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Direct conversion of ethanol into ethylene oxide on gold based catalysts

Results are presented concerning the behavior of alumina supported gold catalysts and the effects of addition of Li_2O and CeO_x on the oxidation, dehydrogenation and dehydration reactions of ethanol. Pure alumina mainly acts as an acidic catalyst and produces diethyl ether and ethylene. Gold particles play an important role in converting ethanol into ethylene oxide and acetaldehyde. Addition of Li_2O influences the selectivity by suppressing the formation of diethyl ether and ethylene. With the $\text{Au}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ catalysts a high selectivity toward ethylene oxide can be obtained. The influence of the oxygen concentration in the gas flow is investigated. It is suggested that at low concentrations the role of oxygen is mainly to prevent coke formation on the catalytic surface.

6.1 Introduction

Due to the diminishing availability and the high prices of crude oil and natural gas much attention is paid to the use of alternative resources. Ethanol is receiving much interest since it has a reasonably high hydrogen content and it can be produced by the fermentation of corn and other renewable resources. One of the possible options is the production of hydrogen by partial oxidation or steam reforming [1]. In addition, selective oxidation of ethanol may also be important for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities [?, 2]. Ethanol can be converted to e.g. acetaldehyde, ethylene, ethyl acetate, ethane, carbon monoxide/hydrogen and as this paper will show, ethylene oxide, in addition to its total oxidation products carbon dioxide and water. Ethanol is commercially used for ethylene oxide production in a two step reaction by the Chemtex corporation. First ethanol is converted to ethylene after which the ethylene is oxidized with O_2 over a silver based catalyst. This paper reports a direct, one step, conversion of ethanol into ethylene oxide.

Ethanol is also a simple probe molecule for the investigation of surface reactions on metals [1, 3, 4] and oxides [5, 6]. On most surfaces the ethanol molecules first dissociate to ethoxy species. These ethoxy species are further oxidized to acetaldehyde or dehydrated to ethylene. On metal surfaces acetaldehyde either desorbs or decomposes to CO and methane [7]. In addition, coupling and bimolecular hydrogenation reactions may occur resulting in the production of higher hydrocarbons such as diethyl ether, ethyl acetate, acetic acid or ketene [?, 8, 9].

Highly dispersed gold on metal oxides supports exhibits an extraordinarily high activity in various low-temperature oxidation reactions [10–16]. The gold particle size is of huge importance for high oxidation activity. This motivated us to investigate the reactions of various alcohols on γ - Al_2O_3 supported gold catalysts. In a recent publication results have been presented of non-oxidative ethanol dehydrogenation of ethanol on silica supported gold catalysts [17]. It was shown that the gold particle size affects the activity just as was reported for oxidation reactions. This effect of particle size was attributed to the role of step sites on the gold surface. Previously reported results show that ceria has a promoting effect on the activity of Au/ Al_2O_3 in CO and other oxidation reactions [15, 18]. It was argued that the active oxygen was supplied by the ceria. In addition, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [19]. A detailed study of Gluhoi et al. [20, 21] on the effects of addition of (earth) alkali metals to a Au/ Al_2O_3

catalyst revealed that the main role of the (earth) alkali metals is to stabilize the gold nanoparticles. Hence, the alkali metal acts as a structural promoter. The oxidative dehydrogenation of ethanol to acetaldehyde is known to be catalyzed by materials possessing strong base sites such as Li_2O [22].

In this study we investigated the behavior of $\text{Au}/\text{Al}_2\text{O}_3$ catalysts in the dehydrogenation, dehydration and oxidation reactions of ethanol. In addition, the promoting effects of Li_2O and CeO_x have been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2 and for making H_2 from ethanol by reforming [23]. Earlier work concerning the oxidation of methanol revealed that addition of Li_2O has a great effect on the acidic sites of $\gamma\text{-Al}_2\text{O}_3$ and so influences the selectivity to products which are not formed on these acidic sites [24]. Similar results have been found for copper and silver based catalysts [?, 25].

6.2 Experimental

6.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and Li_2O on alumina were prepared by pore volume impregnation of $\gamma\text{-Al}_2\text{O}_3$ (BASF, de Meern) with the corresponding nitrates. After calcination at 350°C these oxides were used as support for the Au particles. The prepared mixed oxides had an intended Ce/Al and Li/Al ratio of 1/15. The gold catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent. The appropriate amount of $\text{HAuCl}_4\cdot 3\text{aq}$ (99.999% Aldrich chemicals) was added to a suspension of purified water containing $\gamma\text{-Al}_2\text{O}_3$ or the mixed oxide. The intended M/Al ratio was 1/75 ($\text{M} = \text{Au}$). This ratio of 1:75 is equal to 0.53at% M and results in 5wt% for gold. 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 . The catalysts were thoroughly ground to ensure that the macroscopic particle size was around $200\mu\text{m}$ for all the catalysts used in this study.

6.2.2 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 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 [26].

6.2.3 Activity measurements

Activity tests of the catalysts were performed in a micro reactor system. A oxygen flow balanced in argon was bubbled through a vessel containing absolute ethanol. This gas flow was led to a lab scale flow reactor made from quartz with a internal diameter of 1 cm. In the reactor the catalyst was placed on a quartz bed. The amount of catalyst used was 0.2g for the Au/ γ -Al₂O₃ catalysts. For catalysts containing CeO_x and/or Li₂O the amount of catalyst was adjusted in such a way that the amount of gold was similar for all the catalysts with and without additives. Prior to activity experiments the catalysts were reduced with H₂ (4 vol% in Ar) at 400 °C for 2 hours.

Two different ratios of oxygen/ethanol were used for the oxidation of ethanol: 1:1, and one with excess oxygen (6:1). For the decomposition reaction a argon flow was bubbled through the vessel. Typically, a total gas flow of 40ml⁻¹(GHSV \approx 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, an activated molecular sieve and a Hayesep Q column (Alltech). All possible reaction products were calibrated by injecting a dilute solution directly into the GC or in case of gases as ethylene and ethylene oxide the gas flow from lecture bottles was diluted with argon and led to the GC. Mass spectrometry confirmed that the analysis of the reaction products by gas chromatography was correct. To distinguish the different components the relative intensity ratios of masses 15,29,43,44,45 were used.

