Catalytic Conversion of Biofuels

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Catalytic Conversion of Biofuels

Ph.D. Thesis, June 2008

Center for Sustainable and Green Chemistry

Department of Chemistry

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Preface

This thesis is submitted in candidacy for the Ph.D. degree from the Technical University of Denmark (DTU). The work presented herein has been carried out at Center for Sustainable and Green Chemistry (CSG), Department of Chemistry, DTU from June 2005 to June 2008 with Professor Claus Hviid Christensen as supervisor. This Ph.D. scholarship was funded by The Danish Council for Strategic Research (Det Strategiske Forskningsråd). The thesis is based on the work reported in the scientific papers. Additional papers that I have contributed to are listed in section 1.2. Miscellaneous publications.

I would like to thank my supervisor Claus Hviid Christensen for giving me the opportunity to work in an inspirational environment and encouraging me to think and work independently as well as for giving me the chance to participate in several international scientific conferences.

As part of the Ph.D. education, I have been on an external stay. In September 2007 I went on a three month stay at the University of Wisconsin, Madison at the department of Chemical and Biological Engineering, joining the research group of Professor J.A. Dumesic. I would like to thank the Otto Mønsted Foundation and The Danish Chemical Society (Kemisk Forenings Rejsefond) for their generous grants making theis stay possible.

I would also like to thank the hardworking students with whom I have had the pleasure of working on the gold catalysed oxidation of ethanol. I will especially like to thank the undergraduate students Sofie E. Christiansen and Marie Louise D. Thomsen.

I would also like to thank Søren K. Klitgaard and Kresten Egeblad for recording the TEM images of the gold catalysts.

Finally, I would like to thank the people at CSG for making the last three years enjoyable in both socially and work related situations; there was always one willing to lend an ear.

Betina Jørgensen

DTU, Lyngby, June 1st 2008

Abstract

This thesis describes the catalytic conversion of bioethanol into higher value chemicals. The motivation has been the unavoidable coming depletion of the fossil resources. The thesis is focused on two ways of utilising ethanol; the steam reforming of ethanol to form hydrogen and the partial oxidation of ethanol to form acetyl compounds. The steam reforming has been covered by a literature study of the research work done so far giving an introduction to the use of ethanol as a feedstock. The partial oxidation of ethanol has been studied experimentally using gold and vanadium based heterogeneous catalysts, and two different experimental methods, namely, a batch system and a continuous flow system.

In the batch reaction the process was carried out in the liquid phase using a gold catalyst and atmospheric air as the oxidant. Experiments were conducted at moderate pressures and temperatures (90-200 °C, 30-45 bar) with an aqueous solution of ethanol. It was possible to produce acetic acid in yields above 90 %. Two different support materials were investigated ($MgAl_2O_4$ and TiO_2) and there did not seem to be any significant effect in changing the support. The kinetics of the reaction was also investigated and a simple kinetic model proposed, which could be fitted nicely to the experimental data. By changing the concentration of ethanol, it was possible to shift the selectivity towards ethyl acetate instead of acetic acid. However a concentration above 60 wt% was required for the ester to become the major product.

In the continuous flow system, the oxidation reaction was carried out as a gas phase reaction using a vanadium based catalyst. For this series of experiments, a 50 wt% aqueous ethanol was oxidized with a diluted gas stream of O_2 in helium, the reaction temperature and pressure were kept at a moderate level (175-200 °C, 2-10 bar). It was found that the reaction product could be controlled by means of the temperature and the space velocity, making it possible to shift between acetaldehyde and acetic acid as the main products. It was possible to achieve both acetaldehyde and acetic acid with selectivities above 90 % at close to full conversion. It was furthermore found that the O_2/ethanol ratio was of importance for the conversion as well as the selectivity, with the conversion decreasing when the ratio was lowered.

Dansk resumé

Denne afhandling beskriver den katalytiske omdannelse af bioethanol til fremstilling af kemikalier med forøget værdi. I afhandlingen er der fokuseret på to reaktionsveje, steam reforming af ethanol til produktion af hydrogen samt fremstilling af acetylprodukter ved katalytisk partiel oxidation af ethanol. Steam reformingen bliver dækket med et litteraturstudie af forskningen, der er blevet publiceret ind til nu, hvilket giver en introduktion til brugen af ethanol som ”råmateriale”. Oxidationen af ethanol er blevet undersøgt eksperimentelt ved brug af to forskellige katalysatorsystemer samt to forskellige forsøgsmetoder, nemlig i et batchsystem og et kontinuert flow system.

I batchprocessen fandt reaktionen sted i væskefasen ved brug af en guldkatalysator og luft som oxidationsmiddel. Forsøgene blev udført under moderate tryk og temperaturer (90-200 °C, 30-45 bar) med en vandig ethanolopløsning. Det var muligt at fremstille eddikesyre med udbytte over 90 %. To bærematerialer blev undersøgt ($MgAl_2O_4$ og TiO_2), hvilket ikke viste nogen umiddelbar effekt på aktiviteten. Ydermere blev kinetikken for reaktionen undersøgt og en simpel opstillet kinetikmodel kunne tilpasses pænt med de eksperimentelle data. Ved at ændre på koncentrationen af ethanol var det endvidere muligt at ændre selektiviteten fra eddikesyre til ethylacetat; en koncentration på over 60 wt% var dog påkrævet for at esteren blev hovedproduktet.

I det kontinuerte flow system blev oxidationsreaktionen udført i gasfase over en vanadiumbaseret katalysator. Til denne serie af eksperimenter blev der brugt en 50 wt% vandig ethanol, som blev oxideret af O_2 fortyndet med helium. Reaktionstemperaturen og trykket blev holdt på et moderat niveau (175-200 °C, 2-10 bar). Selektiviteten kunne kontrolleres ved hjælp af *space velocity*, hvorved det var muligt at skifte mellem acetaldehyd og eddikesyre som hovedprodukt. Det var muligt at opnå selektiviteter for både acetaldehyd og eddikesyre, som lå over 90 % med fuld omdannelse af ethanol. Det blev endvidere fundet, at O_2/ethanol forholdet havde en væsentlig indflydelse på både omdannelse og selektivitet med en faldende omdannelse, når forholdet blev formindsket.

List of Contents

1.1. Publications included in appendix

1. Christensen, C. H., Jørgensen, B., Rass-Hansen, J., Egeblad, K., Madsen, R., Klitgaard, S. K., Hansen, S. M., Hansen, M. R., Andersen, H. C., Riisager, A., Acetic Acid by Aqueous-Phase Oxidation of Ethanol with Air Using Heterogeneous Gold Catalysts, *Angew. Chem. Int. Ed*. 45 (2006) 4648.

2. Rass-Hansen, J., Falsig, H., Jørgensen, B., Christensen, C. H., Bioethanol: Fuel or Feedstock?, *J. Chem. Technol. Biotechnol.* 82 (2007) 329.

3. Westermann, P., Jørgensen, B., Lange, L., Ahring, B. K., Christensen, C. H., Maximizing renewable hydrogen production from biomass in a bio/catalytic refinery, *Int. J. Hydrogen Energy* 32 (2007) 4135.

4. Jørgensen, B., Christiansen, S. E., Thomsen, M. L. D., Christensen, C. H., Aerobic Oxidation of Aqueous Ethanol using Heterogeneous Gold Catalysts: Efficient Routes to Acetic Acid and Ethyl Acetate, *J. Catal.* 251 (2007) 332.

5. Jørgensen, B., Fehrmann, R., Christensen, C.H., Riisager, A., Selective gas-phase oxidation of aqueous ethanol with dioxygen using nanoparticle vanadia/anatase catalyst, *Top. Catal.* (2008) accepted

1.2. Miscellaneous publications

1. Jørgensen, B., Taarning, E., Christensen, C. H., Den Fornybare Kemiske Industri, *Dansk Kemi* 88 (2007) 26.

2. Klitgaard, S. K., Egeblad, K., Falsig, H., Frey, A. M., Jørgensen, B., Hansen, D., Johansen, L., Christensen, C. H., Guld og flyvende grise – en opdagelsesrejse ind i nanokemiens verden, *LMFK-Bladet* 3, 2007.

3. Jørgensen, B., Rass-Hansen, J., Christensen, C. H., Bæredygtig kemi, i *Kemiske Horisonter,* DTU, (2006)

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2. Introduction

The focus of this thesis is, as the title suggests, the *catalytic conversion of biofuels*, more specifically the catalytic conversion of ethanol. The initial scope of the work was to investigate different routes for converting bioethanol into other more valuable products. The motivation for this is the unavoidable depletion of fossil resources, which has given ground for many new challenges within chemistry. As this thesis will hopefully clarify, there are several options for utilizing bioethanol besides the, at present, most common usage as a fuel or fuel additive in the transportation sector. Furthermore, the thesis presents two alternative routes for producing acetic acid from aqueous ethanol.

In the thesis, the first part is used for explaining the basic concepts and motivations for the reader. In the first chapter, chapter 3, the basic concepts; renewable resources, the application of bioethanol, and green chemistry are described. In chapter 4, a small yet extensive review are given on the work done within production of hydrogen from ethanol via the steam reforming reaction, a reaction which has experienced a tremendous growth of interest during the last ten years. Then, an introduction to the production and application of acetic acid is given, followed by a short summary of heterogeneously gold catalysed oxidations.

In the last part of the thesis, focus is on the experimental work performed during my Ph.D.-studies. The experimental section is divided into two, namely the liquid-phase partial oxidation of ethanol (chapter 8) and the gas-phase partial oxidation of ethanol (chapter 9). The liquid-phase reactions were carried out in a batch reactor using gold catalysts. Gold catalysis is among the currently fastest growing fields within catalysis, making the work contemporary and relevant. The use of a renewable feedstock as well as the abundant and inexpensive oxidant (air) further increased the relevance of this work in a green chemisty context. The focus was on the partial oxidation of ethanol to form acetic acid, which was investigated thoroughly. Based on the results, a simple kinetic model was proposed. The possibility to tune the selectivity by minor alterations of the reaction conditions were also investigated, this showed the possibility to switch the product from acetic acid to ethyl acetate.

For the gas-phase oxidation of ethanol, a continuous flow fixed bed system was used. For this series of experiments, a vanadium based catalyst was used. Although not as highly profiled as gold catalysts, the use of vanadium for selective oxidation is not an inconsiderable field of research. For partial oxidation of ethanol with oxygen, several parameters were investigated and again it was found possible to switch the selectivity dramatically with only minor moderations of the reaction conditions, in this case between acetaldehyde and acetic acid.

Finally, the thesis is ended with concluding remarks.

3. Basic concepts

3.1. Renewable resources

Within the last decades, there has been a continuously growing interest in finding alternatives to the fossil resources. This interest has been fuelled by the facts that it has become clear that the fossil resources are not inexhaustible and that the environmental effect of their usage has become a major political topic.

Presently, the modern society is highly dependent on fossil resources, they are used for producing heat, electricity and transportation fuels etc. For the heat and electricity production, some alternatives have been implemented to some extent in some countries. Among these alternatives is wind power, which has been very popular in Denmark, where ca. 18 percent of the electricity is produced by wind mills [1]. A down side to the wind power is that the energy production is dependent on the weather conditions, since it, so far, has not been possible to effectively store the excess electricity produced during windy periods. Some geographical locations have the advantage of alternative sources of energy; this can be geothermal heat as in e.g. Iceland or hydropower, which is used extensively in e.g. Norway. These energy sources can be considered sustainable since they only utilise a renewable resource and they do not produce any carbon dioxide. With the Kyoto protocol, the focus on CO_2 emissions has become more substantial in all the participating countries, and especially heat and power generation have been the centre of attention. The Kyoto protocol is a protocol developed to reduce the emission of greenhouse gasses internationally and hereby reduce the impact they have on the climate. The protocol has been developed by the United Nations Framework Convention on Climate Change [2]. Members that have ratified the protocol have agreed to lower their CO_2 emissions; in Denmark a cut of 21 % of what the emissions were in 1990 before the end of 2012 is required [2].

Nuclear power is another alternative to the fossil fuelled power plant, there is, however, in many places a large resistance against it due to the radioactive waste that can lead to severe problems.

Another renewable resource is biomass; this can either be in the form of agricultural waste or other biomass based compounds such as corn. The co-feeding of straw with coal has been implemented at several power plants in Denmark; this requires some modification of the plant. In 2006, 1.4 mill tons of straw were used for power generation in Denmark [1]. With the burning of straw and other biomass, large amounts of CO_2 are released. This CO_2 have, of course, been consumed during the growth of the plants so in fact the process is CO_2-neutral. One might argue that the same is the case for oil; however, the production of oil has taken thousands of years whereby the consumption of CO_2 cannot be included in the carbon cycle. For biomass, the lifespan is much shorter which is why the carbon cycle is considered closed.

3.1.1. Biomass

The typical components of biomass are cellulose, hemicellulose and lignin, which go under the collective name lignocellulose. In some types of biomass, such as corn and sugarcane, also significant amounts of starch are present. The average composition of the three components in lignocellulose is 40-50 % cellulose, 20-30 % hemicellulose and 15-25 % lignin [3]. Starch and cellulose consist of glucose units, which for cellulose are connected via β-1, 4 glycoside bonds giving long linear chains resulting in a very rigid structure. Starch consists of two different glucose polymers amylose and amylopectin; the latter consists of branched chains and the former of straight chains, for both the glucose units are connected by α-1, 4 glycoside bonds. The differences in bonding give very different compounds, with starch being water soluble to some degree, whereas cellulose is completely insoluble in water and most other solvents.

Hemicellulose is a bit more complex than the cellulose since it consists of both pentoses and hexoses (e.g. xylose and glucose). The chemical composition is heterogeneous polysaccharides, which are branched and have no overall repeated structure. The last compound is lignin. It is even more complex and consists of many different monomers among those also aromatic building blocks. As for the hemicellulose, there is no overall structure of the compound. Just like hemicellulose and cellulose, lignin is insoluble in most solvents. At fairly moderate temperatures, it is though possible to decompose lignin [4]. Cellulose and hemicellulose can be depolymerised by specialised microorganisms or by chemical decomposition methods, which are most frequently used to break the polymers down into sugars. Among the chemical decomposition methods are acid hydrolysis, which is the most common method to depolymerise cellulosic feedstocks. Once the cellulose and hemicellulose is broken down to the sugars, further conversion can be pursued either chemically or biologically. Especially fermentation processes have been a focus point for producing higher value products [5].

3.1.2. Production of renewable hydrogen

In the transportation sector, there are several demands for a suitable energy carrier. Among these requirements storage is often one of the main issues. Hydrogen has by some been named the future fuel for the transportation sector, in order to implement a so-called hydrogen society large alterations of the current infrastructure are, however, necessary [6]. Furthermore, the production of hydrogen has not yet been made sustainable using renewable resources. The main part of all hydrogen produced today is obtained via steam reforming of methane, a fossil resource. The process is very energy demanding and produces large amounts of carbon dioxide [7].

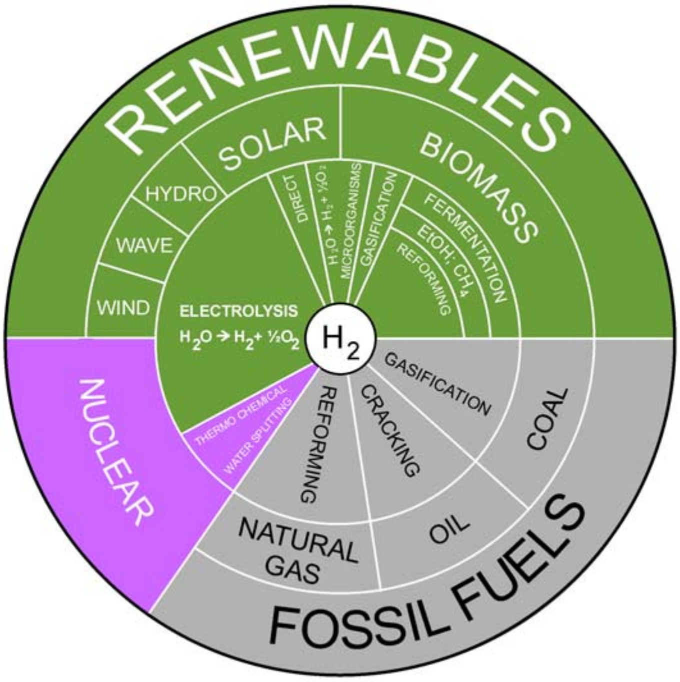

Figure 3.1.: Schematic illustration of different routes for the production of hydrogen.

