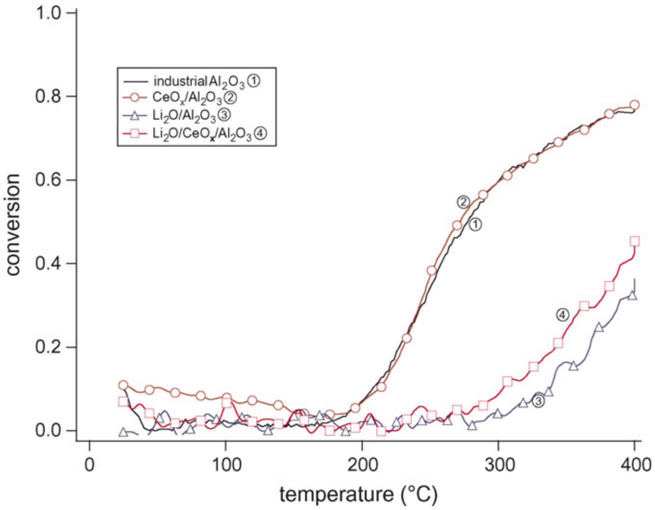

Fig. 2. Conversion of methanol in the absence of oxygen on different supports.

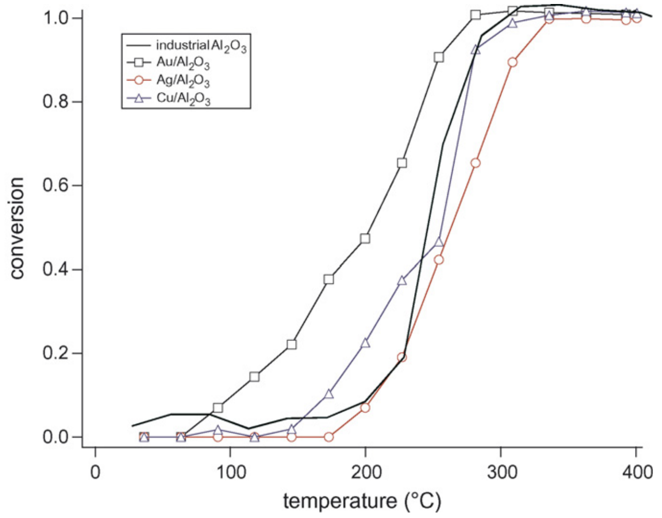

Fig. 3. Conversion of methanol on different metal catalysts. CH_3OH:O_2 ratio of 1:1.

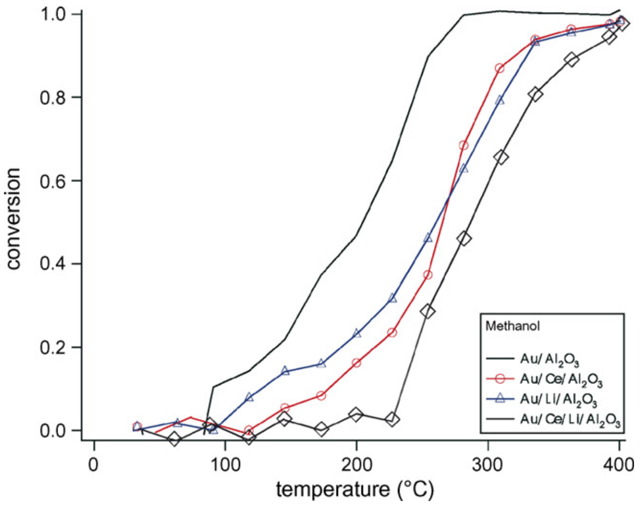

Fig. 4. Conversion of methanol on Au-based catalysts on different metal supports CH_3OH:O_2ratio of 1:1.

From Table 4 it can be seen that Au/Al_2O_3 has a selectivity of 60% to formaldehyde at temperatures above 250 °C, which is much lower than for the Al_2O_3 support only. By adding CeO_x and/or Li_2O this selectivity to CH_2O is decreased to under 10% at 400 ° C as shown in Table 4. The selectivity to $CO_2$is increased by adding $CeO_x$and/or Li_2O and also improved compared to the selectivity of the Li_2O/Al_2O_3 and CeO_x/Al_2O_3 supports. In Fig. 5 the conversion of methanol over Ag catalysts on different support oxides is shown. The selectivity to possible products is shown as well in Table 5. It can be seen from Fig. 5 that Ag/γ-Al_2O_3 shows CH_3OH-conversion above 200 °C, and reaches maximum conversion at 350 °C. After addition of CeO_x or Li_2O CH_3OH-conversion starts at the significantly higher temperature of 250 °C. These values are rather similar to the values for the support materials. However, the adddition of Ag results in a large increase in maximum conversion for the lithium containing support: the maximum conversion is increased to 90%. From Table 5 it can be seen that Ag/γ-Al_2O_3 has an equal selectivity to formaldehyde and CO_2. By adding CeO_x the selectivity to formaldehyde is decreased to 15% at 400 °C.