The experiments were carried out at atmospheric pressure. Each reaction test consisted of at least two heating-cooling cycles from room temperature up to 400°C, with a rate of 2°C/min in order to monitor possible catalyst deactivation and hysteresis processes.

6.3 Results

6.3.1 Characterization

The average gold 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 (CO oxidation) are shown in table 6.1. The catalysts without additives contain small particles of 3-4nm. With ceria and Li₂O added the average particle size is lower than the detection limit. HRTEM data of comparable catalysts have been published in earlier papers of our group [20, 21]. 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.

6.3.2 Activity of catalyst supports without gold particles

In table 6.2 the results of the supports without gold, in the dehydrogenation of ethanol in the absence of oxygen are presented. The most active support is γ -Al₂O₃ without additive. The main products are the dehydration products diethyl ether and ethylene. Also some trace amounts of acetaldehyde are found at temperatures up to 300°C. Addition of ceria to the γ -Al₂O₃ results in formation of CO at temperatures above 300°C, at the expense of diethyl ether and ethylene. Addition of Li₂O to the alumina catalysts lowers the ethanol conversion compared to the γ -Al₂O₃ only catalyst. Addition of Li₂O results in a higher selectivity towards ethylene. No acetaldehyde is found. The catalyst which contains both Li₂O and CeO_x show a behavior with the typical characteristics of both Li₂O/Al₂O₃ and CeO_x/Al₂O₃ catalysts.

Table 6.1: Catalyst characterization by ICP and XRD

Catalyst	Metal loading (wt%)	Average particle size (nm)
Au/Al ₂ O ₃	4.6±0.1	4.3±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±0.3	3.2±0.1
Au/CeO _x /Li ₂ O/Al ₂ O ₃	4.0±0.2	<3.0

Table 6.2: conversion and selectivities of ethanol dehydrogenation on the used supports. TC = total conversion(%), S_1 = selectivity toward diethyl ether, S_2 = selectivity toward ethylene, S_3 = selectivity toward CO

Catalyst	Temperature (°C)	TC	S_1	S_2	S_3
Al_2O_3	200	38	92	8	0
	250	70	86	14	0
	300	100	30	70	0
	400	100	0	100	0
CeO_x/Al_2O_3	200	5	80	20	0
	250	30	13	84	3
	300	100	3	69	28
	400	100	0	64	36
Li_2O/Al_2O_3	200	0	0	0	0
	250	31	84	16	0
	300	72	69	31	0
	350	90	67	33	0
	400	100	50	50	0
$Li_2O/CeO_x/Al_2O_3$	200	10	80	20	0
	250	37	81	19	0
	300	100	45	50	5
	400	100	34	58	8

In addition, measurements have been performed for an ethanol/ O_2 mixture of 1 . For the Al_2O_3 and Li_2O/Al_2O_3 catalysts there were no significant differences in activity and selectivity compared to the measurements without oxygen. On the CeO_x containing catalyst some increase in CO formation is recorded, up to 50% selectivity for the CeO_x/Al_2O_3 catalyst and 21% selectivity for the $Li_2O/CeO_x/Al_2O_3$ catalyst.

6.3.3 Ethanol dehydrogenation reaction in the absence of O_2 over the gold based catalysts

In the dehydrogenation of ethanol in the absence of O_2 over the Au-based catalyst there is a significant difference between the first heating stage and the following cycles, which in the figures are represented by the first cooling stage. The results of the 2nd and further heating/cooling stages resemble that of the 1st cooling stage,

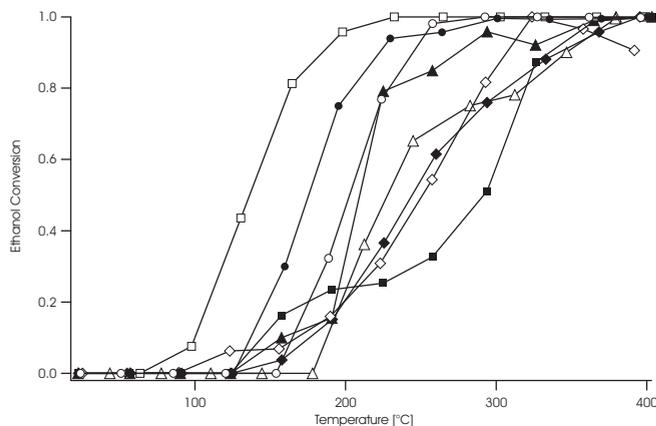


Figure 6.1: Ethanol conversion vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). \circ Au/Al₂O₃, \diamond Au/Li₂O/Al₂O₃, \square Au/CeO_x/Al₂O₃ and \triangle Au/Li₂O/CeO_x/Al₂O₃

which is depicted in the figures shown. The ethanol conversion as a function of reaction temperature is presented in figure 6.1. In the first heating stage (closed symbols) the ethanol conversion starts at 150-200 °C, the Au/Al₂O₃ catalyst being the most active and the Au/CeO_x/Al₂O₃ the least active catalyst with a onset temperature of 250 °C. However, in the first cooling stage and the following cycles(open symbols) the behavior is different. The catalyst which shows the largest difference is the Au/CeO_x/Al₂O₃ catalyst, with a temperature of 50% conversion of 130 °C compared to 300 °C in the first heating stage. The performance of the other catalysts are similar to the first heating stage.

The product selectivities are presented in figures 6.2,6.3,6.4,6.5. The detected products were ethylene, acetaldehyde, diethyl ether, hydrogen and ethylene oxide. No CO₂, H₂O and CO were detected. Only in the first heating stage ethylene oxide is produced, see figure 6.2. Selectivities up to 50% to ethylene oxide were obtained at 300 °C for the Li₂O containing catalysts. The Au/Al₂O₃ and Au/CeO_x/Al₂O₃ catalyst produced ethylene oxide at lower temperatures around 250°C but only with low selectivity. In the following cooling and heating stages no ethylene oxide was produced.