Other routes to hydrogen could involve splitting of water. At present this method is, however, only economically feasible in areas where energy is in excess. Figure 3.1 shows an illustration of the different routes to hydrogen both renewable and current conventional processes. As it can be seen in Figure 3.1, there are several ways to produce hydrogen from renewable resources (the green area) either by utilising biomass or by electrolysis of water. The route from ethanol to hydrogen will be covered thoroughly in chapter 4.

It is not only the production of hydrogen that stalls the implementation of the hydrogen society; also the safe storage of hydrogen has not been satisfactory developed yet. Since hydrogen is a gas at ambient pressure and temperature it needs to be treated very differently from the current liquid fuels, gasoline and diesel. Many different solutions have been proposed either to store the hydrogen in gas cylinders or to chemically or physically bind the hydrogen in a solid material.

Hydrogen is to be used in a fuel cell, this has several advantages. Firstly, the only product formed is water and furthermore the efficiency of a hydrogen fuel is much higher than a combustion engine. Energy efficiencies above 50 % have been reached and for a standard combustion engine the efficiency only reaches 25 %. In order to use the hydrogen in a fuel cell it needs to be very pure, which subsequently leads to challenges within the purification, since even traces of CO can poison the catalyst in the fuel cell. The research within fuel cells is under constant development, and there are several types of fuel cells using different feedstocks e.g. hydrogen or methanol, but also the operational conditions vary a great deal [8].

3.1.3 The chemical industry

It is, however, not only the energy sector that is dependent on the fossil resources; also the chemical industry is highly reliant on them. In fact, more than 90 % of all carbonaceous chemicals are produced from fossil resources. Actually, our whole society can be said to be built on petrochemical products, such as plastic containers, computers, and insulation for electrical wiring and many more.

Some of the petrochemical processes are not too environmentally friendly but they have been optimized for several years to give high yields, which makes it hard to compete with them as long as the cost of fossil resources is low.

The requirements for new processes are high; they should be environmentally friendly, use renewable feedstocks and be economically feasible all at the same time. On the other hand before the fossil fuels made their entrance, the chemical industry was actually mainly based on biomass feedstocks, and some of these experiences could still be useful for the scientists of today [9]. It is also important to keep in mind that major developments and discoveries have been done within chemistry and chemical engineering over the past 60 years, giving an advantageous starting point for the utilisation of renewable feedstocks, although a lot of research is still needed.

3.2. Bioethanol

Bioethanol is one of the best known chemicals currently produced from renewable resources. The main application of bioethanol is at present as a fuel or fuel additive for combustion engine driven vehicles.

Bioethanol is produced by fermentation of biomass, and is typically divided into two categories, first generation and second generation bioethanol. First generation bioethanol is produced from sugar/starch rich feedstock such as sugar cane and corn, which is somewhat simple to convert into ethanol. Since the feedstock only consists of glucose, the microorganism is simpler to optimise to give high yields of ethanol [3]. The exact choice of feedstock varies with the location and hereby the availability. In Brazil, one of the leading producers of bioethanol, the preferred feedstock is sugarcane, whereas in USA, the preferred feedstock is corn. Brazil, in fact, produces so much bioethanol that it is mandatory to use a gasoline ethanol mixture for fuel; bioethanol is furthermore an important export commodity in Brazil [10]. One possible disadvantage with first generation ethanol is that the feedstock can also be used for food production, which gives ground for ethical considerations. There are therefore mixed opinions regarding first generation bioethanol, nevertheless numerous first generation plant have been constructed and still more are currently being built.

As an alternative to using a feedstock that could be used for production of food is the second generation bioethanol concept. Here the feedstock is e.g. agricultural waste such as straw. Straw and the other possible feedstocks typically consist of lignocellulose and are harder to depolymerise to the sugar monomers. Furthermore it is not only glucose that is produced in the hydrolysis but also pentoses e.g. xylose, which requires more, or more complex, microorganisms that selectively ferment more than one particular sugar [3]. Second generation bioethanol production is not yet commercially but several pilot plant have been constructed. For instance, the Danish company Biogasol has a viable operational pilot plant, which has optimised the fermentation to utilise as much of the feedstock as possible with an as low as possible energy consumption [11].

In general, the production of bioethanol is a thoroughly investigated process that is continuously being optimised.

3.2.1. Bioethanol fuel or feedstock?

As mentioned above bioethanol is currently mainly used as a fuel or fuel additive, the energy content of bioethanol is, however, lower than that of gasoline, one litre of ethanol correspond to 2/3 litre of gasoline in terms of heating value. Furthermore the combustion of ethanol in an engine may require alterations of the engine, if the ethanol content is higher than 85 % due to a higher octane number [12]. On the plus side ethanol is much less toxic than the regular fuel additives such as MTBE. There is a growing interest in using bioethanol in other application areas. This is probably induced by the fact that the annual consumption of gasoline and other liquid fuels exceed the production of bioethanol by an order of magnitude, and even with a continuous growth in the production of bioethanol it is not likely that bioethanol can “fill the shoes” of gasoline. Furthermore in order to use bioethanol as a fuel it has to be pure without any water. Since ethanol and water form an azeotrope this last purification is quite costly, and it would be desirable to find a usage for bioethanol that circumvent this step.

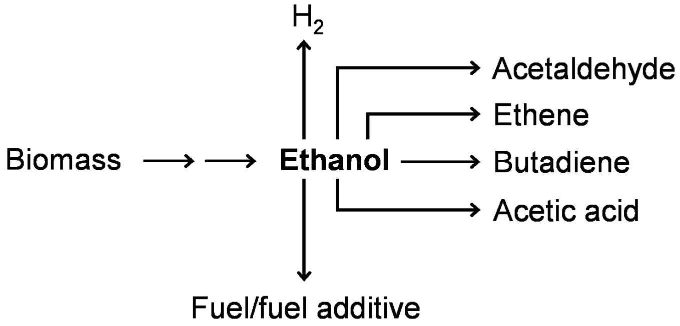

Figure 3.2.: Schematic of some of the applications of bioethanol

Rather than using bioethanol as fuel it could be used as a feedstock in the chemical industry instead; several compounds can be produced from ethanol rather easily. Among those are acetyl compounds (e.g. acetaldehyde and acetic acid), ethene, butadiene and also hydrogen.

The acetyl compounds are considered commodity chemicals and are presently produced in petrochemical processes. These compounds will be covered more thoroughly in chapter 5, and in chapters 8 and 9, alternative reaction routes are proposed and demonstrated in practice.

As for the hydrogen, one method to produce it from renewables is the steam reforming of ethanol. In chapter 4, a short review of this research subject will be given. The incentive to convert bioethanol into hydrogen is the fact that the expensive purification can be omitted, furthermore when using hydrogen in a fuel cell the overall energy utilisation is better than if the ethanol were used in a combustion engine [13].

3.3. Green chemistry

With the increasing focus on the environmental impact of the chemical industry, several incentives have been made; two of the most important are the E factor and the 12 principles of green chemistry.

The E factor was proposed by R.A. Sheldon in 1992 and it is a way of describing the atom efficiency of a given industrial process [14]. The E factor is defined as the mass ratio of waste to desired product; the waste is everything but the desired product and might be a harsh way of determining the environmental effect of a process since valuable and environmentally benign compounds are all considered waste. In order to make the E factor depict a more balanced picture, water is not considered waste and should in general be omitted from the calculations. The E factors for some segments of the chemical industry have been calculated, but even if the segment has a low E factor it does not mean that is produces less waste than a segment with a much higher E factor. When comparing oil refining and the production of pharmaceuticals the latter has a much higher E factor, nevertheless the production scale is a great deal smaller yielding a significantly smaller overall amount of waste [15].

Table 3.1.: Industrial values for E factor.

Industry segment	Product tonnage	E Factor (kg waste/kg product)
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5–50
Pharmaceuticals	10–10^3	25–100

With regards to the classification of the waste, the E factor has been further developed to take into account the nature of the waste; this has led to the environmental quotient (EQ). EQ is the E factor multiplied with an unfriendliness quotient (Q) which is an arbitrarily assigned value chosen for the given waste; this gives a more reasonable expression of the environmental impact of the process [15].

The 12 principles of green chemistry were introduced in 1998 by P. Anastas and J. Warner; the principles provides a guideline on how to implement green chemistry [16]. The 12 principles are:

1. Prevent waste: Design chemical synthesis to prevent waste, leaving no waste to treat or clean up.
2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.
3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. Use renewable feedstock: Use raw materials and feedstocks that are renewable rather than depleting.
5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions.
6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible.
7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials.

8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these are necessary, use innocuous chemicals.
9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.
10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of by-products.
12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

3.3.1. Application of the principles of green chemistry

In order to illustrate how the principles have been embraced in the work described in this thesis, the steam reforming of ethanol and/or the oxidation of ethanol to form acetyl compounds processes are in the following viewed with the principles in mind.

As the following chapters will describe, the amount of waste has been sought to be kept at a minimum. This is e.g. the case when air or oxygen is used as oxidant instead of inorganic oxidants, which can produce vast amounts of salts (principle 1). For the production of acetic acid the feedstock has been changed from the conventional methanol to ethanol which is less toxic and the use of additives has also been eliminated. Air must also be categorised as a more innocuous reactant than CO. Furthermore the processes in question do not produce any significant amount of side-products. The CO_2 formed in the steam reforming can be re-entered in the carbon cycle and help supply new biomass (principles 2-3). As the previous sections should have made clear the use of renewable feedstocks has been one of the main focuses in his thesis, in particular it has been achieved by using bioethanol as the feedstock (principle 4). Another main focus is the use of catalysts, which is the centre of attention for all the reactions described in this thesis. With all of the catalysts being heterogeneous, the separation and reuse is simplified (principle 5). The sixth principle is not of relevance for the production of acetic acid and hydrogen, since chemical derivatives do not play a part in the reactions. The atom efficiency of the reactions is kept high by using air/oxygen as the oxidant, this way all oxygen is incorporated in the products (principle 7). In order to make the reactions less hazardous water has been used as the solvent or in some cases no solvent has been used (principle 8). The reaction conditions were chosen with the ninth principle in mind keeping the reaction temperature and pressures at moderate levels. The conditions were of course chosen so that the reaction still proceeded willingly.

Having worked with acetic acid and hydrogen the tenth principle is not as significant as it would have been in the production of pharmaceuticals. Since the two reactions do not produce any significant amount of by-products other than carbon dioxide, pollution is minimal, when the CO_2 is disregarded as a pollutant (principle 11). The addition of oxygen to organic compound might seem hazardous, but the reaction conditions seem more harmless than e.g. the use of 35 bars of pure CO used in the leading process for production of acetic acid (principle 12).

It is clear that there are several ways of "greening" a chemical process, it is though rarely that a process can/does accommodate all of the twelve principles. This does however not eliminate the process for being considered green, several considerations has to be taken into account in order to classify a process as green. Fulfilling a certain amount of the principles is a way to achieve the status as green. The principles do however not consider everything; one thing the principles do not consider is remediation. Remediation is, however, as long as new atom efficient processes have not prevailed, an important aspect in minimizing the environmental effect of the chemical industry.

4. Steam reforming of ethanol

Steam reforming of methane is the main route for production of hydrogen today and it can be considered very well investigated. Similarly the steam reforming of ethanol has also been investigated thoroughly [17-19]. Steam reforming of ethanol could be a more sustainable way to produce hydrogen, since the feedstock can be produced from biomass and not fossil resources. In this chapter a summary of the research work so far is given with the main emphasis on the catalyst used. This literature study is intended to form basis for a scientific literature review.

4.1. Introduction

Steam reforming (SR) of ethanol is the reaction between ethanol and water to form hydrogen and carbon dioxide, eq. 4.1. It is, however, not possible to get H_2 and CO_2 as the only products, CO is almost always present in the product gas. With the right choice of catalyst, the product selectivity can be very close to the theoretically obtainable.

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \tag{4.1}$$

In general terms steam reforming of ethanol can be divided into two (or three) classes, namely conventional steam reforming and oxidative steam reforming, which to some extent also includes autothermal reforming.

The conventional steam reforming of ethanol is similar to the primary production of hydrogen, steam reforming of natural gas/methane. The reaction temperature is, however, typically somewhat lower in ethanol steam reforming, since ethanol reacts more willingly than methane whereby some energy is saved. Still, the steam reforming reaction takes place at elevated temperatures.

The oxidative steam reforming (OSR) differs from the conventional SR in the way that a small amount of oxygen is added to the feed stream (O_2/EtOH molar ratio 0.1 - 1.0) [20-25]. The addition of oxygen reportedly decreases the coke formation, and thereby prolongs the lifetime of the catalyst [20; 22]. Moreover, the addition of oxygen also favours oxidation of CO and diminishes formation of methane [21].

For auto-thermal SR, some of the added oxygen is used to oxidise some of the ethanol, H_2 or CO, which then provides all the heat required for the SR. The ethanol is very likely to combust in the oxygen rich mixture and the combustion produces some soot and coke which can deactivate the catalyst. Furthermore formation of hot spots may occur and cause sintering of the catalyst [26].

4.2. Thermodynamics

The thermodynamics of ethanol steam reforming have been investigated by several different methods e.g. by using response reactions and by stoichiometric and non-stoichiometric considerations given different approaches to the calculations [27-30]. When the thermodynamic calculations are made many parameters must be taken into account e.g. the ethanol water ratio, temperature, pressure and all the conceivable products. The thermodynamic calculations are to calculate the equilibrium composition of the product gas. The overall reaction considered for the thermodynamics for steam reforming of ethanol is shown in equation 4.2.

$$C_2H_5OH + 3H_2O = 2CO_2 + 6H_2,\ \ \Delta H^\circ_{298} = 174\ \text{kJ/mol} \tag{4.2}$$

This, of course, is the optimal overall stoichiometry for production of hydrogen [31]. However, many other reactions influence the reaction equilibrium at given conditions, and at equilibrium a mixture of CO, CH_4, CO_2, H_2 and water is found.

$$C_2H_5OH + H_2O \rightarrow 2CO + 4H_2,\ \ \Delta H^\circ_{298} = 256\ \text{kJ/mol} \tag{4.3}$$

$$C_2H_5OH + 2H_2 \rightarrow 2CH_4 + H_2O,\ \ \Delta H^\circ_{298} = \text{-}157\ \text{kJ/mol} \tag{4.4}$$

$$C_2H_5OH \rightarrow CO + CH_4 + H_2,\ \ \Delta H^\circ_{298} = 49\ \text{kJ/mol} \tag{4.5}$$

$$C_2H_5OH \rightarrow \tfrac{1}{2}CO_2 + \tfrac{3}{2}CH_4,\ \ \Delta H^\circ_{298} = \text{-}74\ \text{kJ/mol} \tag{4.6}$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2,\ \ \Delta H^\circ_{298} = 68\ \text{kJ/mol} \tag{4.7}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O,\ \ \Delta H^\circ_{298} = 45\ \text{kJ/mol} \tag{4.8}$$

Reaction 4.3 is the incomplete steam reforming of ethanol forming CO instead of CO_2, reaction 4.4 is the hydrogenation of ethanol forming water and methane. Reaction 4.5 and 4.6 involve C-C-bond breaking thereby producing methane. Reaction 4.7 is the dehydrogenation of ethanol to form acetaldehyde, and reaction 4.8 the dehydration of ethanol forming ethylene.

The addition of oxygen to the feed stream affects the thermodynamics significantly, since the reaction pathways are altered, due to the occurrence of additional reactions. The overall reaction for the oxidative/autothermal steam reforming of ethanol is given in equation 4.9 shown below [19].

$$C_2H_5OH + 2H_2O + \tfrac{1}{2}O_2 \rightarrow 2CO_2 + 5H_2,\ \ \Delta H^{\circ}_{298} = -50\ \text{kJ/mol} \tag{4.9}$$

The oxygen can furthermore react according to the following reactions.

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \tag{4.10}$$

$$C_2H_5OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O,\ \ \Delta H^{\circ}_{298} = \text{kJ/mol} \tag{4.11}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{4.12}$$

$$C + O_2 \rightarrow CO_2 \tag{4.13}$$

For both SR and OSR the water gas shift reaction (WGS) is of great importance, since it can improve the yield of hydrogen significantly.

$$CO + H_2O = CO_2 + H_2,\ \ \Delta H^{\circ}_{298} = -41.2\ \text{kJ/mol} \tag{4.14}$$

Carbon formation can take place by several routes with the most conceivable being the Boudouard reaction and the polymerisation of ethene, both illustrated below [18].

