

# Catalytic behavior of Cu, Ag and Au nanoparticles. A comparison

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# Dehydrogenation, dehydration and oxidation of propanol over gold based catalysts

Our recent results concerning the formation of ethylene oxide from ethanol on gold based catalysts [1] motivated us the investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide. In this exploratory study we found that gold based catalysts are capable of converting propanol to acetone and propylene. Minute traces of propylene oxide are found. It is suggested that the conversion of 1-propanol to acetone and 2-propanol is proceeding via a propylene oxide intermediate.

# 7.1 Introduction

The major industrial application of propylene oxide (about 65%) is as a monomer for the production of polyether polyols for use in making polyurethane plastics. Propylene oxide is also used in the production of propylene glycol (using about 30% of propylene oxide) and propylene glycols ethers(about 5%).

Industrial production of propylene oxide is currently performed in three different processes, which are complex and have economic and environmental disadvantages [2]. The chlorohydrin method uses chlorine and propylene. The two other methods use hydroperoxide and a second chemical (iso-butene or benzene) which results in production of the coproducts styrene or tert-butyl alcohol. Using Enichem TS-1 technology [3,4] DOW and BASF propylene is oxidized with hydrogen peroxide tot propylene oxide and water. In this process no side products other than water are formed.

As the current production methods have disadvantages, much research is devoted to the development of new catalysts and new processes to improve the propylene oxide production. One of the methods under study is the use of gold-titania catalysts, which are potentially attractive since propylene oxide is produced out of propylene, hydrogen and oxygen in a single reactor under mild conditions. Unfortunately, however, the conversion levels (2%) are too low for industrial application [5].

Our recent results concerning the oxidation of ethanol on gold based catalysts, which show a high selectivity towards production of ethylene oxide [?, 1] motivated us the investigate the possibility of converting 1-propanol and/or 2-propanol directly to propylene oxide. The catalytic decomposition of 2-propanol is also a simple probe reaction to study surface reactions on metals and investigate the acid-base properties of metal oxides. The decomposition occurs in two parallel reactions, dehydration on acidic sites to give propylene and dehydration to give acetone on basic or redox sites [6].

In this exploratory study we investigated the performance of gold based catalysts in the dehydrogenation, dehydration and oxidation reactions of 1-propanol and 2-propanol. In addition, the effects of adding  $Li_2O$  and  $CeO_x$  have been investigated in line with the large effects found with the addition of  $Li_2O$  and  $CeO_x$  on methanol [7] and ethanol [1] oxidation over  $Au/Al_2O_3$ . We did not include the  $Au/Li_2O/CeO_x/Al_2O_3$  catalyst in this study, as the addition of both  $CeO_x$  and  $Li_2O$ 

to the gold based catalyst did not show any synergistic effects in methanol and ethanol oxidation [1, 7].

Previously reported results show that ceria has a promoting effect on the activity of the  $Au/Al_2O_3$  catalyst in CO oxidation [8, 9]. It was argued that the active oxygen was supplied by the ceria, rather than from the gas phase. In addition, it was reported that the size of the ceria particles has a great influence on the activity of the catalyst [10]. A detailed study of Gluhoi et al. [11, 12] 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 particles i.e that of a structural promoter in the investigated reactions. Comparable results have been found for copper and silver based catalysts [13]. The oxidative dehydrogenation of ethanol to acetaldehyde is known to be catalyzed by materials possessing strong base sites such as  $Li_2O$  [14].

# 7.2 Experimental

#### 7.2.1 Catalyst preparation

Mixed oxides of ceria (denoted as  $\text{CeO}_x$ ) and  $\text{Li}_2\text{O}$  on alumina were prepared by pore volume impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (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 HAuCl<sub>4</sub>.3aq (99.999% Aldrich chemicals) was added to a suspension of purified water containing  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or the mixed oxide. The intended M/Al ratio was 1/75 (M= 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 $\mu$ m for all the catalysts used in this study.

#### 7.2.2 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

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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 a 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 [15].

## 7.2.3 Activity measurements

Prior to activity experiments the catalysts were reduced with H<sub>2</sub> (4 vol% in Ar) at 400 °C for 2 hours. 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 propanol. The oxygen/propanol ratio used was: 1:1, 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 online 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 at atmospheric pressure. Each measurement contains of multiple temperature programmed cycles of heating and cooling, with a rate of 2/°C min. The detected products were also confirmed with as mass spectrometer.

# 7.3 Results

# 7.3.1 Characterization

The average particle size of the fresh catalysts could not be determined by XRD because the size of the particles was below the detection limit of 3nm. The results of the characterization of the catalysts after the reaction are shown in table 7.1. The catalysts without additives contain small particles of 3-4nm. With ceria and  $\text{Li}_2\text{O}$  added the average particle size is lower than the detection limit (3nm). HRTEM data of comparable catalysts have been published in earlier papers of our group [11, 12]. 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.