In Fig. 6 the oxidation of methanol over Cu catalysts on different support oxides is shown. The selectivity of different catalysts to possible products is shown in Table 6. Fig. 6 shows that CH_3OH-conversion on Cu/γ-Al_2O_3 starts at 150 °C, reaching its maximum at 300 °C. Adding CeO_x tends to rise the starting temperature of CH_3OH-conversion, but has no effect on maximum conversion. Addition of Li_2O decreases the maximum conversion to 60% at 400 °C. The observed conversions are rather similar to those of the support materials, although the conversion of the Cu/γ-Al_2O_3 catalyst starts at lower temperatures. Table 6 shows that copper catalysts show a high selectivity (90%) to CO_2. Adding Li_2O decreases the CO-formation at high temperatures. Copper increases the selectivity to CO_2 compared to all the used support materials.

3.5. The effect of oxygen on supported gold catalysts

In Fig. 7 the results of the measurements of the methanol only flow over the gold-based catalysts are shown. Upon comparison to Fig. 2 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_2O, where a maximum conversion of 50% is found in the presence of Li_2O, whereas in the absence of Li_2O a conversion of almost 100% is found. As can be seen in Table 7 Au/γ-Al_2O_3 and Au/CeO_x/γ-Al_2O_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_2O decreases the selectivity to formaldehyde to 45%, with an increase of selectivity to CO_2. For the Au/γ-Al_2O_3 catalyst also a long during experiment was done for 65 h at 300 ° C with methanol in the absence of oxygen. This resulted in a stable 88% conversion and a selectivity to CH_2O of 90%, without apparent coke forming.

Table 3
Selectivity of the M/Al_2O_3 catalysts, CH_3OH:O_2ratio = 1

Catalyst	Temperature	S_1	S_2	S_3
Au/Al_2O_3	250	60	0	40
	300	58	8	36
	400	40	40	20
Ag/Al_2O_3	250	50	–	50
	300	53	4	43
	400	40	20	40
Cu/Al_2O_3	250	20	–	80
	300	10	–	90
	400	–	20	80

S_1 = CH_2O, S_2 = CO, S_3 = CO_2.

Table 4
Selectivity of the Au-based catalysts on different metal supports, CH_3OH:O_2ratio = 1

Catalyst	Temperature	S_1	S_2	S_3
Au/Al_2O_3	250	60	0	40
	300	58	8	36
	400	40	40	20
Au/CeO_x/Al_2O_3	250	75	5	20
	300	30	10	60
	400	5	20	75
Au/Li_2O/Al_2O_3	250	76	–	24
	300	38	10	50
	400	–	30	70

S_1 = CH_2O, S_2 = CO, S_3 = CO_2.

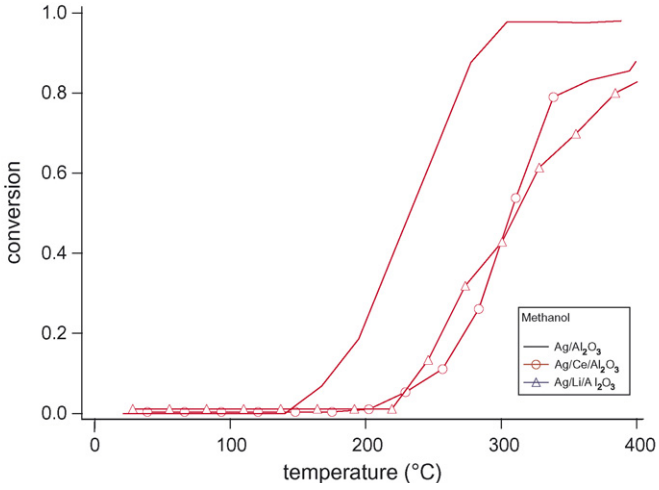

Fig. 5. Conversion of methanol on Ag-based catalysts on different metal supports $CH_3OH:O_2$ ratio of 1:1.