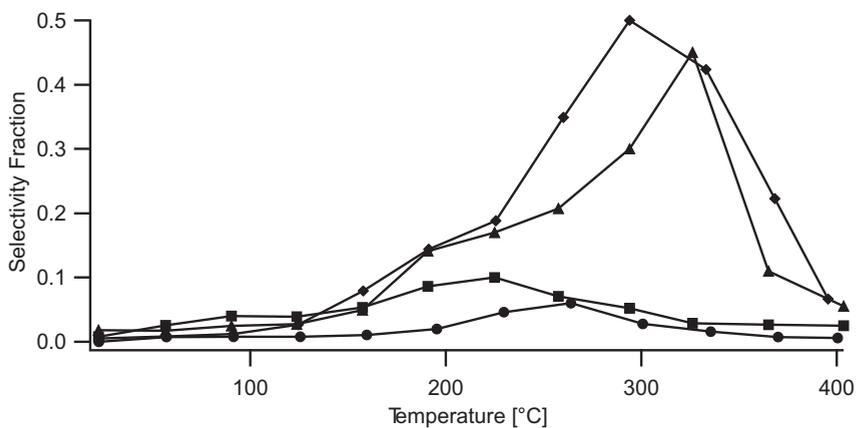


Figure 6.2: Ethylene oxide selectivity vs temperature in the absence of oxygen. First heating stage. ● Au/Al₂O₃, ◆ Au/Li₂O/Al₂O₃, ■ Au/CeO_x/Al₂O₃ and ▲ Au/Li₂O/CeO_x/Al₂O₃

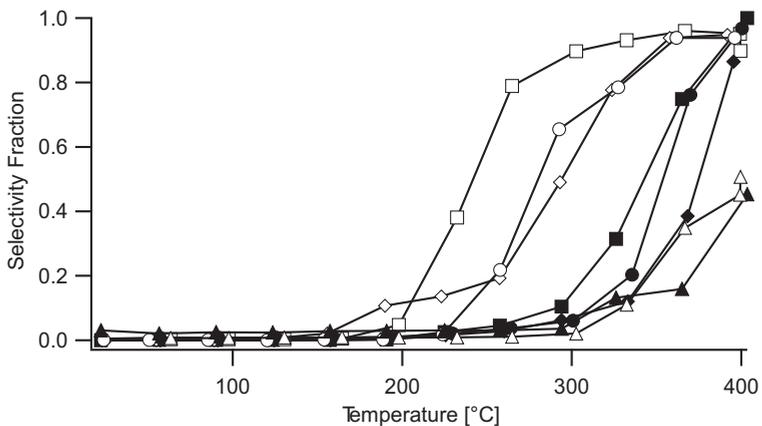


Figure 6.3: Ethylene selectivity vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al₂O₃, ◇ Au/Li₂O/Al₂O₃, □ Au/CeO_x/Al₂O₃ and △ Au/Li₂O/CeO_x/Al₂O₃

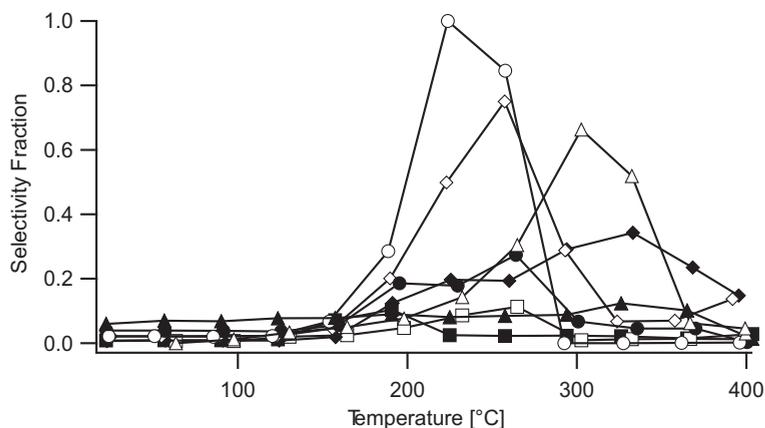


Figure 6.4: Diethyl ether selectivity vs temperature in the absence of oxygen. First heating stage(closed symbols), cooling stage(open symbols). \circ Au/Al₂O₃, \diamond Au/Li₂O/Al₂O₃, \square Au/CeO_x/Al₂O₃ and \triangle Au/Li₂O/CeO_x/Al₂O₃

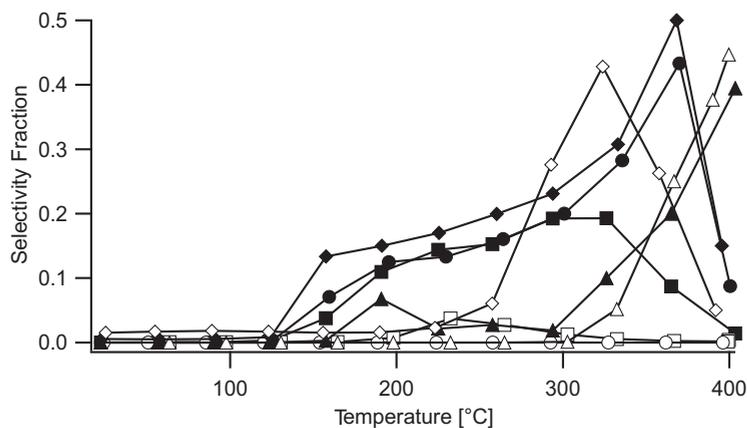


Figure 6.5: Aldehyde selectivity vs temperature in an ethanol/O₂ mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). \circ Au/Al₂O₃, \diamond Au/Li₂O/Al₂O₃, \square Au/CeO_x/Al₂O₃ and \triangle Au/Li₂O/CeO_x/Al₂O₃

Ethylene formation is presented in figure 6.3. In the first heating step the formation of ethylene starts at 320 °C. The selectivity increases to 100 %} at 400 °C on the Au/Al₂O₃ and Au/CeO_x/Al₂O₃ catalysts. On the Au/Li₂O/Al₂O₃ catalyst the formation starts at 350 °C and reached a maximum selectivity of 85 % at 400 °C. The Au/Li₂O/CeO_x/Al₂O₃ catalyst shows the least ethylene formation. The formation of ethylene starts at 350 °C and has a maximum selectivity of 45 % at 400 °C. In the cooling step and the following cycles the ethylene formation already starts at the lower temperatures of 200-250 °C, with the exception of the Au/Li₂O/CeO_x/Al₂O₃ catalyst which shows low selectivity to ethylene at higher temperatures.