Catalyst	Metal loading	Average particle size		
	(wt%)	(nm)		
$Au/Al_2O_3$	4.6±0.1	4.3±0.1		
$Au/CeO_x/Al_2O_3$	$4.1 {\pm} 0.1$	<3.0		
$Au/Li_2O/Al_2O_3$	4.5±0.3	$3.2{\pm}0.1$		

Table 7.1: Catalyst characterization by ICP and XRD

### 7.3.2 Activity of catalyst supports without gold particles

The results of the activity of the used supports are summarized in tables 7.2 and table 7.3. Addition of oxygen to the feed does not result in a significant change in the activity and selectivity. For all used supports only acetone and propylene are formed, with small differences in selectivity. At temperatures of 400°C propylene is the only product. When 2-propanol is used temperatures of 100% conversion are lower compared to the oxidation of 1-propanol.

Table 7.2: conversion and selectivities of 1-propanol oxidation on the used supports. The propanol/ $O_2$  ratio is 1. TC = total conversion,  $S_1$  = selectivity toward propylene,  $S_2$  = selectivity toward acetone

Catalyst	Temperature (°C)	TC	$S_1$	$S_2$
$Al_2O_3$	200	8	50	50
	250	80	75	25
	300	100	25	75
	400	100	0	100
$CeO_x/Al_2O_3$	200	5	80	20
	250	30	85	15
	300	100	69	28
	400	100	0	100
Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	200	0	0	0
	250	31	84	16
	300	72	69	31
	350	90	39	61
	400	100	0	100

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Catalyst	Temperature (°C)	TC	$S_1$	$S_2$
Al <sub>2</sub> O <sub>3</sub>	200	15	70	30
	250	90	64	36
	300	100	20	80
	400	100	0	100
$CeO_x/Al_2O_3$	200	5	80	20
	250	30	85	15
	300	100	0	100
	400	100	0	100
$Li_2O/Al_2O_3$	200	0	0	0
	250	0	0	0
	300	60	67	33
	350	90	33	67
	400	100	0	100

Table 7.3: conversion and selectivities of 2-propanol oxidation on the used supports. The propanol/O<sub>2</sub> ratio is 1. TC = total conversion,  $S_1$  = selectivity toward propylene,  $S_2$  = selectivity toward acetone

# 7.3.3 Propanol dehydrogenation in the absence of O<sub>2</sub> on gold based catalysts

The results of the measurements of 1-propanol or 2-propanol in the absence of  $O_2$  are presented in tables 7.4 and 7.5. On the gold based catalysts no significant differences are found compared to the bare supports. Propylene and acetone are the only formed products. Hence gold nanoparticles are not active in propanol dehydrogenation.

# 7.3.4 1-Propanol oxidation in a propanol/O<sub>2</sub> mixture of 1

In figure 7.1 the activity and selectivity of the Au/Al<sub>2</sub>O<sub>3</sub> catalysts is presented. Compared to the bare support  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> the onset temperature of the conversion is lowered by 30°C and the selectivity toward acetone is increased. No other products are formed. On the Au/CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst 1-propanol is converted to propylene, acetone and CO<sub>2</sub> as shown in figure 7.2. The addition of gold to the ceria/Al<sub>2</sub>O<sub>3</sub> supports results in formation of CO<sub>2</sub> at temperatures above 350°C. In figure 7.3 the results are depicted of the Au/Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> catalyst.

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Catalyst	Temperature (°C)	TC	$S_1$	$S_2$
$Au/Al_2O_3$	200	16	50	50
	250	85	76	24
	300	100	40	60
	400	100	5	95
$Au/CeO_x/Al_2O_3$	200	10	80	20
	250	40	88	10
	300	100	65	35
	400	100	0	100
Au/Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	200	1	100	0
	250	37	86	14
	300	73	75	25
	350	92	49	51
	400	100	2	98

Table 7.4: conversion and selectivities of 1-propanol dehydrogenation. TC = total conversion,  $S_1$  = selectivity toward propylene,  $S_2$  = selectivity toward acetone

Table 7.5: conversion and selectivities of 2-propanol dehydrogenation. TC = total conversion,  $S_1$  = selectivity toward propylene,  $S_2$  = selectivity toward acetone