Boudouard reaction

$$2CO \rightarrow CO_2 + C, \quad \Delta H^{\circ}_{298} = -171.5\,kJ/mol \tag{4.15}$$

$$C_2H_4 \rightarrow 2C + 2\,H_2 \tag{4.16}$$

4.3. Reaction pathways and kinetics

The reactions listed above do not give an insight to the reaction pathway, which is imperial for understanding the kinetics of the overall reaction. The steam reforming can take place via several pathways, some are more favourable than others but nevertheless almost impossible to avoid. In the review by Ni *et al.*, the reaction pathways for ethanol steam reforming are summarised [19]. However, in the case of oxidative and autothermal reforming more reactions need to be analysed in order to describe the system correctly. Some of the possible reactions have already been introduced in the previous section, but here the typical sequence of the reactions, the reaction pathway, is discussed.

There is a general agreement in literature that the first step is either the dehydration of ethanol to produce ethene or the dehydrogenation of ethanol to acetaldehyde, which means that the reaction pathway splits up into two main pathways [18]. Ethene is known to polymerise on some catalytic surfaces, where it decomposes and forms carbon known as coke (eq. 4.16) [18]. Another possibility is that the ethene is reformed to produce CO_2, hydrogen and CO [32]. The acetaldehyde can either go through decarbonylation to form methane, which can then be reformed or it can be reformed directly [17].

The formed carbon monoxide can take part in the desired water gas shift reaction (4.14) where it reacts with water to form hydrogen and CO_2. CO can also react according to the Boudouard reaction where two molecules of CO react to form CO_2 and carbon. It does at present not seem possible to elucidate the exact reaction pathway in more detail than this.

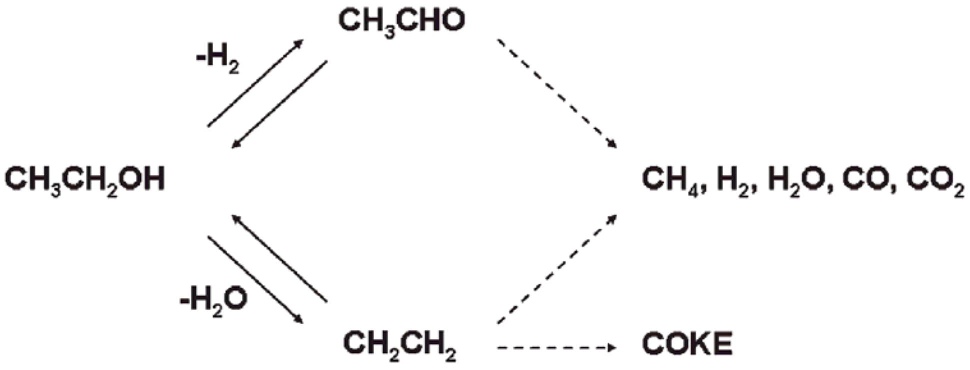

Figure 4.1.: Schematic illustration of the two main reaction pathways [13].

The kinetics of the ethanol steam reforming reaction has mainly been investigated for nickel catalysts, but it should be noted that the kinetics can vary a significantly with the active specie of the catalyst. Most of the kinetic studies seem to suggest that the reaction takes place via an Eley-Rideal mechanism [33; 34] but also Langmuir-Hinshelwood kinetics has been proposed [35]. There is a general agreement that steam reforming of ethanol is a first order reaction in ethanol [36; 37]. However, the kinetics has not been the main focus of the studies investigating ethanol SR, and there is still much more work to be done in order to completely elucidate the kinetics of the reaction, which also depends on the reaction conditions.

4.4. Experimental conditions

There are several parameters to vary during steam reforming of ethanol. In the standard steam reforming experiments the major parameters are; temperature, space velocity, steam to ethanol ratio, and pressure. For the oxidative reforming also the oxygen to ethanol ratio is of importance. The reaction temperature has been varied from as low as 523 K to 1273 K the most common temperature region is though from 673 to 973 K. The reaction temperature is often determined by which catalyst material is used, but also other parameters can influence it. The effect of gas hourly space velocity (GHSV) has been investigated and it was found that the best results were achieved at low values corresponding to a long residence time [38]. The steam to ethanol ratio seems to have an effect on the formation of carbon with excess water minimizing the carbon formation [32].

Many different ratios of water to ethanol have been investigated but the majority is in the range 3 – 13 mol/mol. With the addition of oxygen to the feed gas the deposition of carbon seems to be reduced most likely due to the continuous reoxidation of the carbon formed. The addition of oxygen has also been found to progress the sintering of the dispersed metal particles due to the possible formation of hot spots [38].

Figure 4.2.: Example of an experimental setup for steam reforming of ethanol, here with three parallel reactors.

4.5. Ethanol steam reforming catalysts

Many different catalysts have been investigated for use in the ethanol SR. They can be divided into two main groups; supported metal catalysts and metal oxides. In the following, a summary of the different studies within the field of reforming of ethanol will be given.

4.5.1. Supported metal catalysts

The supported metal catalyst have been categorised accordingly to which metal is considered the active component, and they are listed after how often they are used.

4.5.1.1. Nickel catalysts

Nickel has been found to be an excellent catalyst for steam reforming of ethanol; it is a fairly inexpensive metal making it economical to use compared to noble metals. However, there are also some drawbacks. Nickel is not so resistant to coke formation, which in the long term leads to significant deactivation of the catalyst. Nickel is currently the main catalyst for steam reforming of methane and it has therefore also been an obvious choice for the reforming of ethanol [39].

Several supports have been investigated and in the following an overview of the reported results is given. Due to the large variation in the reaction conditions, they are not all directly comparable but should, at least, give an indication of which are the most promising catalysts.

The mechanism for steam reforming over Ni is thought to involve C-C bond cleavage, which unfortunately also leads to coke formation [40]. However, Freni *et al.* report that Ni is very selective towards acetaldehyde suggesting that steam reforming over Ni takes place via dehydrogenation of ethanol [41], which should be the favoured route in order to avoid coke formation [13].

Alumina (Al_2O_3) is the most frequently used support material reported in literature [20; 34; 42-65], but also other metal oxides have been reported. The use of La_2O_3 as a support material seems to reduce the deactivation of the catalyst due to a reduction of the formation of coke [45; 47; 52; 58; 66]. The use of the more basic support MgO also seems to reduce the formation of coke [41; 45; 58; 67-72], both pure and promoted with alkali metals. Biswas *et al.* reported the use of a mixed metal oxide support consisting of CeO_2 and ZrO [73] this has also been investigated by others [43, 74-76]. In general, CeO_2 appears to become more and more important as a support material, for SR with Ni alone several applications have been reported [43; 44; 62; 72; 75; 77-80]. More complex oxides such as YSZ (yttrium supported zirconia) have also been investigated [44; 45; 76].

Steam reforming of ethanol over nickel catalysts has been carried out at temperatures varying from 523 K to 1273 K, and with varying steam to ethanol ratio. The concentration of the active component also varies significantly ranging from 1 to 40 wt%. Due to the various reaction conditions, the activity and the selectivity of the catalysts are difficult to compare quantitatively, however, the activities are moderate or good in all cases until deactivation occurs. The best results are 100 % conversion of ethanol with a hydrogen yield of 5.8 mol/mol compared to the theoretical of 6.0 mol/mol, a 30 wt% nickel catalyst was used and the reaction temperature at 873 K [74].

Comas *et al.* have studied the effect of the oxygen/ethanol ratio on nickel catalysts. The results showed that in the range of no oxygen to a ratio of 0.6 mol/mol, the carbon deposition is reduced, and due to this the CO and CO_2 yields increase slightly [20]. Furthermore, the CH_4 and H_2 yields remain constant. In the oxygen range of 0.6 to 1, the H_2 yield increases while the CH_4 decreases slightly (T= 773 K). The results imply that carbon deposited on the catalyst could be oxidised and hereby removed from the catalyst surface when oxygen is added. Furthermore, when the oxygen/ethanol ratio is higher than 0.6 also the methane can be oxidised [20]. Fierro *et al.* has also looked into the oxidative reforming of ethanol. They used a mixed copper and nickel catalyst and ran the reaction at lower temperatures, which lead to the formation of acetaldehyde [22].

Frusteri *et al.* have recently performed a comparative study of SR and auto-thermal SR using Ni catalysts [72]. Their study shows that under auto-thermal SR conditions the catalysts deactivates significantly slower than without adding oxygen to the reaction. Furthermore, the study shows that there is a considerable effect of the support. When CeO_2 is used as the support the stability was increased due to CeO_2 ability to store and release oxygen. In general, the MgO supported catalysts were found to be more active [72].

Alloys of nickel and copper showed a lower coke deposition than the pure nickel providing a longer lifespan for the catalysts [21]. Tests were conducted at 973 K and gave selectivity towards H_2 higher than 70 % (molar) and a conversion of ethanol close to 100 %. Furthermore, the catalyst showed good long-term stability producing a hydrogen rich mixture (33%), which can be used in fuel cells [22]. The group of Carrero, Vizcaíno and Calles has also looked into the use of a mixture of nickel and copper [65, 81]. Instead of using standard metal oxides as a support, three templated oxides were used as supports (MCM-41, SBA-15 and ZSM-5) [65, 81]. Their results were compared to similar catalysts supported on SiO_2 and Al_2O_3 and they showed that with the templated oxides there were a slight improvement in selectivity and a decrease in coke formation.

Bergamaschi *et al.* investigated a combined nickel and copper catalyst supported on ZrO_2. They found that at 823 K it was quite active and stable giving a good yield of hydrogen [40].

3.5.1.2. Cobalt catalysts

Cobalt is the second most investigated active transition metal for the steam reforming of ethanol. Cobalt has, like nickel, been chosen as catalyst due to its relatively lower cost compared to noble metals, and because it has been reported that cobalt is very active for splitting of C-C bonds at relatively low temperatures 623-673 K [82; 83]. Especially the group of Llorca *et al.* have investigated the used of Co thoroughly [82-88].

Several different metal oxide supports have been examined but as for the Ni catalysts, Al_2O_3 and MgO have been preferred [35; 44; 45; 68; 71; 82; 84; 89-95], but also ZnO and SiO_2 have been frequently used [44; 78; 82; 84-86; 88-90; 92; 93; 96-99]. In recent years, also ZrO_2 has been chosen as one of the preferred support materials [32; 40; 92; 94; 99, 100].

The effect of the support has been investigated by the group of Llorca who has also investigated more exotic support materials such as Sm_2O_3 [82; 84]. The overall findings showed that, of the chosen support materials, ZnO gives the highest conversion and selectivity towards hydrogen [82]. For the TiO_2 supported catalyst, a severe deactivation was recorded after only 8 h on stream at 723 K, whereas Sm_2O_3 and V_2O_5 showed no sign of deactivation in the same time range [84]. Haga *et al.* have also investigated the effect of the support and found that it has a pronounced effect; especially carbon seems to be a poor choice of support [92].

Urasaki *et al.* have investigated the use of Co supported on perovskite structured supports namely $LaAlO_3$, $SrTiO_3$ and $BaTiO_3$; however the conversion is only 50-60 %. On the other hand the lattice oxygen seem to have an inhibitory effect on the formation of coke [101].

A significant aspect of using a cobalt catalyst is the degree of reduction of the cobalt itself. Freni *et al.* report a loss of activity due to the oxidation of the metallic Co during reaction [68]. On the contrary, others have reported that the Co_3O_4 also is active for the reforming of ethanol [87]. Wang *et al.* have investigated the effect of the preparation procedure for cobalt support on ceria and found that the activity is highest when the cobalt is reduced. On the other hand when the cobalt is incorporated into the CeO_2 crystal lattice, it seems to have a positive effect on inhibiting the formation of carbon [102].

The metal loading has also been investigated; Sahoo *et al.* have studied this using alumina as the support and found that there is a significant increase in activity when going from a loading of 10 % to 15%. Nevertheless, when increasing the loading further to 20 % the activity decreases again [35].

Batista *et al.* have found that cobalt has an activity towards both WGS and methanation. These activities lower the CO content in the product gas which is desirable if the hydrogen is to be used in a fuel cell. Furthermore, the activity seems to be dependent on the choice of support material; in the study alumina gave the lowest CO concentration [89]. Zhang *et al.* have investigated cobalt supported on ceria at several different temperatures ranging from 523 to 823 K, the activity as well as the selectivity towards hydrogen increased significantly when increasing the temperature. Noteworthy for the cobalt catalyst was the considerable amount of acetone found in the product stream [80].

Bergamaschi *et al.* have investigated a mixed metal catalyst consisting of 5% Co and 2% Cu on zirconia microspheres. At 823 K, with a steam to ethanol ratio of three, the catalyst gave full conversion and a selectivity towards hydrogen of 52% [100].

4.5.1.3. Copper catalysts

Copper has been used as a catalyst in the steam reforming of methane and its excellent activity in the water gas shift reaction is also very well known [103]. In general copper-based catalysts have shown promising results when used in reactions involving C_1 species [103]. In methane reforming, copper is mainly used as an additive to the nickel catalyst, whereby the coke formation is decreased and the selectivity toward hydrogen increased [7]. In recent years, as the interest in steam reforming of ethanol has increased, also the use of Cu as a catalyst has been investigated for this reaction.

As for the Ni catalysts, the most frequently reported support for the Cu catalysts is alumina [43; 44; 48-50; 65; 104], but also other metal oxides have been used as support material [32; 40; 41; 43; 44; 81; 98; 99; 104; 105].

Machardo *et al.* have investigated the more uncommon support material Nb_2O_5 and found quite low conversions, below 20 %, but a high selectivity towards hydrogen was reported [104].

For the copper catalysts also templated oxides have been used as support materials. This have been reported by the group of Calles and Carrero, who investigated the templated oxides SBA-15, MCM-41 and ZSM-5 [65, 81].

Freni *et al.* investigated the use of Cu supported on SiO_2 and found that in the temperature range of 623-673 K the conversion of ethanol is complete. Nevertheless, the main product is acetaldehyde. If the temperature is increased to 773 K or higher temperatures, there is a significant increase in the selectivity of ethene and an interrelated decrease in the selectivity of acetaldehyde [41]. Freni *et al.* combined the Cu catalyst with a nickel catalyst in a two bed system where the ethanol was first converted to acetaldehyde which was then reformed over the nickel catalyst. This setup gave full conversion of ethanol and a relative high selectivity toward hydrogen, reaching the thermodynamic equilibrium [41].

The work of Duan *et al.* showed that the preferred support for copper-based catalyst is SiO_2, when compared to the other support materials chosen in the given work (Al_2O_3, CeO_2, TiO_2, and ZrO_2) [44].

A significant part of the reported work regarding SR of ethanol over copper does not use the pure copper as the active specie but a mixture of Cu and Ni. The group of Mariño and Laborde investigated the influence of the Cu/Ni ratio on the activity and the selectivity towards hydrogen at low temperature steam reforming (T= 573 K). They found that when combining the two metals, the activity as well as the hydrogen yield increase [48-50]. The works of Benito et al. show that a copper-based catalyst deactivates rapidly at 973 K unlike the analogues nickel and cobalt catalysts, most likely due to sintering of the copper particles [32; 99]. Nevertheless even at 973 K the copper, when supported on a mixture of ZrO_2 and SiO_2 becomes stable over time although not as active at the corresponding Ni and Co catalysts [99].

Since most of the works concerning copper catalyst have been done at fairly low temperatures, below 673 K, the yield of hydrogen is found to be lower, than other works concerning other metals and higher reaction temperatures [48; 49].

4.5.1.4. Rhodium catalysts

Rhodium is known as an excellent catalyst for steam reforming of ethanol. It has an extended lifetime compared to e.g. Ni catalysts, but due to the rather expensive purchasing price of Rh it is not expected to gain importance as an industrial SR catalyst. However this has not stopped the investigations of rhodiums catalytic abilities towards steam reforming. Once again, the preferred support material is alumina [38; 43-45; 55; 91; 106-112], but also ceria (CeO_2) has been used recurrently [43; 44; 77; 110; 113; 114]. Other works includes MgO and TiO_2 [31; 70; 115; 116]. The catalyst testing has been performed in the temperature range of 423- 1273 K and mainly at ambient pressure but occasionally also at elevated pressures [107]. All testing has been performed with excess water and metal concentrations between 0.2 – 20 wt%. The reported conversions and yields of hydrogen are as expected in the high end.

