Catalysis Today 154 (2010) 127–132

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Direct conversion of ethanol into ethylene oxide on copper and silver nanoparticles
Effect of addition of CeO_x and Li_2O

M.J. Lippits*, B.E. Nieuwenhuys

Leids Instituut voor chemisch onderzoek, Universiteit Leiden, Einsteinweg 55, 2333 CC Leiden, The Netherlands

ARTICLE INFO

Article history:
Available online 24 April 2010

Keywords:
Ethanol oxidation
Ethylene oxide
Alumina
Copper
Silver
Lithium oxide
Ceria

ABSTRACT

The behavior of nanoparticles of copper and silver on an alumina support in the oxidation and dehydrogenation of ethanol is investigated. Pure alumina mainly acts as an acidic catalyst and produces diethyl ether and ethylene. Addition of copper and silver nanoparticles results in a direct conversion of ethanol into ethylene oxide. Addition of Li_2O influences the selectivity by suppressing the formation of diethyl ether and ethylene. Using $Ag/Li_2O/Al_2O_3$ and $Cu/Li_2O/Al_2O_3$ catalysts it is possible to obtain high selectivity towards ethylene oxide at a temperature of 200 °C. It is suggested that at low concentrations the main role of oxygen is to prevent coke formation on the catalytic surface. Addition of CeO_x results in higher selectivities towards CO.

1. Introduction

Selective oxidation of ethanol is increasingly receiving more attention as ethanol can be used for the synthesis of chemical intermediates in the manufacture of high-tonnage commodities. Ethanol can be converted to, e.g. acetaldehyde, ethane, carbon monoxide/hydrogen and ethylene. The ethylene can be further converted over a silver based catalyst to ethylene oxide, which is one of the most important chemical intermediates. It is an intermediate for the production of ethylene glycol and for the production of polyester fibers and plastics such as polyethylene terephthalate (PET). This paper will show that ethanol can be converted directly into ethylene oxide at mild temperatures and atmospheric pressure, in addition to it total oxidation products carbon dioxide and water.

Ethanol is a simple probe molecule to study reactions on metal [1–3] and oxide surfaces [4,5]. 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 [6]. In some cases, coupling and bimolecular hydrogenation reactions occur resulting in production of higher hydrocarbons such as diethyl ether [7,8].

In this study we investigated the low temperature activity of Cu/Al_2O_3 and Ag/Al_2O_3 catalysts in the dehydrogenation, dehydration and oxidation reaction of ethanol. In addition, the promoting effect of adding Li_2O and CeO_x has been investigated. CeO_x is an active oxide for the oxidation of CO to CO_2 and for making H_2 from ethanol by partial oxidation or steam reforming [9,10]. In earlier papers we reported that (earth) alkali metals stabilize gold nanoparticles and hence, act as a structural promoter for Au/Al_2O_3[11,12]. More recently, we reported that Cu and Ag nanoparticles on γ-Al_2O_3 can be stabilized in the same way [13,14]. In another study of our group it was found that highly dispersed gold on suitable metal oxides exhibits interesting behavior toward the oxidation of ethanol and is capable of converting ethanol directly into ethylene oxide. This motivated us to investigate the oxidation of ethanol over γ-Al_2O_3 supported copper and silver based catalysts. It is known for quite a long time that CuO-CeO_2 catalysts are very active and selective in CO (selective) oxidation [10,16]. Ceria has a promoting effect on the activity of the Cu/Al_2O_3 and Ag/Al_2O_3 catalysts in methanol oxidation [14]. It was argued that the active oxygen was supplied by the ceria. The size of the ceria particles has a great influence on the activity of the catalyst [17].

The oxidative dehydrogenation of ethanol to acetaldehyde is known to be catalyzed by materials possessing strong base sites such as Li_2O [18]. Earlier work of our group revealed that addition of Li_2O has great effect on the acidic sites of γ-Al_2O_3 and so influences the selectivity towards products which are not formed on these acidic sites [14,19]. In this paper we show that Li_2O promoted Ag and Cu particles supported on γ-

---

* Corresponding author. Tel.: +31 71 527 4484; fax: +31 71 527 4451.
E-mail addresses: m.lippits@chem.leidenuniv.nl (M.J. Lippits), b.nieuwe@chem.leidenuniv.nl (B.E. Nieuwenhuys).