Catalyst	Temperature (°C)	TC	$S_1$	$S_2$
$Au/Al_2O_3$	200	10	80	20
	250	80	82	18
	300	100	50	50
	400	100	5	95
$Au/CeO_x/Al_2O_3$	200	15	53	47
	250	47	73	27
	300	100	62	38
	400	100	0	100
$Au/Li_2O/Al_2O_3$	200	1	100	0
	250	30	87	13
	300	70	79	21
	350	88	53	47
	400	100	1	99



Figure 7.1: conversion of 1-propanol in the presence of oxygen over  $Au/Al_2O_3$  catalyst. The propanol/ $O_2$  ratio = 1.  $\circ$  propanol conversion,  $\triangle$  acetone selectivity,  $\Box$  propylene selectivity



Figure 7.2: conversion of 1-propanol in the presence of oxygen over Au/CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The propanol/O<sub>2</sub> ratio = 1.  $\Box$  propanol conversion,  $\circ$  acetone selectivity,  $\Diamond$  propylene selectivity, + CO<sub>2</sub> selectivity

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Figure 7.3: conversion of 1-propanol in the presence of oxygen over Au/Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> catalyst. The propanol/O<sub>2</sub> ratio = 1.  $\triangle$  propanol conversion,  $\Diamond$  acetone selectivity,  $\circ$  propylene selectivity, - selectivity other trace amounts

The major products are acetone and propylene, but also some other products are found in minute quantities. Among these are propylene oxide (maximum selectivity of 1%), 2-propanol and oxetane.

#### 7.3.5 2-propanol oxidation in a propanol/O<sub>2</sub> mixture of 1

The oxidation of 2-propanol on the gold based catalysts results in the products acetone, propylene and carbon dioxide. The results are summarized in table 7.6. No indications of other products are found.  $CO_2$  is only formed on the ceria containing catalyst, comparable to the results of 1-propanol.

Catalyst	Temperature (°C)	TC	$S_1$	$S_2$	$S_3$
$Au/Al_2O_3$	200	0	0	0	0
	250	40	80	20	0
	300	100	62	38	0
	400	100	0	100	0
$Au/CeO_x/Al_2O_3$	200	5	60	40	0
	250	55	64	27	9
	300	100	40	50	10
	400	100	0	70	30
Au/Li <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	200	0	0	0	0
	250	25	88	12	0
	300	66	79	21	0
	350	86	56	44	0
	400	100	0	100	0

Table 7.6: conversion and selectivities of 2-propanol oxidation on gold based catalysts. The 2-propanol/ $O_2$  ratio is 1. TC = total conversion,  $S_1$  = selectivity toward propylene,  $S_2$  = selectivity toward acetone,  $S_3$  = selectivity toward CO<sub>2</sub>

### 7.3.6 Discussion

Almost all measured catalysts show comparable activities and selectivities. The conversion of propanol starts around 200°C and two products are formed: propylene and acetone. These two products should be formed in two parallel reactions: dehydration on acidic sites to give propylene and dehydration to give acetone on basic or redox sites. Addition of lithia to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support improves the selectivity to acetone a little bit. However this effect of lithia is much smaller than observed for methanol and ethanol [1, 7]. Probably, the conversion of propanol is much less dependent of the acidic sites of the alumina than methanol and ethanol. Addition of gold nanoparticles results in a higher conversion only when oxygen is present in the gas flow. In the absence of oxygen no effect of gold addition to the supports is detected. This suggests that the gold particles play a important role in activating the oxygen which can react on the interface with propanol adsorbed at the support as C<sub>3</sub>H<sub>7</sub>O species. Addition of ceria in the presence of oxygen improves the oxidation strength of the catalyst resulting in total oxidation of propanol to CO<sub>2</sub>. As the CeO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst does not show CO<sub>2</sub> formation also the gold particles play a role in the oxidation. Ceria

is known to be capable of providing oxygen to gold nanoparticles to assist in oxidation reactions [12]. The most interesting results have been obtained for the 1-propanol oxidation in the presence of  $O_2$  over the Au/Li<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> catalyst. With this catalyst the predominant products are acetone and propylene but also some minute amounts of other products are found, including propylene oxide and 2-propanol. It shows that this catalyst is active in the isomerization of 1-propanol to 2-propanol. It is suggested that the found propylene oxide and 2-propanol products are intermediate products in the conversion of 1-propanol to acetone.

#### 7.3.7 Conclusions

In this exploratory study is found that gold based catalysts are capable of converting propanol to acetone and propylene. No other products with high selectivities are found. The addition of  $CeO_x$  and  $Li_2O$  does not result in major improvement in the investigated reaction. Indications are found that the conversion of 1-propanol to acetone is proceeding via a propylene oxide intermediate. Further investigation is necessary to be able to discriminate between primary and secondary oxidation products and gain clear insight into the mechanism of propanol oxidation to various products.

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