Roh *et al.* investigated the effect of the support material as well as the temperature and found a mixed CeZr oxide to be the most promising support material with respects to achieving high yields of hydrogen [111; 117]. Furthermore, they showed that in the temperature range of 673 to 973 K, at the given reaction conditions a 1 % Rh catalyst gives yields very close to the equilibrium values. Roh *et al.* also proposes that the C-C bond cleavages are facilitated by rhodium whereas the steam oxidation is facilitated by the support [111]. The influence of the Ce/Zr ratio has also been investigated by Diagne *et al.* who achieved the best results at 723 K with a yield of hydrogen nearly as high as stoichiometric [113; 114]. Birot *et al.* investigated a similar system and found that the catalyst promoted the methanation of CO, which led to a decrease in the hydrogen yield [118].

The influence of the rhodium precursor and calcination temperature was investigated by Palmeri *et al.*, who found that the calcination temperature had a slight effect but the precursor a significant effect, which is attributed to the change in crystal structure [116]. Aupretre *et al.* have also investigated the effect of the precursor they find, as Palmeri, $Rh(NO_3)_3$ to be a poor choice of precursor and use $RhCl_3$ instead, Palmeri compared $Rh(NO_3)_3$ to Rh(acac)$_3$ [107; 116].

Rhodium has also been used for autothermal reforming by the groups of Deluga and Wanat [119; 120]. Different kinds of reactors were used, and the catalysts contained either pure rhodium or a rhodium cerium mixture as the active component [119; 120].

Wanat *et al.* conducted tests on a regular catalytic wall reactor (CWR) and an extended CWR [120]. In both, they used a Rh or a Rh/Ce catalyst for SR of ethanol, in the extended CWR they furthermore used a water gas shift (WGS) catalyst (Pt-Ce catalyst) in the extension. By using the extended system, the selectivity towards CO decreases from 60 to ~ 25 %, giving an H_2/CO ratio of 9/1 using the Rh catalyst. The Rh/Ce catalyst additionally improved the H_2/CO ratio giving a value of 18/1 [120]. The WGS catalyst also promotes the methanation of CO, which is undesired since this reaction consumes H_2. Hence it is of great importance to choose the right catalyst for the WGS reaction.

Vesselli *et al.* studied the auto-thermal reforming of ethanol on a rhodium single crystal catalyst under UHV conditions [121]. Experiments showed that the addition of oxygen increased the conversion, tests on supported Rh-catalysts were also conducted and the results were qualitatively in agreement with the results from the UHV experiments [121].

Cavallaro *et al.* studied the auto-thermal reforming of bioethanol in a fixed bed micro reactor made in quartz [26]. A 5% Rh/Al_2O_3 catalyst was used and the S/C ratios were held between 2.1 and 6.3 and the O_2/EtOH molar ration between 0.2 and 1.1. The measurements showed that the conversion of ethanol was very dependent on the contact time, which also had an impact on the selectivity of the product mixture.

4.5.1.5. Noble metal catalysts

In this summary, the noble metals Pt, Pd, Ir, Rh and Ru are considered together. Due to the more extensive studies on rhodium, these have been covered separately. For the noble metals, alumina has once again been the preferred support material [24; 36; 43-45; 106; 110-112; 122-124] but also other metal oxides have been used [13; 21; 23; 70; 80; 125-128]. The reaction conditions are similar as for the other catalysts. In general the noble metals are more resistant towards coking compared to e.g. Ni.

Casanovas *et al.* have investigated palladium on either ZnO or SiO_2 and found that under the given reaction conditions, palladium formed an alloy with zinc, which seemed to be selective for the dehydrogenation of ethanol [125]. The promotion of the dehydrogenation of ethanol correlated with the use of palladium as a catalyst for oxidation of alcohols [129]. In the work of Frusteri *et al.* Pd on MgO was found to be a very poor choice of catalyst showing a low selectivity and high deactivation rate even at 923 K [71]. Also Liguras *et al.* reported of an inferior activity of Pd when compared to Pt, Ru and Rh, here Rh was the superior catalyst [112]. A more thorough investigating of the ruthenium catalyst was also reported describing very good long term stability [112]. In the work of Erdõhelyi *et al.* Pt, Pd, Ir, Rh and Ru on both alumina and ceria have been investigated and they found that the Ru/Al_2O_3 was superior at the given reaction conditions, though the Pt/CeO_2 also had a stable high conversion, the selectivity towards hydrogen was lower [110].

Koh *et al.* have compared cluster-derived Ru and Ru-Pt catalysts and found that this preparation method gave a more active catalyst, which was ascribed to the smaller metal particle size. The addition of Pt did not improve activity but seemed to repress the formation of coke, whereby stability was increased [123].

Noble metal catalysts have also been tested in the oxidative SR, Pd, Pt, Ru and Rh on Al_2O_3 were tested at temperatures between 923- 1073 K. The rhodium and the ruthenium catalysts showed much better performances than Pd and Pt. There were much less undesired by-products such as ethylene and methane giving a higher selectivity towards hydrogen [21].

In addition experiments have been made with platinum catalysts, where the alumina support had been modified by addition of cerium and lanthanum. The catalyst modified by La differed very little from the Pt/Al_2O_3 catalyst. The addition of Ce led to a more active catalyst, which was attributed to the strong interaction between Pt and Ce. When the alumina was modified by both La and Ce the promoter effect was diminished, due to a decrease in the Ce Pt interactions [24].

In the work of Cai *et al.* an iridium based catalyst was found to be very active and stable under oxidative reforming conditions [128], Zhang *et al.* reached the same conclusion [80].

4.5.2. Oxide catalysts

Not only pure metals have been used as the catalytic active specie also metal oxides have shown catalytic activity worth pursuing. These oxides are either used separately, in mixtures, or on a support metal oxide [26; 55; 85; 87; 130-137]. Some of the metal oxides introduce oxygen to the ethanol whereby it is partly oxidised to the aldehyde or acid [137; 138]. Oxides of elements from many different groups in the Periodic Table have been investigated, though the main part originates from the fourth period in the Periodic Table. One thing that should be noted is when using oxides more by-products are detected in particularly acetaldehyde and acetone [138].

Llorca *et al.* investigated the steam reforming of ethanol over a wide range of oxides and found that TiO_2 and Sm_2O_3 promote carbon formation [137]. The more acidic alumina yielded ethylene, and the basic MgO acetaldehyde. From the oxides tested, ZnO seemed to have the highest activity and selectivity towards hydrogen even at lower temperatures [137], in fact when compared to Co supported on ZnO, the improvement of adding a metal was not remarkable [85].

High surface area CeO_2 has been investigated at high temperatures (1073-1273 K) and found to be very active and somewhat selective towards hydrogen. When using ceria as a pre-reforming catalyst prior to a Ni/Al_2O_3 catalyst the results are further improved [55].

Also an industrial dehydrogenation catalyst has been investigated; this was a mixture of several oxides where CuO was the main specie [139]. The experiments were conducted at fairly low temperatures 323 – 573 K, whereby the WGS was prevailing due to thermodynamics. However, in addition to CO_2 and H_2, acetaldehyde, acetone and methane were also detected in the outlet.

Nishiguchi *et al.* used CuO pure and supported on alumina, silica and ceria, and found that CuO supported on CeO_2 was the most promising catalyst [138]. Cavallaro *et al.* investigated oxide mixtures consisting of CuZnAl, NiCuSi and CuZnCrAl oxides; they found that neither coke nor oxygenated side-products were generated in any significant amount [131]. Galetti *et al.* also studied quaternary metal oxides (CuCoZnAl) achieving hydrogen yields as high as 5.2 mol/mol ethanol at 873 K [136].

Velu *et al.* conducted several tests on OSR of ethanol using metal oxide mixtures as catalysts [25]. At 573 K the conversion of ethanol was reported to be complete. The composition of the outlet differed depending on whether the oxides were rich in either Cu or Ni. Ni was found to promote splitting of C-C bonds and addition of Ni to the Cu catalyst minimized the production of acetaldehyde. Also the substitution of Co for Cu has been investigated; experiments showed that the Co/Ni catalyst had an improved catalytic performance with lower selectivities toward undesired by-products [25].

Dong *et al.* reported of a mixed calcium aluminium oxide promoted with potassium, that yielded quite good hydrogen production and stability, though not as high as the reference Rh/Al_2O_3 catalyst [133]. Different spinels was investigated and the highest hydrogen yield was achieved with $ZnAl_2O_4$ followed by the nickel and copper based spinels [134].

A $NiO/ZnO/ZrO_2$ catalyst was found to be very active and stable, and at 923 K it was possible to completely repress the formation of methane [135]. Srinivas *et al.* have investigated a similar catalyst (NiO/CeO_2/ZrO_2) and found it to be stable for more than 500 hours [132].

Vargas *et al.* studied a Ce-Zr-Co fluorite-type oxide although initial results were promising the catalyst deactivates quite rapidly [130].

Goula *et al.* measured the homogeneous steam reforming of ethanol, i.e., without any catalyst present [122]. The results showed that the selectivity changed profoundly as the temperature was altered. At lower temperatures the dehydrogenation reaction was prevailing, but at temperatures above 823 K the decomposition or the reforming of ethanol took over giving higher selectivities towards hydrogen. This correlated with the thermal decomposition of ethanol described by Fishtik *et al.* [27].

4.5.3. The effect of promoters

The catalysts, although already showing good activities, have been found to be improved with addition of so-called promoters, often alkali metals. Frusteri *et al.* have investigated the effect of adding Li, Na and K to a MgO supported nickel catalyst and found that the addition of Li and Na seem to improve the reduction of NiO but lowers the dispersion [70]. The addition of Li and K seem to repress the sintering of the metal particles hereby stabilising the catalyst [69; 70]. Rass-Hansen *et al.* thoroughly investigated the effect the addition of Ag and K has on the formation of coke when using a Ni/$MgAl_2O_4$ catalyst [13]. They found that Ag promoted coke and K suppressed the coke formation. Liberatori *et al.* have also investigated the effect of silver and their findings also show an increased growth of carbon [63]. It has been postulated that the addition of potassium neutralises the acidic sites of the support, whereby the general performance of the catalyst is improved [48-50]. Roh *et al.* found that the loading of potassium was of great importance for the activity of a rhodium based catalyst. They find that a loading of 0.5 % K had a promoting effect, but a loading of 5 % K lowered the initial activity significantly [117].

Youn *et al.* investigated the effect of adding molybdenum to a nickel catalyst, and found that 3-5 % Mo improved the yield of hydrogen and the stability of the catalyst. These improvements were ascribed to the fact that the Ni –Al interaction was decreased and the molybdenum seemed to prevent incorporation of nickel into the alumina lattice, furthermore, Mo seemed to act as a barrier preventing the growth of the nickel paticles [140].

The addition of noble metals to cobalt catalysts was investigated by Profeti *et al.*, who found that the addition of the noble metals contribute to a decrease in reduction temperature, this was determined by TPR measurements [95]. Biswas and Kunzru investigated the effect of doping a nickel catalyst with copper, calcium or cobalt. The addition of Cu had the greatest effect at lower temperatures, at 673 K the conversion was more than doubled when 5 wt% Cu is added, nickel lconcentration was 30 wt%. As for the addition of Ca the activity was improved but there were also a significant change in the composition of the products, indicating that calcium enhanced WGS at temperatures below 873 K. The addition of cobalt seemed to have a negative effect on both the conversion and the selectivities, yielding measurable amounts of ethene, acetone and acetaldehyde at all temperatures; this could be caused by non-reduced Co-species [75].

A more indirect way of promoting the reaction is addition of CaO to the feed stream, hereby the equilibrium of the WGS is shifted. CaO reacts as a CO_2-adsorber whereby CO_2 is removed from the gas stream leading to a different composition, which favours the production of hydrogen [141].

4.5.4. The optimal catalyst

Based on the above mentioned reports it is not simple, if even possible, to choose the “perfect” catalyst for the steam reforming of ethanol. As it has been shown, many parameters need to be taken into account and it is not only the catalyst that determines the activity and the stability of the catalyst.

It, however, seems that in particular the steam to ethanol ratio, and the ethanol to oxygen ratio have an effect on the product distribution as well as the stability of the catalysts.

When choosing the catalyst not only the activity, selectivity, and stability need to be taken into account, in order to the make the catalyst feasible to the industry also the cost has to be considered.

Based on the above mentioned findings the best catalyst should consist of rhodium and ceria (CeO_2), due to the cost of Rh it might be more feasible to use a nickel catalyst promoted with e.g. potassium. The reaction conditions are also very important and a steam to ethanol ratio around 8 is preferred, furthermore the addition of oxygen might help on the long term stability of the catalyst due to the suppression of carbon formation. A low gas

hourly space velocity and temperature around 873 K is also preferred. When looking at the energy consumption it would however be desirable to run at lower temperature.
It has been possible to get hydrogen yields as high as 5.8 mol hydrogen/ mol ethanol with a nickel based catalyst at 873 K, with the catalyst being stable for 25 h [74].

The field of steam reforming of ethanol is rapidly growing and as the previous section has shown but there is still room for improvement. The major challenge is to find a catalyst that is active and stable at lower temperature. It does however seem clear that the process very well could be the future route for making hydrogen.

5. Industrial production of acetic acid

Acetic acid is a bulk chemical and the annual production reaches more than 9.5 mill ton. Acetic acid has a wide range of applications. One of its main applications is in the production of polymers consisting of either vinyl acetate monomers (VAM) or cellulose [142]. The corresponding polymer poly vinyl acetate (PVA) is mainly used in the paint industry, whereas cellulose acetate is used to produce acetates fibres that are used in e.g., cigarette filters. The pure acetic acid is also used as a solvent in the chemical industry, where it is used in the production of terephtalic acid [143]. The derivates of acetic acid e.g. acetic anhydride and ethyl acetate also have a wide range of applications.

In 1960 BASF commercialised the first methanol carbonylation process to produce acetic acid. The homogeneous BASF catalyst was iodide promoted cobalt and the reaction conditions were rather harsh (680 bar, 250 °C) [144]. Today, acetic acid is mainly produced by carbonylation of methanol [145]; the biggest process is the Monsanto process. The Monsanto process is a homogeneous catalysed process using a rhodium based catalyst and methyl iodide as a promoter. Compared to its predecessors the process run at moderate temperature and pressure (150-200 °C, 30-60 bar) [146; 147]. The rhodium catalyst is expensive and is deactivated quite easily since the active rhodium specie is oxidised whereby the activity is lost. Furthermore the iodide promoter is carcinogenic and the feed stock methanol and carbon monoxide are both acquired from the petrochemical industry. In 1996 BP came with an altered process, the Cativa process, which uses an iridium based catalyst but otherwise are very similar to the Monsanto process [148]. Some of the other industrial production methods include the oxidation acetaldehyde, direct oxidation of either ethane or ethene and the fermentation of carbohydrates or ethanol [145]. Figure 5.1 gives a schematic overview of the different production routes.

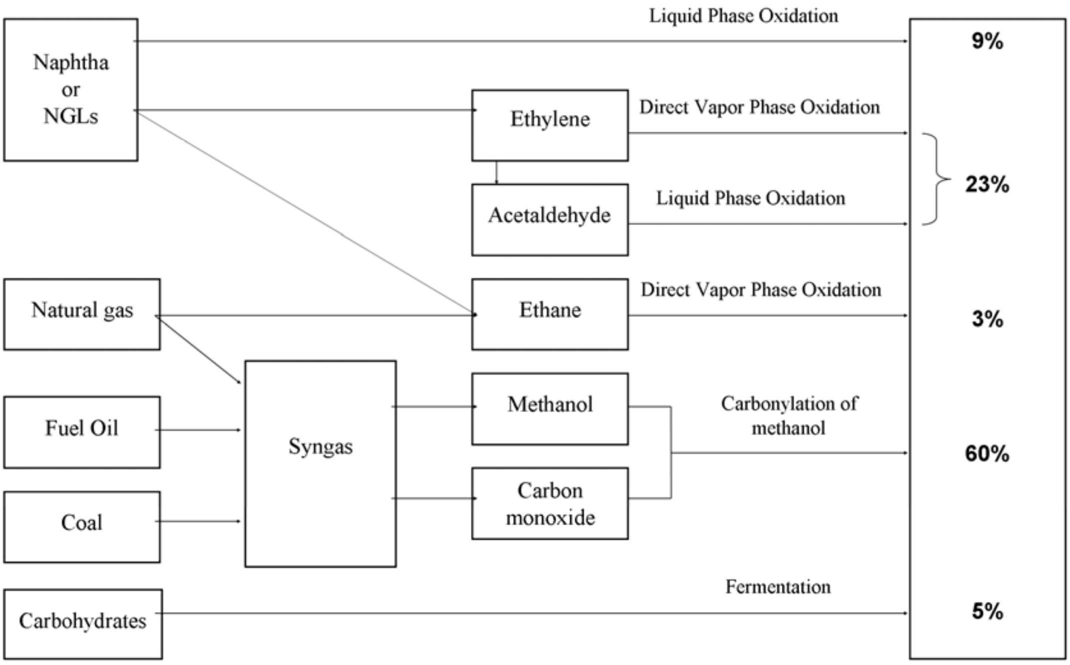

Figure 5.1.: Schematic illustration of the current industrial routes for production of acetic acid.