0920-5861/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2010.03.019

Al_2O_3 can be used for the production of ethylene oxide from ethanol.

2. Experimental

2.1. Catalyst preparation

Mixed oxides of ceria (denoted as CeO_x) and/or Li_2O with alumina were prepared by pore volume impregnation of γ-Al_2O_3(BASF) with the corresponding nitrates. After calcination at 350 °C these oxides were used as supports for the Cu or Ag based catalysts. The prepared mixed oxides have an intended atomic ratio Ce/Al and Li/Al of 1/15. The copper and silver catalysts were prepared via homogeneous deposition precipitation using urea as precipitating agent. An appropriate amount of $Cu(NO_3)_2\cdot$ 3aq or $AgNO_3$ was added to a suspension of purified water containing γ-Al_2O_3 or the mixed oxide. The intended M/Al atomic ratio was 1/75 (M = Cu or Ag). This ratio of 1:75 is equal to 0.53 at% M and resulted in 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 $Ag[NH_3]_2^+$ 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 particle size was estimated from XRD line broadening after subtraction of the signal from the corresponding support by using the Scherrer equation [20].

2.3. Activity measurements

The amount of catalyst used was 200 mg for the Ag/γ-Al_2O_3 and Cu/γ-Al_2O_3 catalysts. For the catalysts containing CeO_x and/or Li_2O the amount of catalyst was adjusted in such a way that the amount of metal atoms (Ag or Cu) was similar for all the catalysts with and without additives. Prior to activity experiments the catalysts were reduced with H_2 (4 vol% in Ar) at 400 °C for 2 h. Activity tests of the catalysts were performed in a micro reactor system. An oxygen flow balanced in argon was bubbled through a vessel containing absolute ethanol. For the oxidation an ethanol oxygen ratio of 1:1 was used. For the decomposition reaction a argon flow was bubbled through the vessel. Typically, a total gas flow of 40 ml^{-1} (GHSV $\approx 2500\,h^{-1}$) was maintained. The effluent stream was analyzed on-line by a gas chromatograph (HP 8590) with a CTR1 column (Alltech) containing a porous polymer mixture and an activated molecular sieve and a Hayesep Q column (Alltech). The experiments were carried out under atmospheric pressure. Each measurement is composed of multiple temperature programmed cycles of heating and cooling, with a rate of 2 °C/min. Mass spectrometry confirmed that the analysis of the reaction products with GC was correct. Unless otherwise stated the results of the first cooling stage are depicted in the figures.

3. Results

3.1. Characterization

For the fresh Ag and Cu particles the average size 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 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 [12,21,22]. 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 γ-Al_2O_3 support was investigated 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%).

3.2. Activity of catalyst supports without metal particles

In Table 2 the results are presented concerning the dehydrogenation of ethanol in the absence of oxygen, for the supports without Cu and Ag. The most active support is the γ-Al_2O_3 without additive. The main products are the dehydration products diethyl ether and ethylene. In addition, some trace amounts of acetaldehyde are found at temperatures up to 300 °C. Addition of ceria to the γ-Al_2O_3 results in formation of CO at the expense of diethyl ether and ethylene, at temperatures above 300 °C. The formed hydrogen is converted to water. Addition of Li_2O to the alumina catalysts lowers the ethanol conversion compared to the γ-Al_2O_3-only catalyst,

Table 1
Catalyst characterization by ICP and XRD.

Catalyst	Metal loading (wt%)	Average particle size (nm)
Ag/Al_2O_3	2.3 ± 0.1	4.5 ± 0.1
$Ag/CeO_x/Al_2O_3$	1.7 ± 0.1	3.3 ± 0.1
$Ag/Li_2O/Al_2O_3$	2.2 ± 0.1	< 3.0
$Ag/CeO_x/Li_2O/Al_2O_3$	1.6 ± 0.1	< 3.0
Cu/Al_2O_3	1.5 ± 0.1	3.5 ± 0.1
$Cu/CeO_x/Al_2O_3$	1.0 ± 0.1	< 3.0
$Cu/Li_2O/Al_2O_3$	1.4 ± 0.1	< 3.0
$Cu/CeO_x/Li_2O/Al_2O_3$	1.0 ± 0.1	< 3.0

Table 2
Conversion and selectivities of ethanol dehydrogenation on the used supports. TC = total conversion, S_i = selectivity.