The formation of acetaldehyde is shown in figure 6.5. In the first heating step acetaldehyde formation starts at 160 °C on all catalysts except for the Au/Li₂O/CeO_x/Al₂O₃ catalyst. On that catalyst acetaldehyde is not observed below 300 °C. At the same temperature the Au/Al₂O₃ and Au/Li₂O/Al₂O₃ catalysts show a second increase in acetaldehyde formation. This increase was not observed for Au/CeO_x/Al₂O₃ which has the lowest selectivity for acetaldehyde. In the cooling step and following cycles only the Li₂O containing catalysts show significant selectivities to acetaldehyde at high temperatures.

On the Au/Al₂O₃ and Au/CeO_x/Al₂O₃ only traces of acetaldehyde were detected. In the first heating step there is a low selectivity to diethyl ether on the Au/Al₂O₃ and Au/CeO_x/Al₂O₃ catalysts between 200-300 °C as shown in figure 6.4. In the following steps much higher selectivities were obtained. The Au/Al₂O₃ and Au/Li₂O/Al₂O₃ showed maximum selectivity between 200-270 °C. The Au/Li₂O/CeO_x/Al₂O₃ catalysts showed a maximum selectivity at 300 °C.

6.3.4 Ethanol oxidation in an ethanol/O₂ mixture of 1.

The conversion of ethanol using an ethanol/O₂ mixture of 1 is presented in figure 6.7. In the first heating step the reaction starts at higher temperatures compared to the cooling step. In the subsequent cycles the behavior is rather similar to that of the first cooling step. The conversion starts at 100 °C and reaches a maximum at about 275 °C. The Au/Li₂O/Al₂O₃ shows the best activity. The oxygen conversion (shown in figure 6.6) starts at higher temperatures compared to the ethanol conversion. The addition of Li₂O or CeO_x lowers the temperature of oxygen uptake by 50 °C. The oxygen conversion starts at 150 °C and reaches a maximum conversion at 250 °C for the CeO_x containing catalysts, and for Au/Al₂O₃ and Au/Li₂O/Al₂O₃ the oxygen conversion reaches maximum conversion at 350 °C.

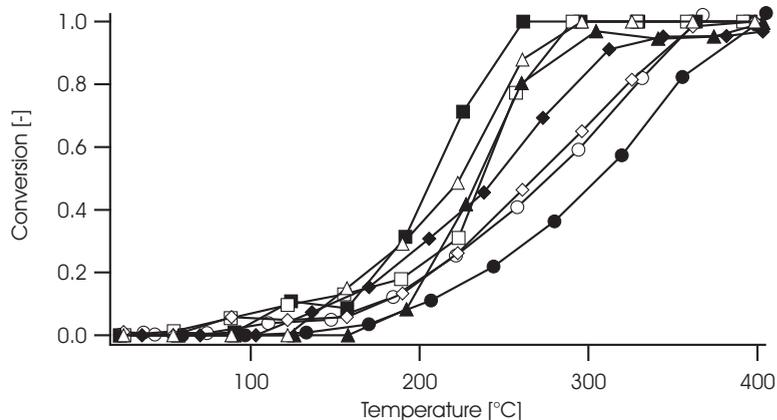


Figure 6.6: Oxygen conversion vs temperature in an ethanol/O₂ mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). \circ Au/Al₂O₃, \diamond Au/Li₂O/Al₂O₃, \square Au/CeO_x/Al₂O₃ and \triangle Au/Li₂O/CeO_x/Al₂O₃

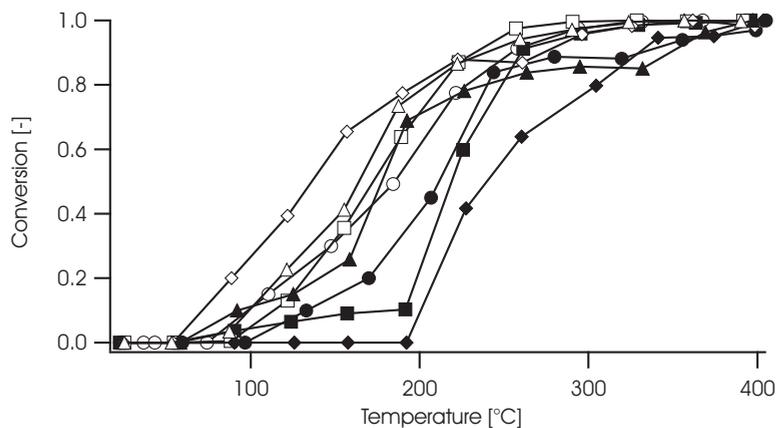


Figure 6.7: Ethanol conversion vs temperature in an ethanol/O₂ mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). \circ Au/Al₂O₃, \diamond Au/Li₂O/Al₂O₃, \square Au/CeO_x/Al₂O₃ and \triangle Au/Li₂O/CeO_x/Al₂O₃