Prior to the advent of petrochemistry acetic acid was produced by oxidation of ethanol. This is still utilised in the production of vinegar, where microorganisms are used to oxidise the ethanol. However, very few microorganisms can survive in highly acidic media. The consequence of this is that a fairly low amount of acetic acid can be produced before the microorganisms are inhibited.

The oxidation can also be chemically catalysed; as far back as 1820 E. Davy reported that if ethanol was heated over platinum black a change in the platinum takes place [149]. This is not the exact truth as it was proved by Döbereiner. He repeated the experiment and analysed the liquid and found that it had become more acetic leading to the right conclusion that the reaction that took place were not a change in the platinum but an oxidation of the ethanol in the solution [150]. Based on this work several others have used noble metal to catalyse the oxidation of ethanol and other alcohols [129; 151; 152].
Idriss has investigated the partial oxidation of ethanol over CeO_2 supported noble metals including platinum, palladium and rhodium. He found that at the given conditions the Pt

and the Pd catalyst led to the formation of acetaldehyde, whereas the Rh catalyst led to CO [153]. Platinum on graphite has also been investigated and it was found to catalyse the formation of acetaldehyde, the experiments were carried out at fairly low temperatures and low conversions [154]. Sheng *et al.* used a mixed Rh-Pt catalyst and could at low temperatures produce acetaldehyde, but at temperature above 550 K methane became the main product [144].

Within the last few years, focus on greener oxidation routes have increased significantly. The oxidation of alcohols to form acids or aldehydes/ketones is one of the most useful reactions in organic chemistry. It is however seldom that the reaction is carried out using an environmental benign oxidant, and the oxidant often used in quantitative amounts. Some of the proposed/recommended oxidants are pyridinium chlorochromate (PCC) and chromium trioxide, with the latter oxidising primary alcohols all the way to the acid [156]. With the growing focus on environmentalism and the depletion of the fossil resources the demand for more green and sustainable routes has gained ground. This has opened up the field of catalytic oxidations of ethanol using air or oxygen as the oxidant.

6. Heterogeneous gold catalysed oxidations

One of the catalysts that have been found to be well suited for mild oxidation using air as the oxidant is gold.

It is only within the last two decades that gold has emerged as an effective catalyst in particularly oxidation reactions. The oxidation of carbon monoxide was one of the first reactions where gold reportedly had superior activity even at very low temperatures. Prior to this discovery gold had been considered a noble – inactive – material, which only formed very few compounds. Nevertheless as far back as the Middle Ages gold was used a medicinal product. Still at present day gold is found as a compound in remedies all over the world. Gold was also used in its colloidal form to give unique colours on glass and other decorative ornaments [157]. The colours of gold colloids have been found to be very dependant of the actual size of the suspended gold particles, the colours rages from blues to red nuances, and the particle sizes are in the nanoscales with a correlation between colour and size [158].

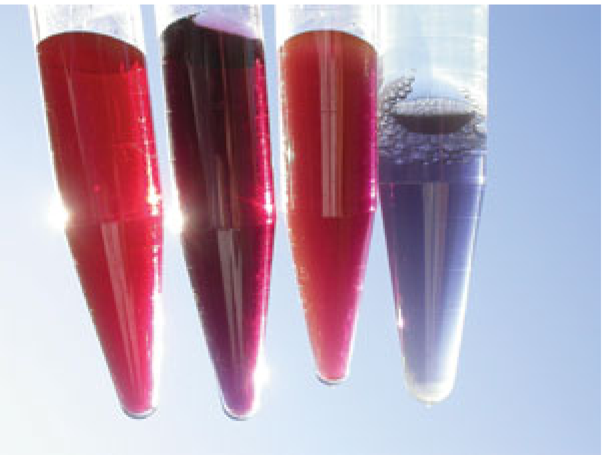

Figure 6.1.: Colourful gold colloids with different gold particle size.

In catalysis it is also nanoscale gold that are found to be active. When looking at nanoscale particles the properties are very different compared to the bulk material. This is in the case of gold very obvious just when looking at the change in colour.

The gold catalysed oxidation of CO was among the first reactions where gold nanoparticles were found to have extraordinaire properties. The reaction has been thoroughly investigated both experimentally as well as theoretically by DFT calculations [159; 160]. It

has been found that the smaller the particle size the higher the activity [161]. Haruta is one of the pioneers within gold catalysis especially in the fields concerning preparation of the catalyst and CO oxidation. The gold catalysed oxidation of CO has been found to be active even at temperatures below 0 °C, and the best suited support material has been found to be Fe_2O_3 among those investigated [162].
The use of gold as a catalyst for the hydroclorination of ethyne was, more or less simultaneously with the CO oxidation, discovered by Hutchings. This reaction has not been investigated as thoroughly as the CO oxidation but is partly responsible for the making gold catalysed reactions among one the fastest growing fields in catalysis [163].

When focusing on the gold catalysed oxidation of alcohols, both supported gold particles and polymer-stabilised clusters have been investigated [164; 165]. Several substrates have been examined, and they include aromatic, aliphatic and allylic alcohols, among which both primary and secondary alcohols have been studied as well as some polyols. The oxidation of aliphatic alcohols is suggested to be more difficult than the analogue oxidation of benzyllic alcohols [166]. Su *et al.* have in addition found that when oxidising a substituted benzyl alcohol the substitute has an important effect, with electron donating groups making the alcohols easier to oxidise and the opposite was the case for the electron withdrawing groups [167]. For the polyols, gold catalysts were reported to exhibit a higher chemoselectivity than analogous supported palladium and ruthenium catalysts [168-170] making it possible to control which one of the alcohol groups in the polyol that is preferentially oxidised. When oxidising aliphatic diols containing both a primary and a secondary alcohol group, it is found that the regioselectivity is highly shifted towards the oxidation of the primary alcohol group [171]. Also the effect of the solvent is noteworthy since in aqueous solution the carboxylic acid is favoured over the aldehyde, but under solvent-free experiments the aldehyde is favoured [168]. For the formation of ester the use of Fe_2O_3 or C as support materials seem, in contrast to CeO_2, TiO_2 and SiO_2 supported catalyst, to be more selective [172]. The group of Prati and Rossi has investigated the oxidation of both simple alcohols and more complex polyols such as glucose [173-177]. Additionally, they have thoroughly studied the reactivity of various diols, in particular ethylene glycol and phenylethane-1, 2-diol [168; 178-181]. In these studies, it was found that that the activity of gold on metal oxides is increased if the particle size is decreased, whereas for gold on carbon catalysts, the activity apparently reaches a maximum at a mean diameter of 7-8 nm [178]. Hutchings *et al.* have worked with both pure supported gold catalysts but also with Au/Pd alloys, for the oxidation of alcohols and aldehydes [168; 182]. The oxidation of glycerol in aqueous soulution were studied by Carrettin *et al.*, they found that, though at moderate temperature (333 K), the oxidation only takes place in the presence of a base nonetheless giving high selectivities [183; 184]. Similarly, others have also conducted oxidations of glycerol with dioxygen using gold catalysts, and here the selectivity was found to vary significantly with the conversion [185]. Taarning *et al.* have also investigated the oxidation of glycerol, their work was conducted in a methanolic solution and the main product was dimethyl mesoxalate [186]. Recently, also the group of Corma has used supported gold catalysts for the solvent-free oxidation of various alcohols. In these studies, it is concluded that nanocrystalline CeO_2 acts as a co-catalyst, which improves the catalytic activity of the gold [187]. It has been demonstrated that the gold catalyst is superior to the palladium catalyst when aiming for a selective oxidation of secondary alcohols to form ketones [165], and also the oxidation of allylic alcohols was investigated in detail [188]. In the case of the allylic alcohols, the chemoselectivity of the gold catalyst was found to be significantly better than for the Pd catalyst, and with gold it was possible to form mainly the α, β-unsaturated carbonyl compound. Idriss *et al.* investigated the gas-phase oxidation of ethanol over an Au/CeO_2 catalyst in the temperature range of 373 to 1073 K; here it was clear that the product composition changed significantly with the temperature [189]. At low temperatures, acetaldehyde was the main product whereas at higher temperatures, the selectivity switched towards acetone and finally to methane.

The effect of promoters have also been investigated, Zheng *et al.* have found that inexpensive promoters such as carbonates and acetates can improve the activity and selectivity significantly [190].

Hutchings has recently made a summary of the achievement made within supported gold catalysis since the discovery of gold’s catalytic properties, wherein certain milestones are highlighted [163]. The industrial application of gold catalysis has not yet prevailed but it is know possible to purchase large quantities of gold catalyst (up to 20 kg) and the amount of patents concerning gold catalysis is rapidly growing [191]. For lab scale investigations it is possible to purchase reference gold catalysts from the World Gold Council. Four different choices of support are possible being TiO_2, Fe_2O_3 on alumina beads, Fe_2O_3 and carbon, with the first two catalysts prepared by deposition precipitation and the latter two by coprecipitation and gold sol respectively [192]. The preparation method of gold catalyst seem to have a great influence on the activity of the catalyst, especially the particle size and size distribution are of great importance. Zheng and Stucky have proposed a preparation method which yields reproducible particle sizes [193]. The main method for producing oxide supported gold catalysts remains nevertheless the deposition precipitation method [161].

EXPERIMENTAL WORK

In my work I have investigated the catalytic oxidation of ethanol both in batch reaction and in a continuous fixed bed setup. The first reaction series were performed in the liquid-phase whereas for the latter the reaction was carried out in the gas-phase.

7. Preparation and characterisation of catalysts

7.1 Preparation of gold catalysts

For the batch reaction a series of gold catalysts were prepared. The catalysts were prepared by the deposition precipitation method, which has been found to be suitable when preparing oxide supported gold catalysts (Haruta). Catalysts on two different supports as well as with different loadings were prepared as follows:

A diluted solution of chloroauric acid ($HAuCl_3 \cdot 3H_2O$, 0.01 mM) was made basic by drop wise adding a saturated solution of sodium bicarbonate till the pH was higher than eight; this was measured with pH-paper. Following this the support material was added and the mixture was left to mature at 50 °C for one hour, during which the gold precipitated and were deposited on the support material. After this the catalyst was filtered and washed with water till this was free of chloride, subsequently the catalyst was dried at 120 °C for 2 hours. Finally the catalyst was calcined at 450 °C for 4 hours, following which the distinctive lilac colour had appeared. As support spinel ($MgAl_2O_4$) and titania (TiO_2) were used and the loading were varied between 1 weight percent and 10 weight percent.

Also a palladium and a platinum catalyst were prepared this was done by the standard incipient wetness method. The precursors used were $PdCl_2$ and $PtCl_4$ which were dissolved in water. These catalysts were calcined at 500 °C for 5 hours.

Figure 7.1.: Two gold catalysts, 1 wt% Au/$MgAl_2O_4$, 1.5 wt% Au/TiO_2

7.2. Characterisation

A number of characterisations were performed on the catalysts in order to elucidate the gold particle size as well as the surface area and the pore volume. The methods used were Transmission Electron Microscopy (TEM), x-ray diffraction (XRD) and nitrogen physisorption measurement.

With the Transmission Electron Microscopy (TEM) it was possible to determine the average particle size and to estimate the size distribution. In Figure 7.2 TEM images of gold on both spinel ($MgAl_2O_4$) and titania (TiO_2) is shown. As it can be seen from the figures the average particle size is between 3 and 6 nm and the gold particles are quite evenly distributed. There is, however, a tendency that the average gold particle size is smaller on the Au/TiO_2 than the $Au/MgAl_2O_4$.

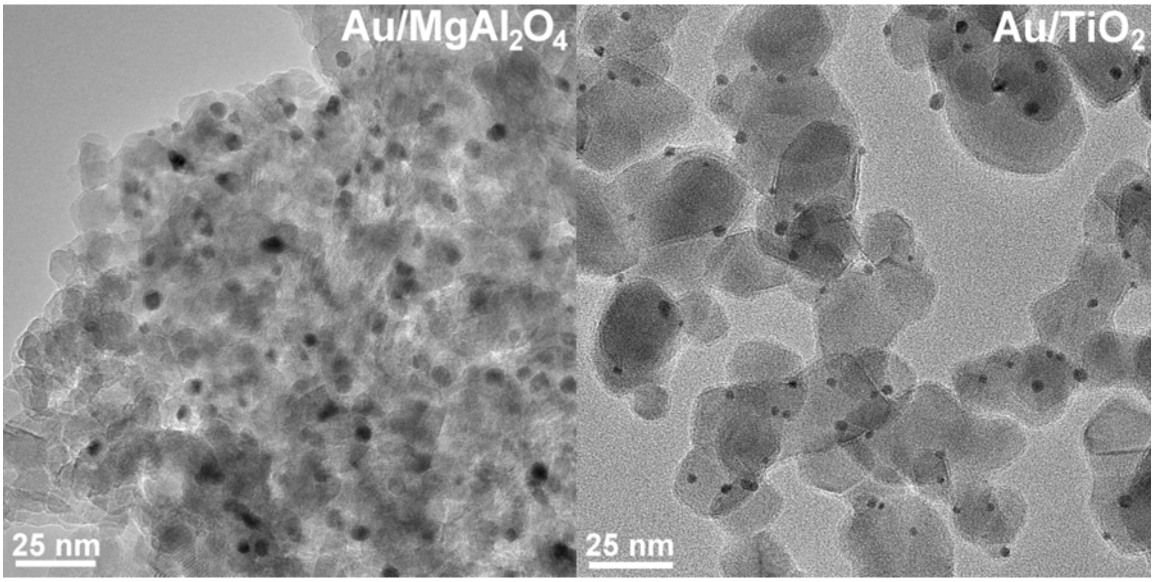

Figure 7.2.: TEM images of $Au/MgAl_2O_4$ and Au/TiO_2 catalysts.

With TEM only a very small sample of the catalyst is analysed so it is a very local method. Commonly the results are though transferred to describe the bulk sample. For each sample, however, several images were taken on different sites of the sample in order to get a broad enough scope. Measurements on used catalysts were also performed although not included in this thesis.

The surface areas of the catalysts were determined by a Micromeritics ASAP 2020 surface area and porosity analyser. The method applied to determining the surface area was physisorption of nitrogen using the Brunauer-Emmet-Teller method (BET), and the pore volume were determined with the Barret-Joyner-Halenda (BJH) method utilising the desorption isotherm.

For the $MgAl_2O_4$ supported catalyst the surface area was determined to be : 60.4 m^2/g, with a pore volume of 0.433 cm^3/g. The gold catalyst purchased from the World Gold Council was also analysed this gave a surface area of 45.6 m^2/g and a pore volume of 0.507 cm^3/g.

Since the form of the titania used for the catalyst from the World Gold Council was not apparent, XRD measurements were conducted in order to clarify which form was used. The diffractogram explicitly showed that the TiO_2 was phase-pure anatase. Since the metal loading was low (1.5 wt%) the gold was not depicted in the diffractogram.

8. Liquid-phase catalytic oxidation of ethanol

The catalytic oxidation of ethanol was investigated in a batch reactor using a gold based catalyst and air as the oxidant. The experiments were conducted in a stirred heated Parr autoclave equipped with a mechanical stirrer and a thermocouple with a volume of 50 ml (exact volume 56 ml including pipelines). In all the experiments an aqueous solution of ethanol was used as the feedstock, which was chosen in order to mimic bioethanol prior to the final distillation. As the oxidant, technical grade pressurised air was used. The aim of the reaction series was to find reaction conditions that were both moderate and which gave a high yield of acetic acid.