Catalyst	Temperature (°C)	TC	$S_{diethyl\ ether}$	$S_{ethylene}$	S_{CO}
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

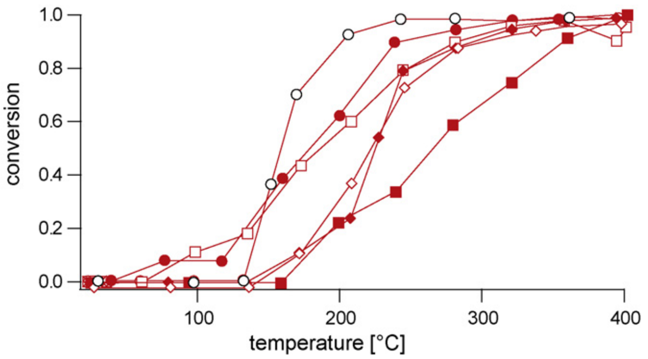

Fig. 1. Ethanol conversion vs temperature. Ethanol dehydrogenation in the absence of oxygen. First heating stage (closed symbols), cooling stage (open symbols). (◯) Cu/Al_2O_3, (◊) $Cu/Li_2O/Al_2O_3$, (□) $Cu/CeO_x/Al_2O_3$.

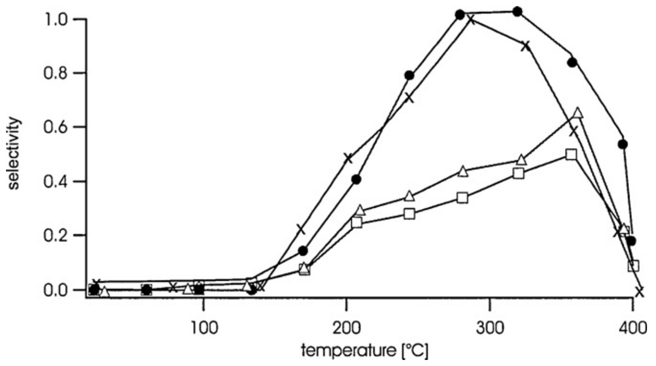

Fig. 2. Ethylene oxide selectivity vs temperature. First heating stage in ethanol-only flow. (×) Cu/Al_2O_3, (•) $Cu/Li_2O/Al_2O_3$, (□) $Cu/CeO_x/Al_2O_3$, (△) $Cu/Li_2O/CeO_x/Al_2O_3$.

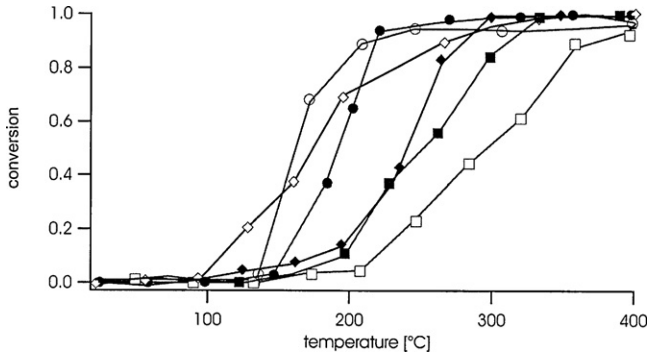

Fig. 3. Ethanol conversion vs temperature. Ethanol/O_2 mixture of 1. First heating stage(closed symbols), cooling stage (open symbols). (◯) Cu/Al_2O_3, (◊) $Cu/Li_2O/Al_2O_3$, (□) $Cu/CeO_x/Al_2O_3$.

and results in a lower selectivity towards ethylene. No acetaldehyde is found. The catalysts which contain both Li_2O and CeO_x show a behavior typical of a mixture of Li_2O/Al_2O_3 and CeO_x/Al_2O_3 catalysts.

Similar measurements have been performed for an ethanol/O_2 mixture of 1 using the supports without Cu or Ag deposited. For the Al_2O_3 and Li_2O/Al_2O_3 catalysts there were no significant differences in activity and selectivity detected, compared to the measurements without oxygen. For the CeO_x containing catalysts an increase in CO formation is recorded. For the CeO_x/Al_2O_3 catalyst a CO selectivity up to 50% was found and for the $Li_2O/CeO_x/Al_2O_3$ catalyst a selectivity to CO of 21% was found.