100

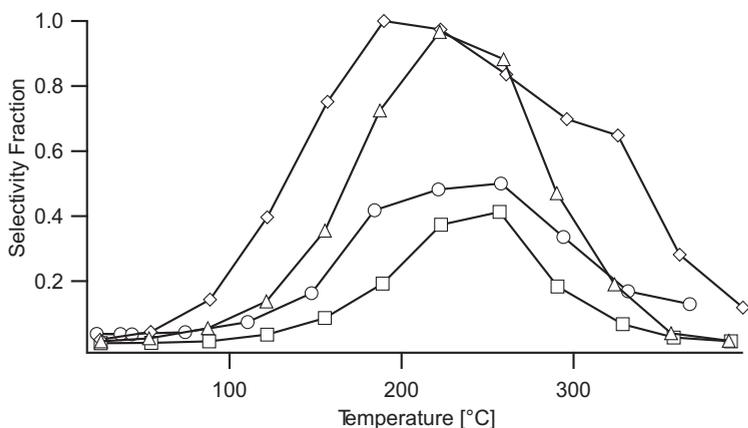


Figure 6.8: ethylene oxide selectivity vs temperature in an ethanol/O₂ mixture of 1. First cooling stage (open symbols). ○ Au/Al₂O₃, ◇ Au/Li₂O/Al₂O₃, □ Au/CeO_x/Al₂O₃ and △ Au/Li₂O/CeO_x/Al₂O₃

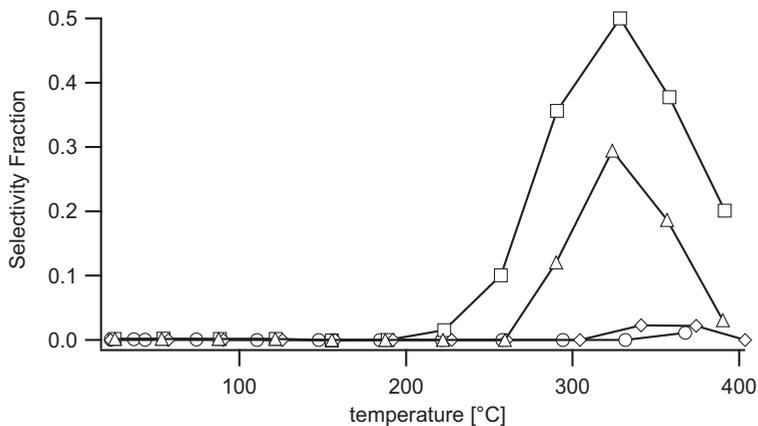


Figure 6.9: Diethyl ether selectivity vs temperature in an ethanol/O₂ mixture of 1. First cooling stage (open symbols). ○ Au/Al₂O₃, ◇ Au/Li₂O/Al₂O₃, □ Au/CeO_x/Al₂O₃ and △ Au/Li₂O/CeO_x/Al₂O₃

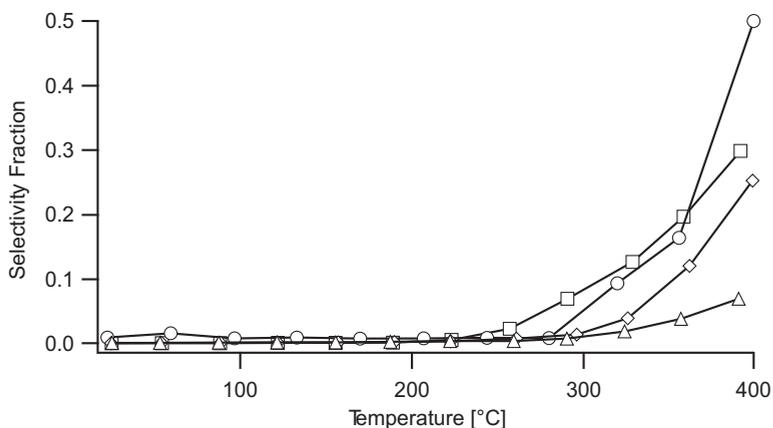


Figure 6.10: ethylene selectivity vs temperature in an ethanol/O₂ mixture of 1. First heating stage(closed symbols), cooling stage(open symbols). ○ Au/Al₂O₃, ◇ Au/Li₂O/Al₂O₃, □ Au/CeO_x/Al₂O₃ and △ Au/Li₂O/CeO_x/Al₂O₃

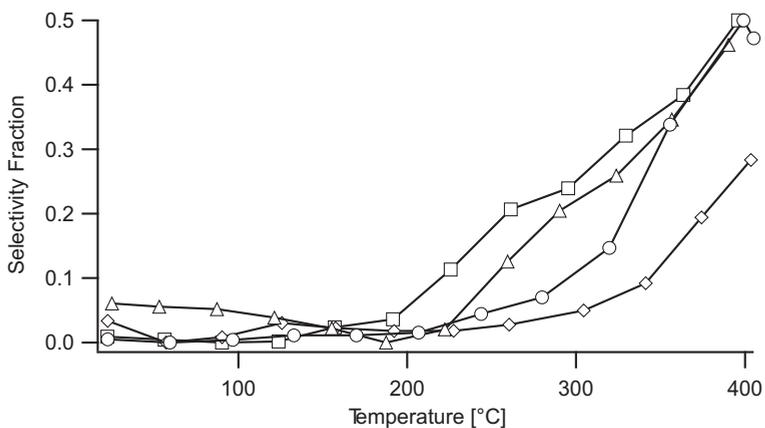


Figure 6.11: CO₂ selectivity vs temperature in an ethanol/O₂ mixture of 1. First cooling stage(open symbols). ○ Au/Al₂O₃, ◇ Au/Li₂O/Al₂O₃, □ Au/CeO_x/Al₂O₃ and △ Au/Li₂O/CeO_x/Al₂O₃

At temperatures between 100 °C and 250 °C the main product is ethylene oxide, as can be seen in figure 6.8. The catalyst with the best performance in ethylene oxide formation is Au/Li₂O/Al₂O₃. A selectivity to ethylene oxide of 88% is reached. With this catalyst also traces of the combination product of ethylene oxide and ethanol (ethoxy-ethanol) were detected. When the gas flow was bubbled through a diluted NaOH solution glycol was produced, which is further evidence that the output gas flow contained ethylene oxide. At temperatures between 250-400 °C diethylether was formed over the two CeO_x containing catalysts, as shown in figure 6.9. The addition of ceria to the Au/Al₂O₃ catalyst also results in more ethane formation (not shown). Also ethylene and CO₂ and traces of CO were formed as shown in figures 6.10 and 6.11. Au/Al₂O₃ showed the highest selectivity to CO₂ production and the Au/CeO_x/Al₂O₃ catalyst showed the highest selectivity to ethylene formation.