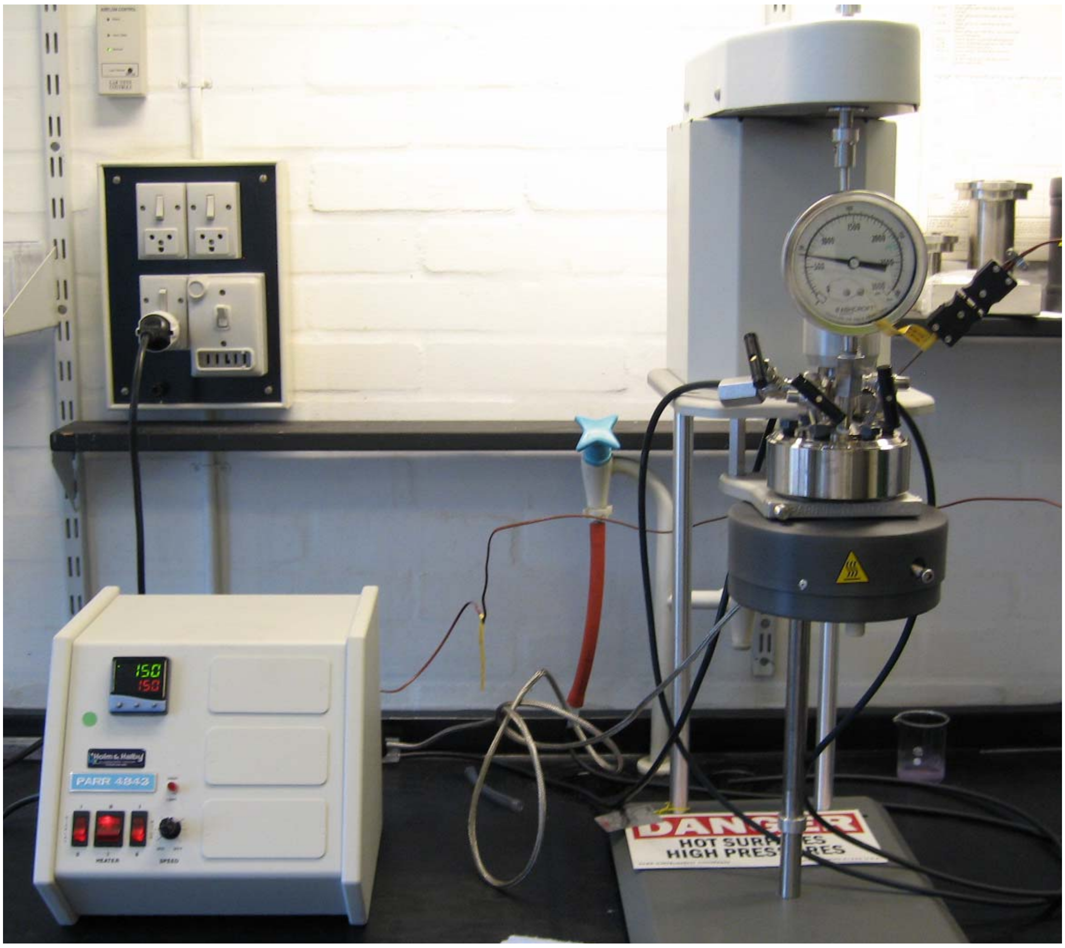

Figure 8.1.: The experimental setup used for the liquid-phase experiments.

Several parameters were investigated, initially the pressure, time and temperature dependences were studied for the spinel supported catalyst. The ethanol concentration was fixed at 5 wt% and the amount of catalyst set to 150 mg. The pressure was varied between 3.0 and 4.5 Mpa, and the temperature between 363 and 473 K with reaction times between 15 minutes and 24 hours.

The average experiment was conducted at 453 K and 3.5 Mpa of air for 4 hours. For each run 10 ml of the feedstock solution together with 150 mg catalyst were loaded in the autoclave, which following was pressurised with air. At the end of the reaction time the reactor was cooled in an ice bath until the temperature was below 268 K, hereby allowing the liquid products to condensate. Following this the excess pressure in the autoclave was reduced and the liquid was analysed on a Shimadzu GC-9A gas chromatograph installed with a Nukol capillary column, 15 m ^{x} 0.53 mm ID, Supelco equipped with a flame ionisation detector (FID). The sample was manually injected and each chromatogram was repeated three times. To verify the results obtained with the GC, the content of acetic acid was for some of the samples also determined by potentiometric titrations with NaOH. The results were within the range of the experimental error. For some of the experiments the reaction gas was collected after the reaction, while reducing the excess pressure, the composition was analysed on a GC equipped with a Thermal Conductivity Detector (TCD). The analysis of the gas was only done qualitatively.

The palladium and the platinum catalysts were also tested at the given reaction conditions for comparison reasons.

After the initial series of experiments the effect of the support was investigated, the new catalyst was gold on TiO_2. Two different Au/ TiO_2 catalysts were tested, one prepared as the gold on spinel and another purchased from the World Gold Council, this was however also prepared by deposition precipitation. Since the catalyst was found to show comparable selectivities the one from the World Gold Council was used in the subsequent experiments. Experiments were performed investigating the effect the reaction time had on the composition of the liquid-phase. Based on these results a proposition for the reaction pathway was made and some investigating measurements were performed. They included changing the feed-solution to an aqueous solution of acetaldehyde and a solution of acetic acid.

In the initial experiments a small amount of ethyl acetate was detected, it was therefore investigated whether it was possible by simple alterations to change the selectivity towards the ester instead of the acid. A series of experiments were conducted where the ethanol concentration was altered. Based on the esterfication reaction it was clear that water most likely was inhibiting the formation of the ester. This was supported by some simple thermodynamic calculations. In order to achieve high enough amounts of oxygen in the reaction mixture without running at dangerously high pressures the reaction time was divided in two parts as described below. Various combinations were investigated and the most favourable was when the reaction first was started with a pressure of 3.5 Mpa for 4 hour following which the autoclave was quenched on an ice bath (cooled below 268 K) and the air let out. Then the autoclave was recharged with a fresh amount of air again 3.5 Mpa and left to react for additionally two hours. The reaction time was started when the autoclave had reached the desired reaction temperature.

8.1. Results

8.1.1. Formation of acetic acid

The formation of acetic acid by the liquid-phase oxidation of an aqueous solution of ethanol was found to be considerably dependant on the reaction temperature. In Figure 8.2 and Figure 8.3 the conversion of ethanol and the yield of acetic acid are shown as a function the reaction temperature over respectively the $MgAl_2O_4$ and the TiO_2 supported gold catalysts.

It can be seen that the analogous experiments with the Au/$MgAl_2O_4$ and Au/TiO_2 catalyst gave very similar results. It is clear that both the conversion and the yield increased with increasing temperature. There is though a difference in the exact form of the two curves depicting the conversion and the yield. This gave the initial indication of the presence of a reaction intermediate. The yield of acetic acid reached, for both catalysts, levels above 90 % at high conversions, the level for the Au/TiO_2 catalyst is slightly higher (95 %) than for the Au/$MgAl_2O_4$ catalyst, but this is close to the experimental uncertainty. It, however, seems that the titania supported catalyst is slightly less active at the lower temperature region.

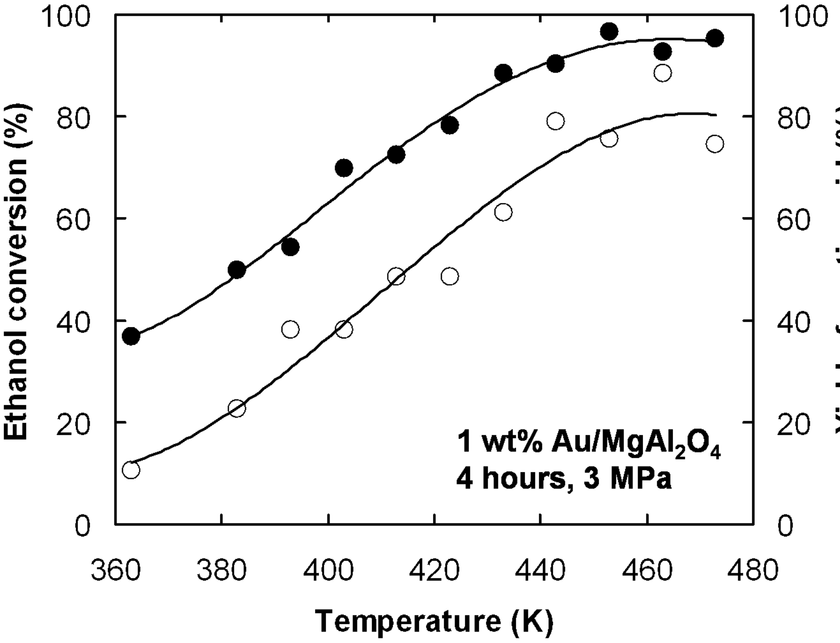

Figure 8.2.: Ethanol conversion and yield of acetic acid as a function of reaction temperature for the Au/MgAl$_2$O$_4$ catalyst.

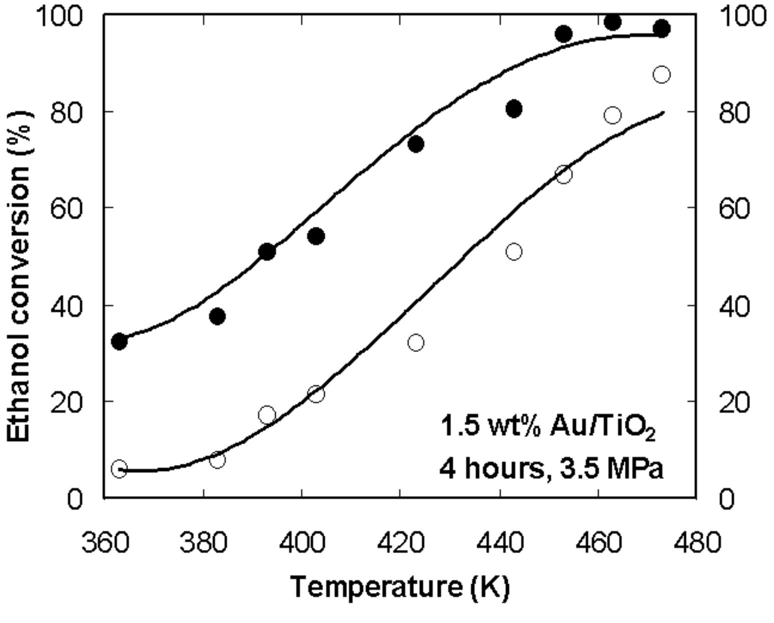

Figure 8.3.: Ethanol conversion and yield of acetic acid as a function of reaction temperature for the Au/TiO$_2$ catalyst.

When investigating the effect of the reaction time again the two catalyst exhibit similar results as shown in Figure 8.4 and 8.5. Here the Au/TiO$_2$ is also found slightly better than the spinel supported catalyst; it might be due to the slightly higher metal loading, 1 wt % versus 1.5 wt %.

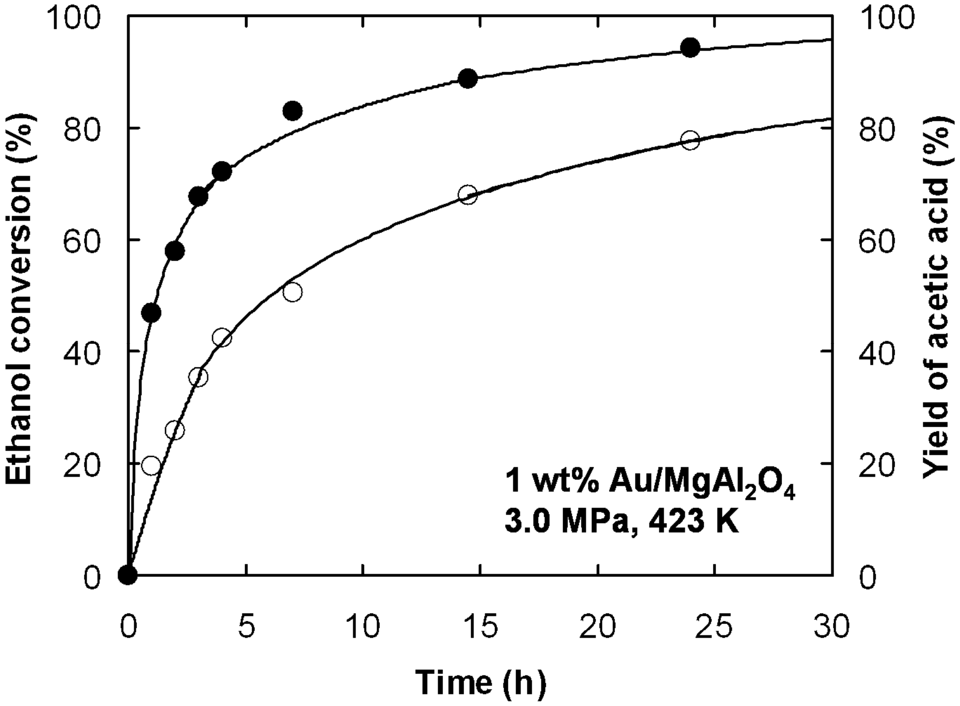

Figure 8.4.: Ethanol conversion and yield of acetic acid as a function of reaction time for Au/MgAl$_2$O$_4$

Overall the results indicate that there is no significant difference between the two metal oxide supports. This does nonetheless not rule out a significant effect of the support material affecting both activity and selectivity in the case of other types of support materials. This could especially be the case if the support was changed to a material not being a metal oxide; such an effect has previously been reported for the selective oxidation of glucose [194]. Preliminary experiments with carbon as the support material does not give nearly as high a conversion of ethanol nor as high selectivity towards acetic acid as the present investigated metal oxide supports. When conducting experiments with the pure support materials (TiO$_2$ and MgAl$_2$O$_4$) the yields of acetic acid was below 2 %, emphasizing that gold plays a significant role in the selective oxidation to form acetic acid.

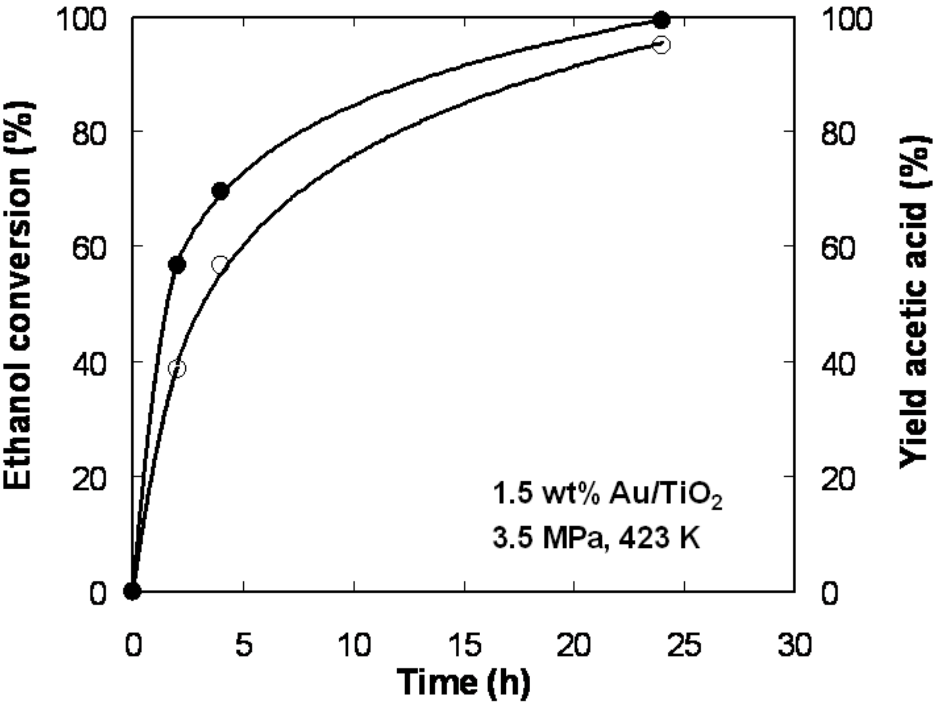

Figure 8.5.: Ethanol conversion and yield of acetic acid as a function of reaction time for Au/TiO_2.

Also the influence of the reaction pressure has been studied. For all the experiments the pressure was kept high enough so that there was at least a stoichiometric amount of oxygen present at the start of the reaction, making the lower limit 3.0 Mpa. The results showed that when the pressure was increased so were both the conversion of ethanol and the yield of acetic acid. With an increase of 1.5 Mpa (from 3.0 Mpa to 4.5 Mpa) the conversion was increased from 80 % to 90 % and the yield from 50 to 65 %. For safety reasons the pressure was not increased to higher than 4.5 Mpa (RT), the yield and conversion would most likely improve even more if the amount of oxygen was increased further, but it was chosen to proceed with air (21 % O_2 in N_2). Figure 8.6 shows the conversion and the yield as a function of the reaction pressure.