3.3. *Ethanol dehydrogenation on copper based catalysts*

In the dehydrogenation of ethanol there is a significant difference between the first heating cycle and the following cycles, which in the figures and tables are represented by the first cooling cycle. The results of the 2nd and further heating/cooling stages resemble that of the 1st cooling cycle. The ethanol conversion as a function of reaction temperature of the first heating step is presented in Fig. 1. The Cu/Al_2O_3 catalyst being the most active. The conversion starts at 140 °C and reaches maximum conversion around 225 °C. The $Cu/Li_2O/Al_2O_3$ is slightly less active and the conversion on both CeO_x containing catalysts starts around 170 °C and reaches 100% conversion above 300 °C. In Fig. 2 the selectivities towards ethylene oxide are presented. Clearly, the Cu/Al_2O_3 and $Cu/Li_2O/Al_2O_3$ are much more selective towards ethylene oxide. The selectivity towards ethylene oxide decreases at high temperatures and then mainly ethylene is formed. 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. Also minor quantities of acetaldehyde and diethyl ether are formed. On the $Cu/CeO_x/Al_2O_3$ catalyst mainly CO is formed next to ethylene oxide. In the following cooling cycle the conversion of ethanol is slightly improved for the $Cu/CeO_x/Al_2O_3$ and Cu/Al_2O_3 catalysts. For the $Cu/Li_2O/Al_2O_3$ catalyst the conversion is about the same. In terms of selectivity there is a big change compared to the first heating cycle. The results are summarized in Table 3. The greatest difference is the absence of ethylene oxide formation. It is only formed in trace amounts. Compared to the results of the support oxides only, the addition of copper results in more ethylene oxide formation.

3.4. *Ethanol oxidation on copper based catalysts*

For an ethanol/oxygen mixture of 1 the results are shown in Fig. 3 and the selectivities in Table 4. Contrary to the measurements without oxygen in the reaction flow, all the heating and cooling steps show the same behavior. The Cu/Al_2O_3 and $Cu/Li_2O/Al_2O_3$ catalysts show ethanol conversion from 140 °C. For the $Cu/Li_2O/Al_2O_3$ catalyst the O_2 conversion starts at higher temperature. $Cu/CeO_x/Al_2O_3$ is the least active catalyst with ethanol and oxygen conversion starting at 200 °C. The $Cu/Li_2O/Al_2O_3$ and

Table 3
Selectivities for Cu based catalysts in ethanol-only flow. First cooling cycle. S_i = selectivity.

Catalyst	Temperature (°C)	$S_{ethylene}$	$S_{acetaldehyde}$	$S_{diethyl\ ether}$	S_{CO}	$S_{ethylene\ oxide}$
Cu/Al_2O_3	200	–	–	100	–	–
	300	80	15	5	–	–
	400	100	–	–	–	–
$Cu/CeO_x/Al_2O_3$	200	–	–	–	100	–
	300	25	5	–	70	–
	400	46	10	8	36	–
$Cu/Li_2O/Al_2O_3$	200	–	–	–	–	–
	300	60	12	12	–	15
	400	70	15	10	–	5

Table 4
Selectivities for Cu based catalysts in an ethanol/O_2 mixture of 1, S_i = selectivity.

Catalyst	Temperature (°C)	$S_{ethylene}$	$S_{acetaldehyde}$	$S_{diethyl\ ether}$	S_{CO}	$S_{ethylene\ oxide}$
Cu/Al_2O_3	200	–	–	–	30	70
	300	15	15	–	20	50
	400	100	–	–	–	–
Cu/CeO_x/Al_2O_3	200	–	–	–	–	–
	300	20	5	-	55	20
	400	60	-	-	40	–
Cu/Li_2O/Al_2O_3	200	–	–	–	10	90
	300	60	12	12	–	15
	400	90	2	2	2	4