6.3.5 Ethanol oxidation in excess oxygen

The results of ethanol oxidation over Au/Al₂O₃ in excess oxygen (ethanol/O₂ = 1/6) are presented in figures 6.12 and 6.13. Ethanol conversion starts from 150 °C and a sharp increase in conversion is observed at 200 °C. At this temperature also the O₂ conversion and the CO₂ production start. At temperatures above 300 °C ethanol is mainly ethanol oxidized to CO₂. The ethylene oxide production can be assigned to the activity of gold as the γ -Al₂O₃ support produces no ethylene oxide. Addition of Li₂O shown in figures 6.12 and 6.14 increases the ethanol conversion between 50 and 200 °C. The main product in this temperature region is ethylene oxide while no oxygen is consumed. The oxygen conversion is similar to the Au/Al₂O₃ catalyst as is the CO₂ production.

In figures 6.12 and 6.15 the effect of addition of CeO_x is shown. The onset of both ethanol and oxygen conversion is shifted to 175 °C. CO₂ production already starts at 200 °C. At temperatures up to 250 °C the intermediate products ethylene oxide, diethyl ether and ethylene are detected.

The results of addition of both Li₂O and CeO_x are presented in figures 6.12 and 6.16. The Au/Li₂O/CeO_x/Al₂O₃ catalyst shows an activity similar to the Au/Al₂O₃ catalyst when the ethanol and oxygen conversion are considered. The selectivity to ethylene oxide is increased and similar to the Au/Li₂O/Al₂O₃ catalyst, but with a lower ethanol conversion. At temperatures above 350 °C some ethylene is formed.

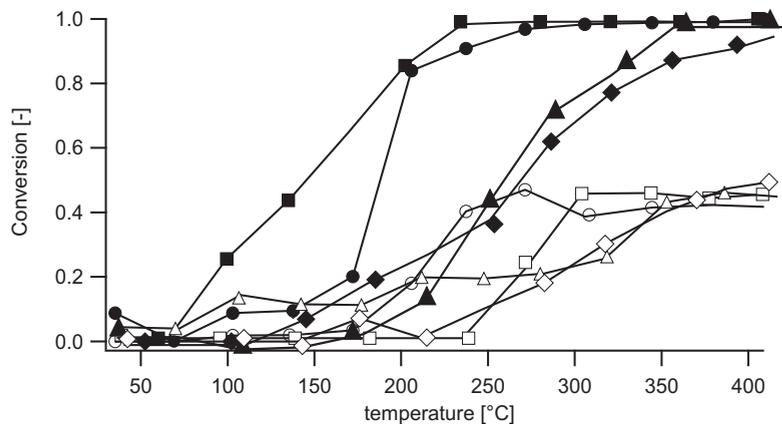


Figure 6.12: Ethanol conversion in excess oxygen. Ethanol conversion(closed symbols) and oxygen conversion (open symbols) vs temperature, First cooling stage.
 ▲ Au/Al₂O₃, ● Au/CeO_x/Al₂O₃, ■ Au/Li₂O/Al₂O₃ and
 ◆ Au/Li₂O/CeO_x/Al₂O₃

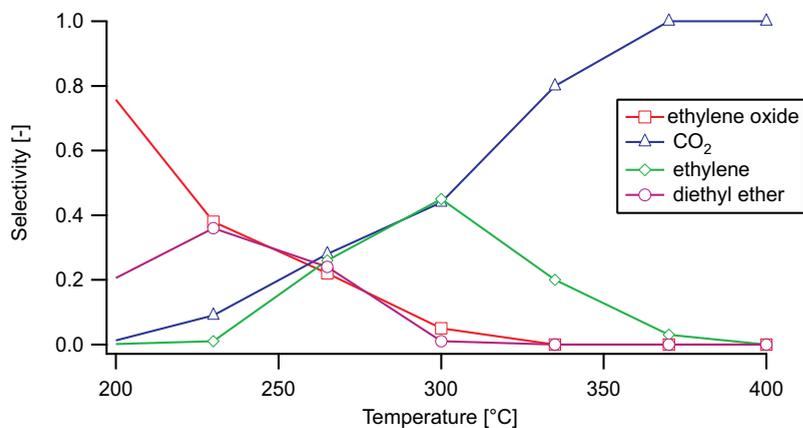


Figure 6.13: Ethanol conversion in excess oxygen. Selectivity vs temperature on Au/Al₂O₃ catalyst. First cooling stage

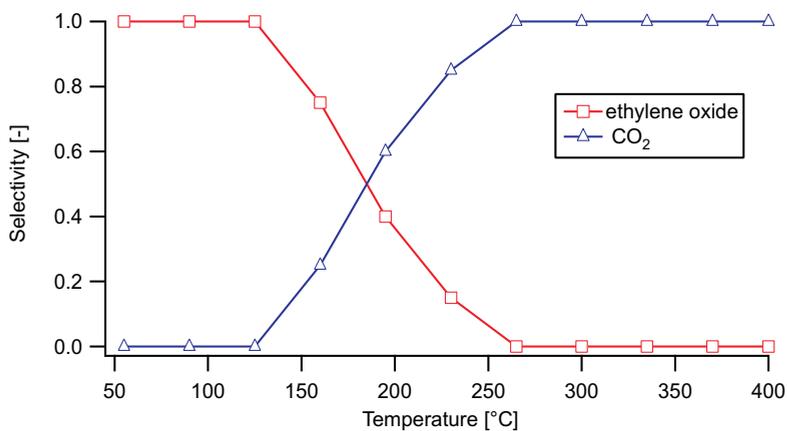


Figure 6.14: Ethanol conversion in excess oxygen. Selectivity vs temperature on Au/Li₂O/Al₂O₃ catalyst. First cooling stage