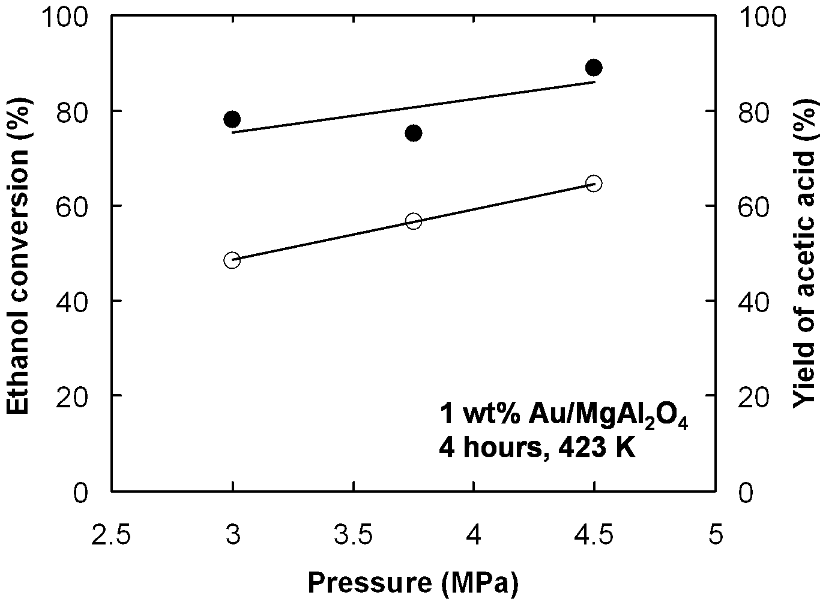

Figure 8.6.: Ethanol conversion and yield of acetic acid as a function of reaction pressure.

The long-term stability of both gold catalysts has been investigated and it was found that the catalysts do deactivate. Measurements show a significant decrease in activity when the catalyst is reused, but it remains active even after several runs. The used catalyst shows no signs of coke formation; which is supported by the colour of the catalyst. TEM images of a catalyst kept under reaction conditions for ten days clearly showed that the gold particle size increased significantly but remained smaller than 10 nm. Furthermore the content of Al, Mg, and Au in solution after a run was measured by ICP-MS, indicating that the support could not tolerate the highly hydrothermal conditions. Small alterations of the catalyst composition might possibly improve the long-term stability. Along these lines, Mirescu *et. al* have presented gold catalysts with quite long lifetimes [194], the reaction conditions in those studies were nevertheless much milder than the conditions used in the above mentioned experiments.

8.1.2. Kinetic investigation

In order to try to elucidate the kinetics of the reaction the composition of the product mixture were thoroughly investigated as a function of the reaction time. Initially it was discovered that not only acetic acid but also acetaldehyde and carbon dioxide were formed.

Furthermore also a trace amount of ethyl acetate appeared in the chromatograms. When lowering the reaction time it was clear that the concentration of acetaldehyde had a local maximum at the low reaction times. Based on this it is proposed that the ethanol is oxidised/dehydrogenated to acetaldehyde which is subsequently further oxidised to acetic acid. This however does not explain the formation of carbon dioxide, and in order to find the origin of the CO_2 the aqueous solutions of either acetaldehyde or acetic acid was subjected to the same reaction conditions. The results showed that the aldehyde was fully converted and the yield almost the same (X= 100 %, Y= 98 %) indicating that this step was not contributing any significant amount of CO_2. After the treatment the acetic acid solution remained the same eliminating the decomposition of the acid as a source of CO_2. It was therefore most likely that another intermediate was the source of the by-product. A possibility is that one hydrogen is first removed from ethanol whereby a surface intermediate is formed, the intermediate is therefore denoted "CH_3CH_2O". This surface intermediate can then either proceed to the aldehyde or decompose and form CO_2. In Figure 8.7 the proposed reaction pathway is illustrated.

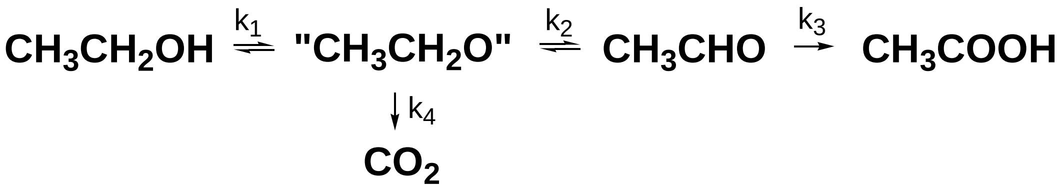

Figure 8.7.: The proposed reaction pathway.

A simple kinetic model was derived and fitted to the experimental data. It was presumed that all of the reactions were first order, hereby simplifying the calculations. Below the rate expressions for each compound is given (equation 8.1-8.5).

$$\frac{dC_{EtOH}}{dt} = -k_1 \cdot C_{EtOH} \tag{8.1}$$

$$\frac{dC_{"CH_3CH_2O"}}{dt} = k_1 \cdot C_{EtOH} - k_2 \cdot C_{"CH_3CH_2O"} - k_4 \cdot C_{"CH_3CH_2O"} \tag{8.2}$$

$$\frac{dC_{AcH}}{dt} = k_2 \cdot C_{"CH_3CH_2O"} - k_3 \cdot C_{AcOH} \qquad (8.3)$$

$$\frac{dC_{AcOH}}{dt} = k_3 \cdot C_{AcOH} \qquad (8.4)$$

$$\frac{dC_{CO_2}}{dt} = 2\,k_4 \cdot C_{"CH_3CH_2O"} \qquad (8.5)$$

The fitting was performed in *MathLab*. In Figure 8.8 the experimental data and the kinetic model are shown. The amount of CO_2 and the surface intermediate have however not been determined experimentally. For each reaction step the corresponding rate constants were obtained, in Table 8.1 these are displayed.

Tabel 8.1.: Fitted values of 1. order rate constants (mol/(l h)).

Rate constant	k_1	k_2	k_3	k_4
Value	1.1	5.1	14.1	1.1

The difference in the values for the rate constants k_2 and k_4 can be supported by the fact that the full oxidation of the intermediate (k_4) involves C-C bond breaking, whereas the dehydrogenation (k_2) only requires C-H bond breaking, which is less demanding. From the values it is obvious that the rate determining step in the formation of acetic acid is the activation of the ethanol (k_1). This step involves the, possibly oxygen-assisted, dehydrogenation of ethanol to form acetaldehyde.

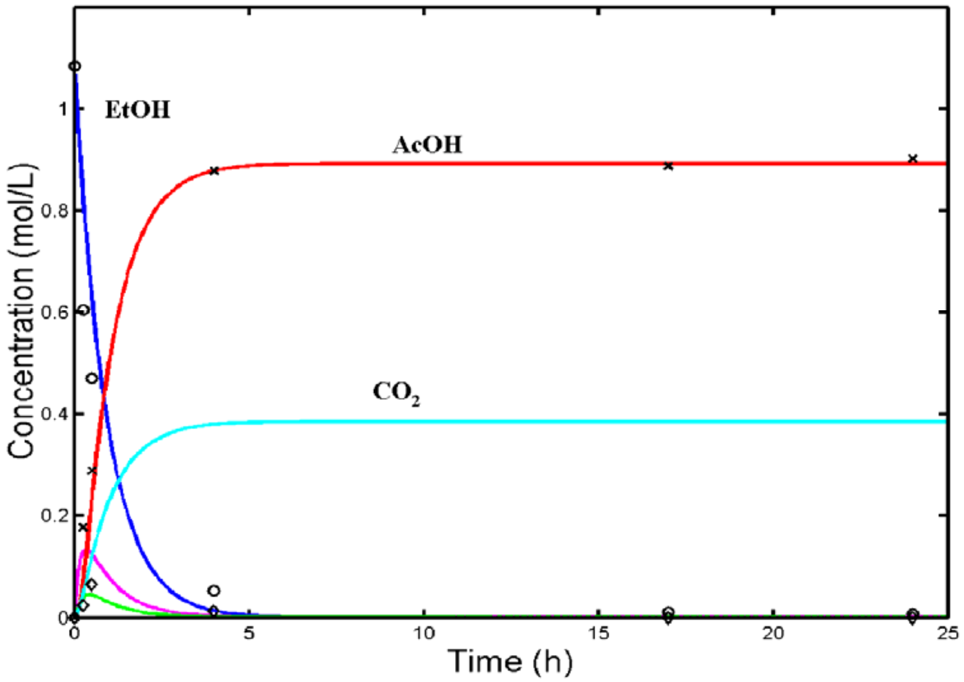

Figure 8.8.: Simple kinetic modelling of the reaction, solid lines theoretical values based on the reaction scheme in Figure 8.7; ○, x, ◊ experimental values (EtOH, AcOH, AcH). The green line represents acetaldehyde and the mauve the surface intermediate.

8.1.3. Formation of ethyl acetate

As for acetic acid ethyl acetate has its application in the paint industry but also as a solvent in the pharmaceutical industry. It is also used as a substitute for methyl ethyl ketone (MEK) and for extractions in the food industry [195]. Ethyl acetate is mainly produced via esterfication of acetic acid.

Others have previously shown that methyl esters can be produced by gold catalyzed oxidation of a methanolic solution of primary alcohol using oxygen as the oxidant both with and without the presence of base [165; 196]. Corma *et al.* has in addition reported that aliphatic primary alcohols can be oxidised to the corresponding ester [187].

The oxidation of an aqueous solution had so far not been studied which lead to the decision to alter the reaction condition used to produce acetic acid in order to produce ethyl acetate. It was found that fairly small alterations could shift the selectivity towards the ester.

The effect of the concentration of ethanol was investigated, since this seemed the most likely way of altering the composition of the products. The increase in concentration gave, as expected, an increase in the selectivity towards ethyl acetate. It was nonetheless necessary to go to concentrations higher than 60 wt % in order to make the ester the main product, below acetic acid remained the main product. At the highest concentration it seems as if the selectivity reached a maximum. In Figure 8.9, the selectivity in the liquid-phase as well as the turnover number (TON) are plotted as a function of the ethanol concentration. The selectivities are based on the moles of products (EtOAc, AcOH and AcH) in the liquid-phase.

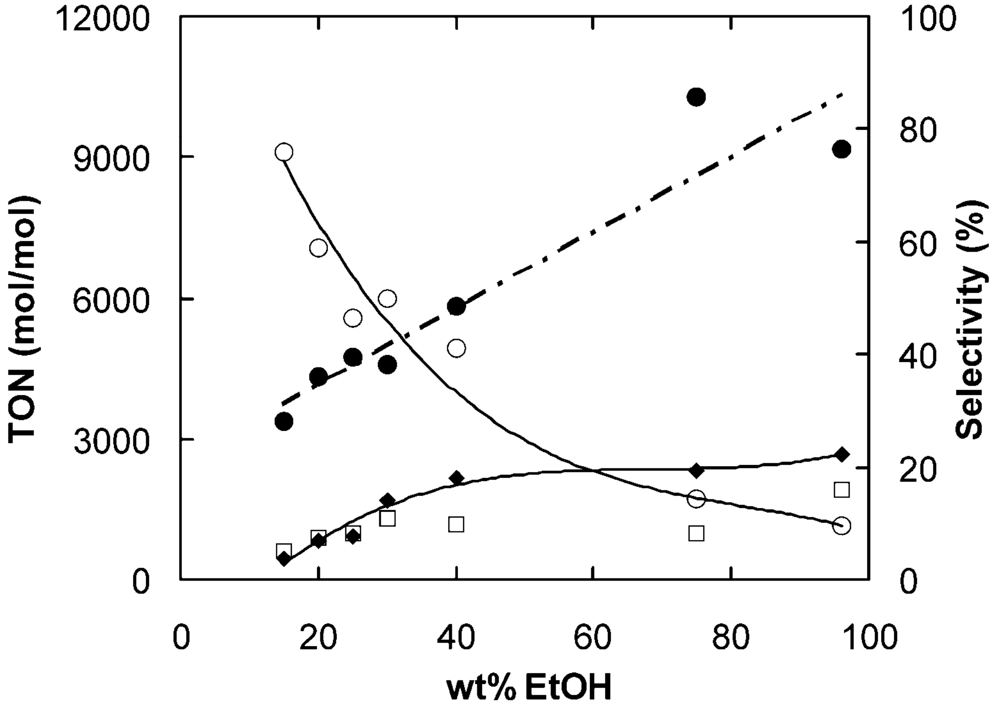

Figure 8.9.: Selectivity and activity of the gold catalyst as a function of the concentration of ethanol. (○ acetic acid, ♦ ethyl acetate, □ acetaldehyde, • TON).

From the figure it can be seen that the selectivity towards acetaldehyde also increases with the increase in ethanol concentration. This could be partially due to the decrease in the oxygen to ethanol ratio. The amount of air is kept constant but with the increase in concentration the ratio is altered. However when focusing on the turnover number (TON) it can be seen that this increased over the whole concentration range indicating that the catalyst remained active even at high concentrations of ethanol, making oxygen the limiting factor. This can also be seen on the conversion of ethanol, which decreased as the concentration was increased, whereby also the oxygen deficiency was increased. Another contributing factor to the decrease in conversion could be the fact that even though the amount of substrate/ethanol was increased the reaction time was kept constant. For the whole concentration range the selectivity towards acetic acid decreased steadily with the increase in ethanol concentration.

The acetic acid to ethyl acetate ratio is under the given reaction conditions largely determined by thermodynamic constraints. Thus the formation of ethyl acetate is limited by the water content in the reaction mixture, since water obviously participates in the equilibrium for the ester formation (eq. 8.6). The water content is determined not only by the amount of water present in the feed but also by the extent of the reaction, and by the selectivity. In particularly significant amounts of water is formed when CO_2 is produced.

$$\mathrm{CH_3CH_2OH + CH_3COOH = CH_3CH_2OOCCH_3 + H_2O} \tag{8.6}$$

Based on the above mentioned results it would be not be possible to produce ethyl acetate directly from the crude bioethanol, a concentration step will be necessary with the present reaction conditions.

8.2. Summary

Based on the results achieved with experiments conducted in the batch reactor it can be concluded that supported gold is a promising catalyst for the liquid-phase oxidation of ethanol. It was possible to achieve high yields of acetic acid with the only by-products being CO_2, acetaldehyde and trace amounts of ethyl acetate. The reaction conditions were fairly mild using air as the oxidant and moderate pressures and temperatures. It was furthermore determined that the two different oxide support materials investigated did not affect the activity considerably.

The reaction pathway was derived from the experimental data, elucidating that the formation of acetic acid goes via the formation of acetaldehyde; furthermore the CO_2 was attributed to the decomposition of the surface intermediate “CH_3CH_2O”. Based on the deduced reaction pathway a simple kinetic model was composed. The kinetic model was fitted to the data with great accuracy revealing the rate determining step as the activation of the ethanol.

In addition it was found that with moderate alterations of the reaction conditions it was possible to shift the selectivity towards ethyl acetate. This though required a higher concentration of ethanol, whereby crude bioethanol is not the ideal feedstock.

Overall the work has to some degree shown the application of gold as a catalyst for oxidation reactions under somewhat moderate conditions. Some minor problems with the long term stability of the catalysts were however also revealed, leaving space for further work.

9. Gas-phase oxidation of ethanol

Metal oxide supported vanadium catalyst have a wide range of applications in industry, and about 5 % of the annual production of vanadium is used for catalysis. Some of the main applications are in the production of sulphuric acid, where V_2O_5 is used in the oxidation of SO_2 to SO_3, and for removal of NO_x in flue gas from power plants, here the catalyst is used for the selective catalytic reduction of the nitrogen oxide species [197]. Many other applications of vanadium have been reported in literature, among these it has been reported that a vanadium based catalyst can catalyse the gas-phase oxidation of ethanol to form acetic acid with high selectivities.

Gubelmann-Bonneau has studied the oxidation of ethanol over a V_2O_5/TiO_2 catalyst immobilised on clay [198]. Gubelmann-Bonneau used a continuous gas-phase flow system, which gave very high selectivities towards acetic acid even at relatively moderate temperatures and pressures (180 °C and 1.7 bar). A diluted stream of ethanol water and oxygen (2.5/5/3/89.5 with the latter being N_2) were reacted over the catalyst giving a selectivity towards acetic acid of 97 %, with the only by-product being CO_2 [198].

Iglesia and co-workers have also investigated the reaction; they used a more complicated catalyst composed of a mixture of niobium, molybdenum and vanadium oxides dispersed on titania. The measurements were preformed at elevated pressure and temperature (16 bar, 237 °C) with a diluted stream of ethanol, water and oxygen (2/20/6.7/70.6, with the latter being He). The reaction gave a high selectivity towards acetic acid (95%) but also a slight amount of acetone [199]. A thorough investigation of the kinetics of the reaction has also been performed elucidating the importance of the presence of water in order to form the acid. The reaction pathway is very similar to the one proposed for the gold catalyzed liquid-phase reaction described in the previous chapter.