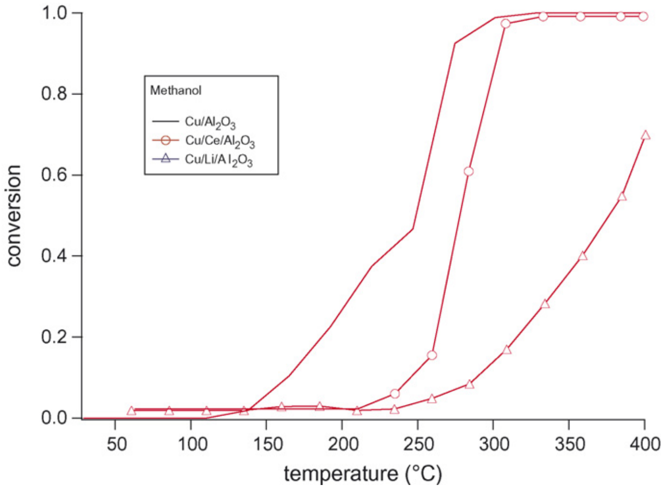

Fig. 6. Conversion of methanol on Cu-based catalysts on different metal supports $CH_3OH:O_2$ ratio of 1:1.

4. Discussion

4.1. Activity of the bare supports and effect of oxygen

The most active support in this study is the acidic γ-Al_2O_3 that is able to produce formaldehyde, with high selectivity. The presence or absence of O_2 does not seem to have a large influence on this selectivity. A part of the activity of the commercially γ-Al_2O_3 support used might be attributed to the presence of impurities, as very pure γ-Al_2O_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 γ-Al_2O_3. Cariati et al. [24] found CO to be the principal product on Al_2O_3. They used a flow of 20% O_2 and 5.5% CH_3OH, 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_2O 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_2O_3support. When Li_2O, which has a basic character, is added the methanol conversion is greatly decreased and the selectivity to CH_2O 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, by the acid sites or further oxidized to $CO_2$with oxygen. Addition of $CeO_x$to Al_2O_3 results in a small decrease in methanol conversion. This catalyst shows selectivity to CO and CO_2 at the expense of CH_2O, 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_2O 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.

4.2. Gold catalysts

Addition of gold to all used supports results in an enhanced methanol conversion. The effect is most pronounced for the Li_2O/Al_2O_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_xas support but CeO_x/Al_2O_3. It might be that in our system the ceria is already 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. Addition of gold affects

Table 5
Selectivity of the Ag-based catalysts on different metal supports, $CH_3OH:O_2$ratio = 1

Catalyst	Temperature	S_1	S_2	S_3
Ag/Al_2O_3	250	50	–	50
	300	53	4	43
	400	40	20	40
$Ag/CeO_x/Al_2O_3$	250	60	–	40
	300	60	–	40
	400	15	25	60
$Ag/Li_2O/Al_2O_3$	250	76	–	24
	300	60	–	40
	400	35	5	50

$S_1 = CH_2O$, $S_2 = CO$, $S_3 = CO_2$.

Table 6
Selectivity of the Cu-based catalysts on different metal supports, $CH_3OH:O_2$ratio = 1

Catalyst	Temperature	S_1	S_2	S_3
Cu/Al_2O_3	250	20	–	80
	300	10	–	90
	400	–	20	80
$Cu/CeO_x/Al_2O_3$	250	20	0	80
	300	–	10	90
	400	–	25	75
$Cu/Li_2O/Al_2O_3$	250	–	–	–
	300	–	–	100
	400	–	15	85

$S_1 = CH_2O$, S_2=CO, $S_3 = CO_2$.

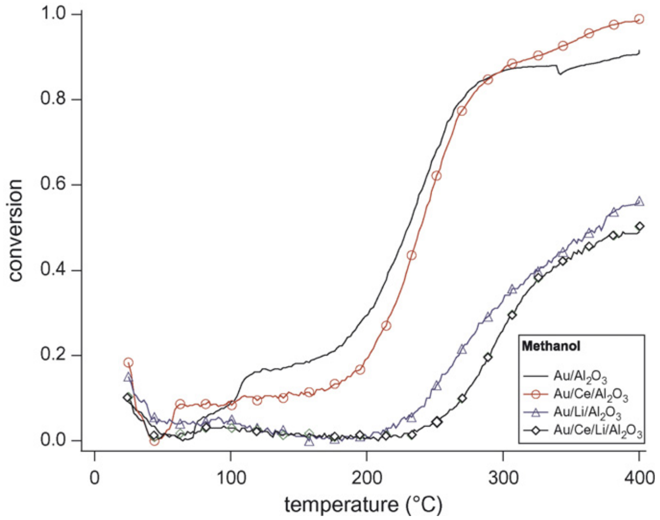

Fig. 7. Conversion of methanol in the absence of oxygen on Au catalysts on different supports.