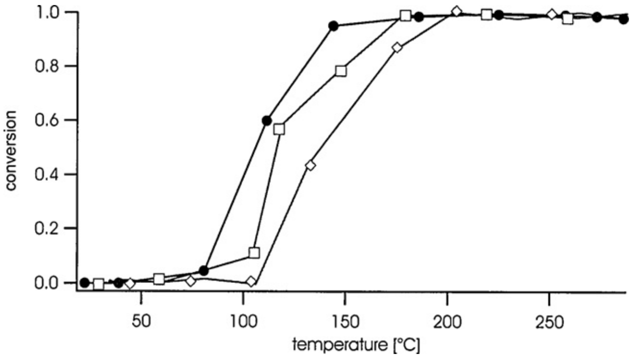

Fig. 4. Ethanol conversion vs temperature. Ethanol dehydrogenation in the absence of oxygen. First cooling stage. (●) Ag/Al_2O_3, (◊) Ag/Li_2O/Al_2O_3, (□) Ag/CeO_x/Al_2O_3.

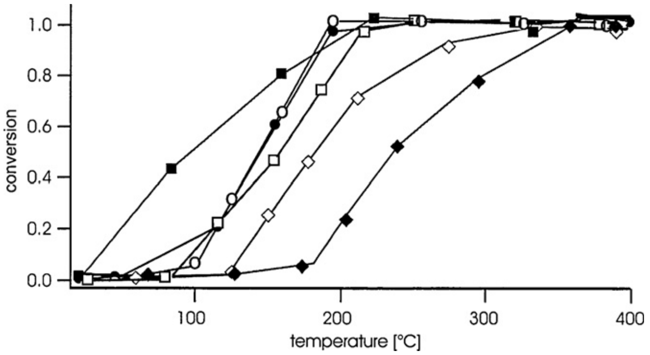

Fig. 5. Ethanol conversion (open symbols) and oxygen conversion (closed symbols) vs temperature. The ethanol/O_2 ratio = 1 (○) Ag/Al_2O_3, (◊) Ag/Li_2O/Al_2O_3, (□) Ag/CeO_x/Al_2O_3.

Cu/Al_2O_3 catalyst show a high selectivity toward ethylene oxide at temperatures up to 300 °C. The selectivity is then shifted towards ethylene and CO. On the Cu/CeO_x/Al_2O_3 catalyst the selectivity to CO is higher and the selectivity to ethylene oxide is much lower. On all catalysts some acetaldehyde and diethyl ether are formed with selectivities under 10%. No H_2 is detected but only H_2O. The Li_2O containing catalyst was also checked for stability. At temperatures of 240 °C no deactivation was found for 72 h.

3.5. Ethanol dehydrogenation on silver based catalysts

The silver based catalysts are already active at a temperature of about 100 °C as shown in Fig. 4, which is a significantly lower temperature than for the copper based catalysts. For the Ag/Li_2O/Al_2O_3 catalyst the onset of ethanol conversion is about 50 °C higher than for the Ag/Al_2O_3 and Ag/CeO_x/Al_2O_3 catalysts. The selectivities are also quite different from the copper based catalyst as can be seen in Table 5. No differences between first heating stage and the other stages are found. Very little ethylene oxide is produced. Instead only ethylene and CO are formed. When Li_2O is added to the Ag/Al_2O_3 catalyst, some improvement to the ethylene oxide selectivity is obtained but it remains under 10%. For the Ag/CeO_x/Al_2O_3 catalyst the selectivity shifts to CO as the temperature is increased. Also increasing amounts of H_2 are detected. On the Ag/Al_2O_3 some diethyl ether is formed at low temperatures and some traces of acetaldehyde are detected.

3.6. Ethanol oxidation on silver based catalysts

In Fig. 5 the results of an ethanol/O_2 mixture of 1 are presented. The Ag/Al_2O_3 and Ag/CeO_x/Al_2O_3 catalyst show ethanol conversion from 100 °C onward. The Ag/Li_2O/Al_2O_3 catalyst is less active and show an onset temperature of 150 °C for the ethanol conversion. For the Ag/Al_2O_3 catalyst the O_2 conversion is similar to the ethanol conversion. This is not the case for the Ag/Li_2O/Al_2O_3 catalyst, where the ethanol conversion starts at 120 °C and the O_2 conversion starts from 190 °C. In this temperature region mainly ethylene oxide is formed. Compared to the ethanol-only flow the activity is not greatly influenced by the oxygen, but the effect of O_2 on the selectivity is much greater; as shown in Table 6. For the Ag/Al_2O_3 catalyst the effect of adding oxygen results in an increased CO production at the expense of diethyl ether, but also a decrease in ethylene. For the Ag/CeO_x/γ-Al_2O_3 catalyst ethylene and CO remain still the two important products, but also other products

Table 5
Selectivities for Ag based catalysts in ethanol-only flow. First cooling cycle S_i = selectivity.