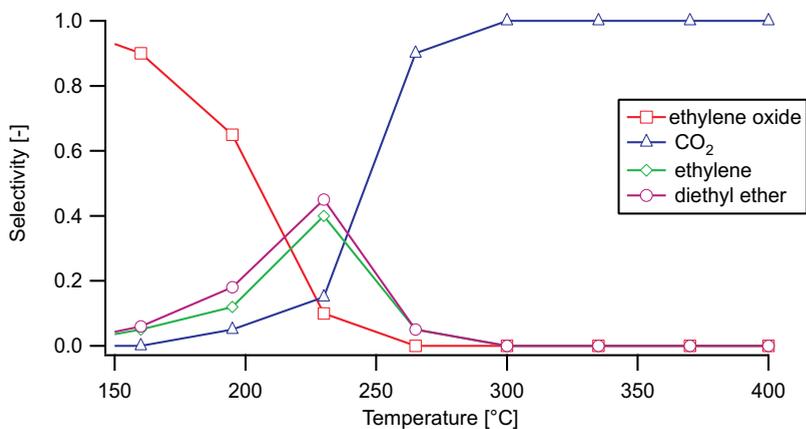


Figure 6.15: Ethanol conversion in with excess oxygen. Selectivity vs temperature on Au/CeO_x/Al₂O₃ catalyst. First cooling stage

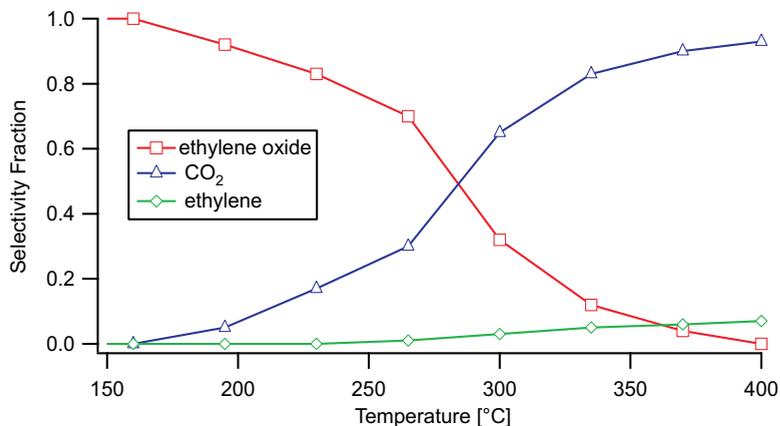


Figure 6.16: Ethanol conversion in excess oxygen. Selectivity vs temperature on Au/Li₂O/CeO_x/Al₂O₃ catalyst. First cooling stage

6.4 Discussion

6.4.1 Activity and selectivity of Au/Al₂O₃

In agreement with literature data [27, 28] the Al₂O₃ support only converts ethanol into diethyl ether and ethylene and a small amount of acetaldehyde. When gold is added to the support, the Au/Al₂O₃ catalyst also produces ethylene oxide which is not observed on the Al₂O₃ support. To our knowledge ethylene oxide production from ethanol in a single reaction has not been reported earlier in the literature. Apparently, the presence of gold nanoparticles is necessary for the formation of ethylene oxide. At temperatures above 325 °C, the addition of gold enhances the formation of acetaldehyde at the expense of ethylene but apparently, a second pathway via the gold particles contributes at temperatures above 325 °C. In the cooling stage and consecutive cycles no difference between Au/Al₂O₃ catalyst and the Al₂O₃ support is observed. This can be explained by carbon deposition during the first heating stage, which deactivates the active gold sites. Indications that carbon deposition is taking place are the color change. The catalyst turns black after the first heating stage. When this black catalyst is used in a temperature programmed oxidation experiment with O₂, CO₂ is formed and the color is restored to the original purple color and also

the activity is restored. Similar results have been found for copper based catalysts [?]. The formation of diethyl-ether and ethylene is not affected by the carbon deposition. The formation of these products is catalyzed by the acid sites of alumina [27], which apparently are not affected by the carbon deposition. Addition of a small amount of oxygen does not influence the onset temperature of the ethanol conversion, but the oxygen prevents the carbon deposition as no deactivation is noticed in the ethylene oxide formation. The decrease of ethylene oxide at temperatures above 250°C is probably due to the further oxidation to CO₂.

6.4.2 Addition of Li₂O to the Au/Al₂O₃ catalyst

Addition of Li₂O has indeed a significant effect on the selectivity in the dehydrogenation of ethanol. The selectivity to ethylene oxide is increased, whereas the selectivities to the acid-catalyzed products ethylene and diethyl ether are decreased. This can be attributed to the absence of strong acidic sites on the Li₂O/Al₂O₃. In the consecutive cooling and heating steps on the Li₂O containing catalyst there is still acetaldehyde formation, although the temperature is shifted compared to the first heating step. As the Li₂O/Al₂O₃ only catalyst does not show any acetaldehyde formation, this activity can be attributed to gold. Apparently as the formation of ethylene oxide is hindered by carbon deposition on the active gold sites, a second type of active gold sites is still active in acetaldehyde formation. This is in agreement with earlier findings that Li₂O acts as a structural promoter for the Au/Al₂O₃ catalyst [25, 29]. Addition of oxygen prevents the blocking of the active sites by carbon deposition and enhances the selectivity to ethylene oxide. Above 300°C the ethylene oxide is further oxidized to CO₂ and ethylene. The same is valid for the measurements with excess oxygen.

6.4.3 Addition of CeO_x to the Au/Al₂O₃ catalyst

The addition of ceria has not a great influence on the catalyst activity in the first heating step of the ethanol dehydrogenation. The temperature shift in diethyl ether formation suggests that this reaction no longer takes place at the acid sites of the alumina but on the ceria surface. In the consecutive cooling and heating stages the addition of ceria results in a slight improvement of the activity. The CeO_x cannot prevent coke formation on the active gold sites. The addition of ceria improves the oxygen conversion in the measurements with oxygen, whereas in the absence of oxygen, the Au/CeO_x/Al₂O₃ shows the worst acetaldehyde selectivity. Possibly, the ceria

increases the acetaldehyde formation by providing oxygen to the ethoxy-species on the gold, which is further oxidized to acetaldehyde. This also applies for the measurements with excess oxygen where the CeO_x containing catalyst shows the highest oxygen conversion and CO_2 formation from 200 °C.