the T50% temperature – and therefore the activity – positively. It can be seen that adding gold does not change the selectivity to formaldehyde much on alumina below 350 °C. Adding gold does increase the selectivity to CO above this temperature. Only above this temperature CO is formed. This effect can be assigned to the presence of gold particles, because this increase is not observed using pure alumina. These observations suggest a possible mechanism of CH_3OH 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_2 production is observed above 350 °C, gold does not oxidise CO further to CO_2, possibly this is caused by the lack of oxygen. An increase of selectivity to CO_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_3OH is adsorbed directly on the gold, and oxidized fully to CO_2. This suggestion is supported by literature data [26], where O–H bond breaking was observed for methanol on the Au(3 1 0) surface.

When $CeO_x$is added to the catalyst, the selectivity to formaldehyde drops completely, while the selectivity to CO and CO_2 is increased to over 80%. Above 300 ° C the formaldehyde is further oxidized to CO and CO_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 [22]. The results of the non-oxidative dehydrogenation of methanol show the same trend as the results with O_2. The Au/Al_2O_3catalyst produces mainly CH_2O at temperatures up to 350 °C. Above this temperature the formaldehyde, which is probably formed on the support is further converted to CO by the gold particles. Measurements in the presence of oxygen showed a higher selectivity toward CO and CO_2. With the addition of Li_2O and CeO_xmore CO and CO_2 are formed. This indicates further oxidation of the formed formaldehyde by the same reasons as mentioned above. In the presence of O_2 more CO_2 is prodcued on Au/Al_2O_3 as would be expected since Au/Al_2O_3 is an excellent oxidation catalyst.

Table 7
Selectivity of the Au-based catalysts on different metal supports during methanol dehydrogenation $S_1 = CH_2O$, $S_2 = CO$, $S_3 = CO_2$

Catalyst	Temperature	S_1	S_2	S_3
Au/Al_2O_3	250	100	–	–
	300	97	3	–
	400	40	60	–
$Au/CeO_x/Al_2O_3$	250	90	–	10
	300	70	5	25
	400	5	60	35
$Au/Li_2O/Al_2O_3$	250	–	–	–
	300	78	–	24
	400	7	35	58
$Au/Li_2O/CeO_x/Al_2O_3$	250	–	–	–
	300	45	40	15
	400	10	50	40

4.3. Silver catalysts

The Ag/Al_2O_3 catalyst is more selective to CO_2 than γ-Al_2O_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_2 or oxidize methanol fully to CO_2. 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_2O_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_3OH is activated on the Ag-particles and oxidized directly to CO_2 at temperatures above 200 °C. In the second mechanism CH_3OH 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_2O/Al_2O_3 support causes the formation of CH_2O 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, 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 oxidizing 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 converted to CO on silver. This reaction is enhanced in comparison to the silver-only catalyst by the addition of ceria.

4.4. Copper catalysts

While addition of gold and silver does not alter the selectivity to formaldehyde very much compared to γ-Al_2O_3, addition of copper leads to 85% selectivity to CO_2. Almost no formaldehyde is formed. This illustrates that Cu is more active in complete oxidation of CH_3OH 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, because Cu/Al_2O_3 is already very efficient in total oxidation of methanol. When Li_2O is added to the Cu/Al_2O_3 catalyst, the conversion drops to 65% at 400 °C, while the selectivity to CO_2 remains 85%. 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_2O 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 oxidized to CO_2 on copper.

4.5. Comparison of the copper, silver and gold catalysts

On all the three γ-Al_2O_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 γ-Al_2O_3 is used as support. The addition of Li_2O to Al_2O_3 results in a drastic decrease in formaldehyde formation. On the silver containing catalyst there is some selectivity to CH_2O at temperatures above 300 °C, which is not observed for the gold containing catalyst, demonstrating that gold is better in total oxidation of methanol.

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_2O on the acidic support: γ-Al_2O_3. Addition of Li_2O 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/Al_2O_3. The results of the Ag/Li_2O/Al_2O_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. The presence of gold particles enhances the catalytic activity, bith in the presence and absence of oxygen and greatly affects the selectivity.

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