Catalyst	Temperature (°C)	$S_{ethylene}$	$S_{acetaldehyde}$	$S_{diethyl\ ether}$	S_{CO}	$S_{ethylene\ oxide}$
Ag/Al_2O_3	200	–	–	100	–	–
	300	40	–	40	20	–
	400	100	–	–	–	–
Ag/CeO_x/Al_2O_3	200	75	–	–	20	5
	300	64	–	–	36	–
	400	32	–	–	68	–
Ag/Li_2O/Al_2O_3	200	60	–	30	–	10
	300	90	–	–	5	5
	400	100	–	–	–	–

Table 6
Selectivities for Ag based catalysts in an ethanol/O_2 mixture of 1, S_i = selectivity.

Catalyst	Temperature (°C)	$S_{ethylene}$	$S_{acetaldehyde}$	$S_{diethyl\ ether}$	S_{CO}	$S_{ethylene\ oxide}$
Ag/Al_2O_3	200	–	10	–	85	5
	300	60	5	–	40	–
	400	16	–	–	84	–
$Ag/CeO_x/Al_2O_3$	200	12	5	33	39	10
	300	24	–	13	54	9
	400	43	–	–	57	–
$Ag/Li_2O/Al_2O_3$	200	–	4	–	–	96
	300	23	–	21	–	54
	400	28	–	38	4	30

are formed. For the $Ag/Li_2O/Al_2O_3$ catalyst there is a big shift from ethylene production towards ethylene oxide when O_2 is added, also diethyl ether is formed at high temperatures. The Li_2O containing catalyst was also checked for stability. At temperatures of 240 °C no deactivation was found for 72 h.

4. Discussion

4.1. Activity of copper based catalysts

In agreement with literature [10,23] the Al_2O_3 support only converts the ethanol into diethyl ether and ethylene and a small amount of acetaldehyde. When copper is added to the support, the Cu/Al_2O_3 catalyst also produces ethylene oxide which is not observed on the Al_2O_3 support. To our knowledge production of ethylene oxide from ethanol in an single reaction has not been reported before in literature. Apparently, the presence of copper nanoparticles is necessary for the formation of ethylene oxide. In another study of our group similar results were found for gold based catalysts. At high temperatures the selectivity resembles that of the support only. However, the addition of copper has a positive effect on the ethanol conversion. Clearly, the copper particles are capable of partly oxidizing the ethanol. Especially when CeO_x is added their is a great improvement in selectivity to carbon monoxide, while much less ethylene oxide is formed. This can be attributed to the capability of CeO_x in supplying oxygen to the copper particles. When no oxygen is added to the gas flow, the formation of ethylene oxide is only observed in the first heating cycle and not in the following cycles. This is probably caused by carbon deposition on the active copper sites. After all the stages indeed carbon deposition was found. Heating the catalyst in an O_2 flow produced CO_2. When this was followed by a pretreatment in hydrogen the catalyst was regenerated. When O_2 was added to the gas flow no deactivation or carbon deposition was found, hence O_2 prevents carbon deposition on the sites that are active in converting ethanol into ethylene oxide. The addition of Li_2O to the γ-Al_2O_3 support results in a great decrease of the conversion, possibly by affecting the strong acidic sites of the alumina [10,14,19]. The addition of lithia to the Cu/Al_2O_3 catalyst does not result in significant changes in conversion and selectivity. Apparently, in the presence of copper nanoparticles the reaction pathways are not dependent on the acidic sites of alumina.