6.4.4 Addition of both CeO_x and Li_2O

Addition of both CeO_x and Li_2O results in a typical behavior of a mixed catalyst. By addition of Li_2O the strong acid sites of Al_2O_3 are reduced, which explains the low selectivity to ethylene shown in figure 6.3. The effect of CeO_x is apparent in the formation of the coupling product diethyl ether. In the measurements with oxygen the $\text{Au}/\text{Li}_2\text{O}/\text{CeO}_x/\text{Al}_2\text{O}_3$ catalyst shows the lowest onset temperature, but the highest temperature of 100% conversion. This also applies for the experiments with excess oxygen where on this catalyst no maximum conversion is reached up to 400 °C.

6.4.5 Comparison of ethylene oxide formation with silver and copper based catalysts

Recently, ethanol dehydrogenation and oxidation have been studied on copper and silver based catalysts [25]. On the copper based catalysts formation of ethylene oxide was found in the first heating stage in ethanol dehydrogenation. In the following cooling stage much less ethylene oxide was formed, as also was observed for the gold based catalyst. On the silver based catalysts no ethylene oxide was detected in the ethanol dehydrogenation reaction. Measurements with an ethanol/ O_2 ratio of 1 show ethylene oxide formation on all three metal based catalysts. In table 6.3 some results of the catalysts with the best performance in ethylene oxide production are presented. In all cases the best selectivity is achieved with the Li_2O containing catalysts. The $\text{Au}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ catalysts show the highest ethanol conversion with good selectivity to ethylene oxide at 200°C. At temperatures of 300°C the selectivity to ethylene oxide is the highest on the $\text{Au}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$ catalyst. At higher temperatures the selectivity to ethylene oxide drops on all catalysts but remains the highest for $\text{Ag}/\text{Li}_2\text{O}/\text{Al}_2\text{O}_3$.

With all three metal based catalysts, the most promising results are found when Li_2O is added, suggesting that the role of Li_2O is very important in the conversion of ethanol into ethylene oxide. The copper and gold based catalysts show some similarity in reactivity and selectivity. The gold based catalyst is the most selective to ethylene oxide. Both show a maximum selectivity around 200°C. At higher temperat-

ures the selectivity decreases with increasing temperature, as ethylene, CO and CO₂ are formed. The silver based catalyst also shows high selectivity to ethylene oxide at 200°C but at lower conversion than the gold based catalyst. At temperatures of 400°C the selectivity to ethylene oxide remains at higher levels, less CO, ethylene and no CO₂ are formed. The silver based catalyst also differs from the copper and gold based catalyst as in ethanol dehydrogenation no ethylene oxide is formed.

6.4.6 Role of gold, lithium, cerium and oxygen

The results presented do not result in a complete picture of the mechanism of ethylene oxide formation from ethanol, but some annotations can be made. As ethylene oxide formation is only observed in the presence of gold-nanoparticles, it can be concluded that the gold-particles contain active sites needed for the formation of ethylene oxide. When an ethanol-only flow is used, these sites are deactivated by carbon deposition. The selectivity then shifts to formation of acetaldehyde, which is not observed on the bare support. Hence, most probably, another active site is present on the gold which is active in formation of acetaldehyde, and this site is not affected by carbon deposition.

It is unlikely that the formation of ethylene oxide is the result of a reaction of ethanol on the gold particles with oxygen from the support as the addition of ceria, which is very capable of supplying oxygen [?, 18] would then increase the formation of ethylene oxide and just the opposite is found.

We believe that the ethylene oxide is formed directly from the ethanol, by abstracting hydrogen. In experiments with varying contact time no indications were found of any intermediates. Also when an ethylene/O₂ flow was used no ethylene oxide was detected. The only carbon containing products were CO and CO₂.

Addition of Li-species results in a great increase in selectivity to ethylene oxide. This promoting effect of lithium may be twofold. First, lithium can act as a structural promoter by influencing the shape and size, and thus the active sites, of the gold particles [20]. Second, it lowers the activity of the alumina support by influencing the acidic sites of the alumina. In this way it favors the reaction pathway in which the gold-nanoparticles are involved.

For the role of oxygen we have made the following observations: Ethanol conversion and ethylene oxide formation start at lower temperature than O₂ conversion. Secondly, we found no apparent relation between O₂ conversion and ethylene oxide formation. These observations led us to believe that the main role of oxygen is to

Table 6.3: comparison of conversion of ethanol and selectivities into ethylene oxide in an ethanol/O₂ mixture of 1.

Catalyst	Temperature (°C)	Conversion	Selectivity
Au/Li ₂ O/Al ₂ O ₃	200	80	95
	300	90	71
	400	100	10
Ag/Li ₂ O/Al ₂ O ₃	200	58	96
	300	90	54
	400	100	30
Cu/Li ₂ O/Al ₂ O ₃	200	70	90
	300	92	15
	400	100	4

prevent coke formation. In the measurements with high O₂ content almost no ethylene oxide is formed, but the ethanol is further oxidized mainly to CO₂. Hence, a low concentrating of oxygen is important for a high ethylene oxide selectivity.

6.5 Conclusions

Gold based catalysts are active in ethanol dehydrogenation, oxidation and dehydration. In a gas flow with a low O₂ concentration a high selectivity to ethylene oxide can be obtained. The presence of O₂ is very important to prevent carbon deposition. With the best performing catalyst, Au/Li₂O/Al₂O₃ a selectivity to ethylene oxide up to 88% is obtained. By improving the oxygen uptake, ceria makes oxygen available to the catalytic reaction sites. No indications are found of a combinatorial effect of Li₂O and CeO_x in these reactions.

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