4.2. Activity of silver based catalysts

The addition of silver to the γ-Al_2O_3 support improves the activity but does not change the selectivity to diethyl ether and ethylene much. These products diethyl ether and ethylene are mainly the result of the catalytic activity of γ-Al_2O_3. A difference between Ag/Al_2O_3 and Al_2O_3 catalyst is the formation of small quantities of CO, showing some oxidation capabilities of the silver particles, which is enhanced by the addition of CeO_x. Addition of Li_2O shifts the selectivity towards ethylene but also introduces another product: ethylene oxide. This is probably caused by the effect of Li_2O on the acidic sites of the alumina, and so increasing the relative weight of the reaction pathway to ethylene oxide. This is in particular the case with O_2 present in the gas flow, where addition of Li_2O results in a great increase in selectivity towards ethylene oxide. Apparently for the silver particles both the presence of Li_2O and O_2 are needed to obtain a good selectivity to ethylene oxide. This is in contrast to copper and gold based catalysts which can also produce ethylene oxide in the absence of oxygen, because those metals have greater oxidation capabilities.

5. Conclusions

Results show that both silver and copper nanoparticles are active in oxidation, dehydrogenation and dehydration of ethanol. They are also capable of converting ethanol directly into ethylene oxide. Indications of multiple catalytic reaction centers and multiple pathways are found. The presence of O_2 is very important to prevent carbon deposition for copper based catalysts. For the silver based catalysts O_2 is also needed to improve the selectivity towards CO. For the silver based catalysts the presence of both Li_2O and O_2 is needed to obtain a good selectivity to ethylene oxide.

Acknowledgements

The authors thank Dr. J.-P. Lange form Shell Global Solutions, Amsterdam for the discussions concerning the results presented in this paper.

References

[1] P.-Y. Sheng, G.A. Bowmaker, H. Idriss, Appl. Catal. A 261 (2004) 171.
[2] J.P. Camplin, E.M. McCash, J. Chem. Soc. Faraday Trans. 92 (1996) 4696.
[3] M.K. Rajumon, M.W. Roberts, F. Wang, P.B. Wells, J. Chem. Soc. Faraday Trans. 94 (1998) 3699.
[4] H. Idriss, E.G. Seebauer, J. Mol. Catal. A 152 (2000) 201.
[5] S.V. Chong, T.R. Griffiths, H. Idriss, Surf. Sci. 444 (2000) 187.
[6] J.L. Davis, M.A. Barteau, J. Am. Chem. Soc. 111 (1989) 1782.
[7] G. Avgouroupoulos, E. Oikonomopoulos, D. Kanistras, T. Ioannides, Appl. Catal. B 65 (2006) 62.
[8] X. Liu, B. Xu, J. Haubrich, R.J. Madix, C.M. Friend, J. Am. Chem. Soc. 131 (2006) 5757.
[9] N. Laosiripojana, S. Assabumrungrat, Appl. Catal. B 66 (2006) 29.
[10] G. Avgouropoulos, H.K. Ioannides, J. Matralis, J. Batista, S. Hocevar, Catal. Lett. 73 (2001) 33.
[11] A.C. Gluhoi, S.D. Lin, B.E. Nieuwenhuys, Catal. Today 90 (2004) 175.
[12] A.C. Gluhoi, Fundamental studies focused on understanding of gold catalysis, Ph.D. thesis, Leiden University, 2005.
[13] M.J. Lippits, A.C. Gluhoi, B.E. Nieuwenhuys, Topics Catal. 44 (2007) 159.
[14] M.J. Lippits, R.R.H. Boer Iwema, B.E. Nieuwenhuys, Catal. Today 145 (1) (2009) 27.
[16] G. Avgouropoulos, T. Ioannides, Ch. Papadopoulou, J. Batista, S. Hocevar, H.K. Matralis, Catal. Today 75 (2002) 157.

[17] S. Carrettin, P. Concepcion, A. Corma, J.M. Lopez Nieto, V.F. Puntes, Angew. Chem. Int. Ed. (2004) 2538.
[18] R.W. McCabe, P.J. Mitchell, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984) 196.
[19] S.R. de Miguel, A.C. Martinez, A.A. Castro, O.A. Scelza, J. Chem. Tech. Biotechnol. 65 (1996) 131.
[20] P. Scherrer, Nachr. K. Ges Wiss (1918) 98.
[21] A.C. Gluhoi, X. Tang, P. Margineau, B.E. Nieuwenhuys, Topics Catal. 39 (2006) 101.
[22] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 232 (2005) 96.
[23] J. Trawczynski, B. Bielak, W. Mista, Appl. Catal. B 55 (2005) 277.