Kwak *et al.* have also done experiments with a vanadium based catalyst; here the support was titania modified MCM-41 or MCM-41 and the experiment were conducted at ambient pressure [200]. At temperatures below 200 °C the reaction favoured the formation of acetaldehyde and at higher temperatures CO_2 became the main product though with a small amount of acetic acid being formed for the titania modified MCM-41, furthermore also ethene was detected. For the MCM-41 supported catalyst acetaldehyde and ethene were the only products [200]. The effect of addition of sodium has also been investigated for the

MCM-41 supported V_2O_5 and it was found that the addition had a promoting effect at sodium vanadium molar ratios below 1.0 with a maximum in reactivity at a ratio of 0.5 [201].

A mixture of SnO_2 and MoO_3 has however also been found to be active in this reaction with a very high selectivity towards acetic acid, the reaction temperature were nevertheless significantly higher (300 - 360 °C) [202].

9.1. Experimental

A series of experiments were conducted in a continuous fixed bed setup. The setup consisted of a fixed bed steel reactor and was connected to a Perkin Elmer Autochem XL gas chromatograph (GC) equipped with a flame ionisation detector (FID). The pressure of the system was controlled with a pneumatic valve from SAMSON. A diluted oxygen gas stream was mixed with an aqueous solution of ethanol in a Controlled Evaporate Mixer (CEM) unit; hereby a uniform gas mixture was led to the reactor. The liquid was stored in a steel container which was pressurised with helium, and fed to the CEM unit via a liquid mass flow controller (LMFC). From the CEM unit and trough to the GC the pipelines and valves were heated above 120 °C in order to avoid condensations. A simple illustration of the setup is given in Figure 9.2. For all measurements a 50 wt% ethanol solution was used and prior to the activity measurements the feed stream was led to the GC via the bypass mode.

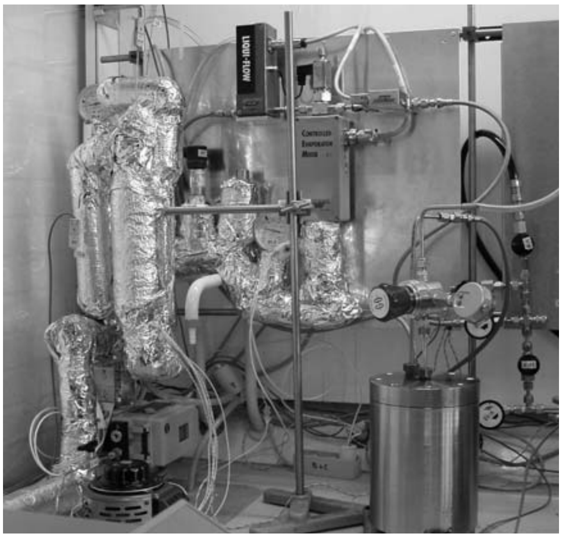

Figure 9.1.: The experimental setup

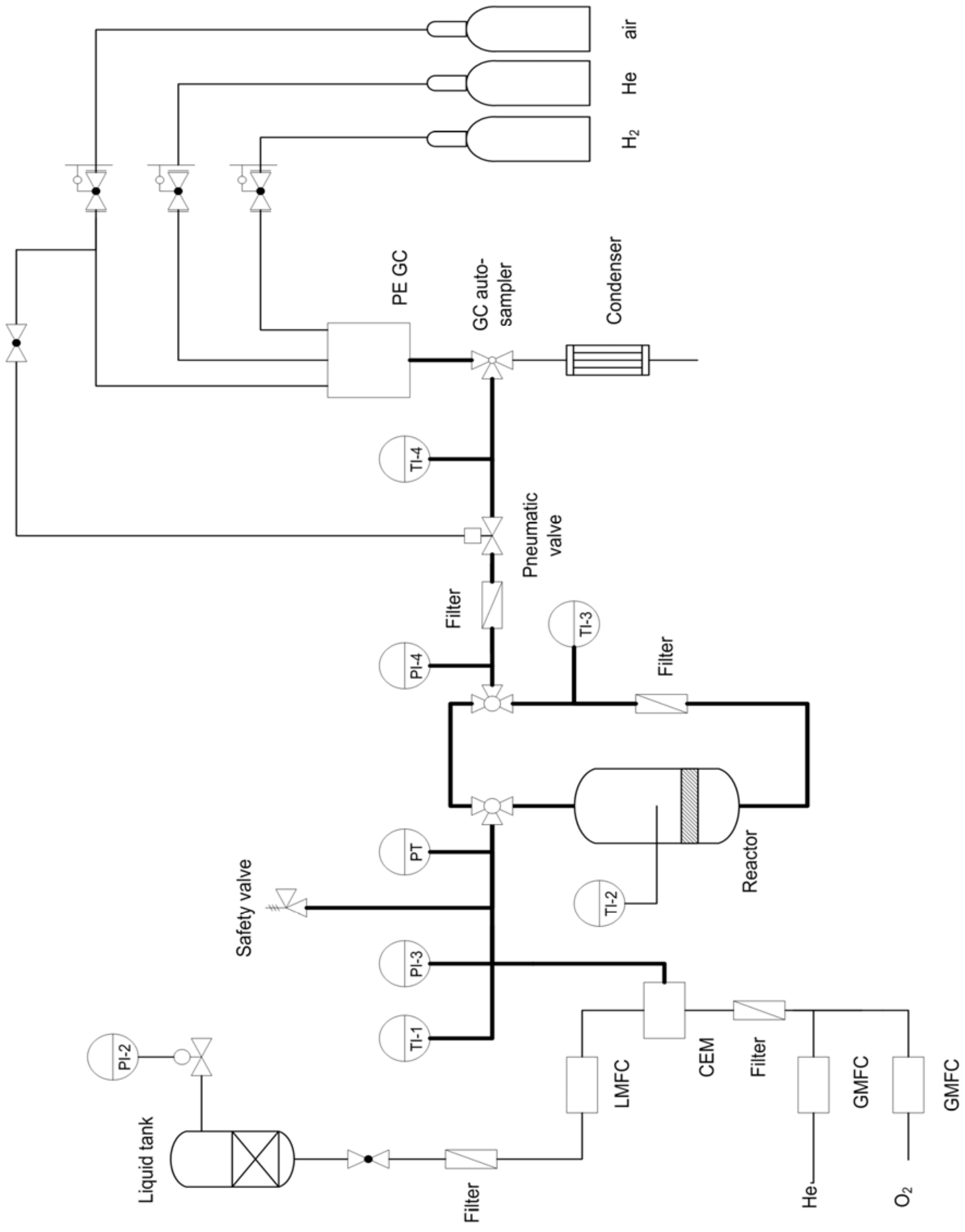

Figure 9.2.: Schematic drawing of the reaction setup, TI = thermocouple, PI = manometer, PT = pressure transducer. Thick piping equals heated pipeline.

As for the cases previous reported in literature, a vanadium based catalyst was used. The catalyst consisted of 15 wt% V_2O_5 dispersed on high surface area TiO_2. (The catalyst was prepared by Steffen B. Kristensen and Andreas J. Kruse). For the measurements the catalyst was diluted with SiO_2 that had been calcined at 273 K for 3 hours, the catalyst to silica mass ratio was 200 mg of catalyst to 800 mg of silica. In order to avoid a significant pressure drop over the catalyst bed the catalyst and SiO_2 were fractionised to a grain size of 180 – 300 μm.

Several reaction conditions were tested and most parameters were investigated including temperature, pressure, O_2/ethanol molar ratio and gas hourly space velocity (GHSV). The initial reaction conditions were 200 °C, 2.7 bar, GHSV: 25000 h^{-1}, with a gas flow of 100 ml/min, O_2/ethanol molar ratio of 3.3, a 50 wt % aqueous ethanol solution and a O_2/He ratio of 1/9. The above mentioned parameters were altered in series, each new condition was left until steady state was reached; this was followed by the chromatograms. The GC analysis was set to take a sample every 16th minute, the chromatograms were analysed with the software TotalChrom. Prior to the catalytic test calibrations curves were made for ethanol and for acetaldehyde and acetic acid, which were the expected products. These products were detected, but based on the molar balance of carbon under some conditions also combustion products, here regarded as carbon dioxide, were formed.

In Table 9.1 the parameters for the reaction conditions in the different reaction series are summarised.

Table 9.1.: Reaction conditions used in this study.

Pressure [bar]	**Temperature [°C]**	**Gas hourly space velocity [h^{-1}]**	**O_2/Ethanol ratio [mol/mol]**
2.7	200	2500, 12500, 25000, 50000	3.3
2.7	175-215	25000	3.3
2.7	175-200	25000	0.5, 1.0
2.0, 2.7, 5.0, 10.0	200	25000	3.3

9.2. Results

Firstly the temperature dependence was investigated with the remaining parameters kept at the initial values. Measurements were done at four different temperatures ranging from 175-215 °C. It was clear that with an increase in temperature the conversion was also increased reaching full conversion at 200 °C; in general the conversion remained moderate at the given temperatures. When looking at the selectivities it was clear to see that the selectivity towards acetaldehyde decreased as the temperature was increased, with an initial selectivity of 95% at 175 °C. It was however necessary to go to temperatures above 200 °C in order to shift the selectivity towards acetic acid, but at 215°C the selectivity towards acetic acid reached 55% in the acetyl products. On the down side at higher temperatures the amount of combustion products also increased. Both the conversion of ethanol and the selectivities are shown as a function of reaction temperature in Figure 9.2.

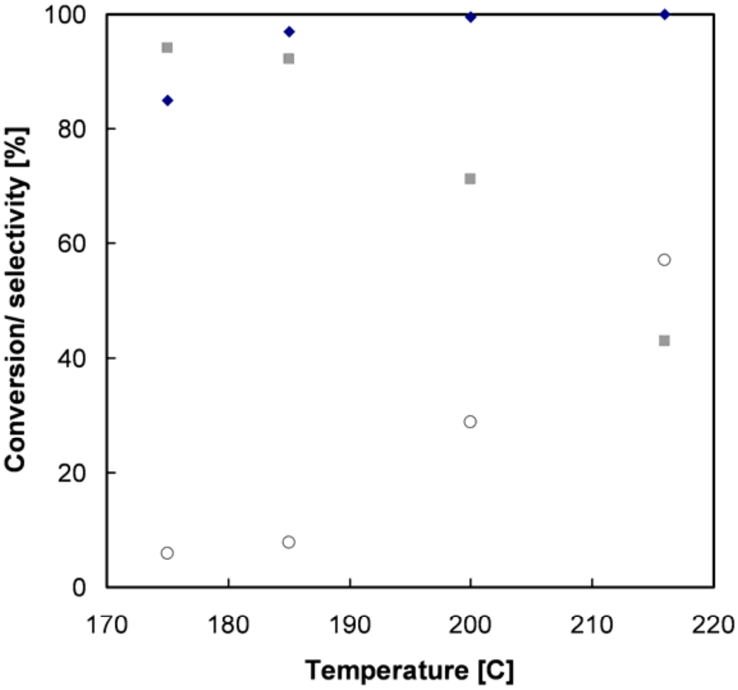

Figure 9.2.: Ethanol conversion (♦) and selectivity of acetaldehyde (■) and acetic acid (○) as a function of the reaction temperature. (P = 2.7 bar, GHSV = 25000 h^{-1}, O_2/ethanol = 3.3).

Keeping the temperature fixed at 200 °C the effect of reaction pressure was investigated. Measurements were done at four different pressures 2.0, 2.7, 5.0, 10.0 bar, and the rest of the parameters were kept constant as for the previous experiments (200 °C, 25000 h^{-1}, and a O_2/ethanol ratio of 3.3). The pressure had a substantial influence on the composition of the offgas. The conversion remained more or less stable at >99 % but the selectivity towards acetaldehyde dropped from 60 to 24 % when the pressure was increased from 2.7 bar to 10.0 bar. The selectivity towards the acetic acid however stayed more or less stable around 20 %. The remaining products were assumed to be combustion products. In Figure 9.3 the results are depicted.

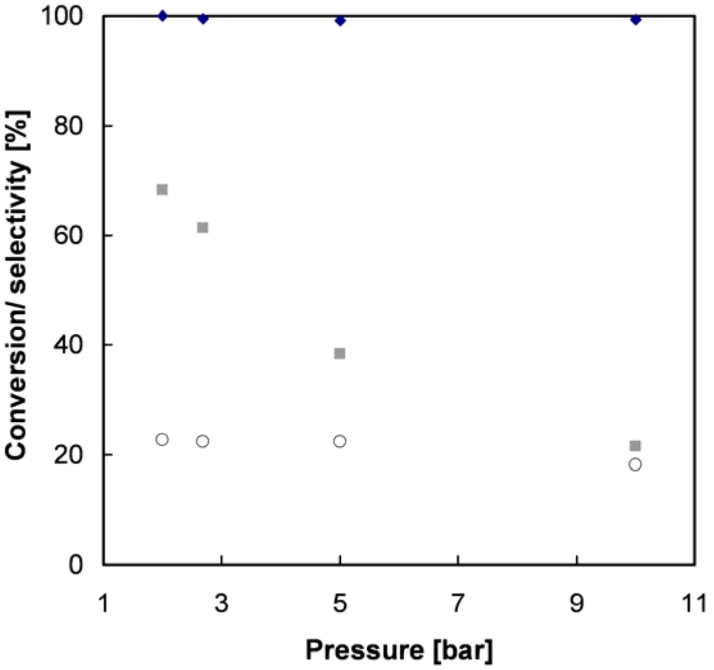

Figure 9.3.: Ethanol conversion (♦) and selectivity of acetaldehyde (■) and acetic acid (○) as a function of the reaction pressure. (T = 200 °C, GHSV = 25000 h^{-1}, O_2/ethanol = 3.3).

When investigating the effect of the gas hourly space velocity (GHSV) four different values were used; 2500, 12500, 25000, and 50000 h^{-1}. The initial total gas flow was either doubled or halved giving the three latter values for GHSV. The pressure was kept at 2.7 bar and the temperature at 200 °C, while the remaining parameters kept as previous. As expected the selectivity towards acetic acid was increased when the space velocity was reduced, hereby increasing the residence time. At this low space velocity the acetic became the main product with a selectivity of 55 %, a value similar to the one achieved at 215 °C. When the space velocity was doubled the selectivity towards acetaldehyde was improved reaching 85 %. The conversion dropped slightly but remained higher than 95%. In order to investigate even lower space velocities a bed of 1 g of pure catalyst was loaded to the system making it possible the perform measurement at a space velocity of 2500 h^{-1}. At this low space velocity the selectivity towards acetic acid was further improved reaching 99 % in regards to the acetyl products (81 % when based on ethanol conversion). The results are depicted in Figure 9.4.

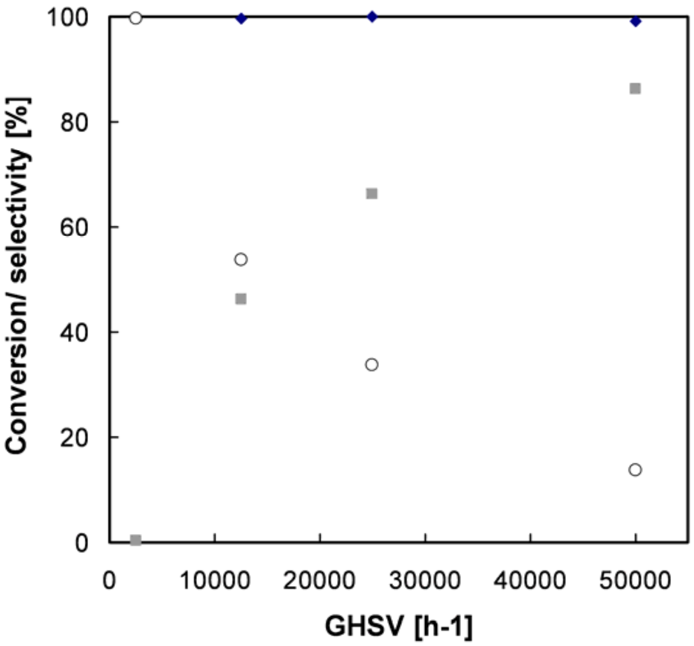

Figure 9.4.: Ethanol conversion (♦) and selectivity of acetaldehyde (■) and acetic acid (○) as a function of the gas hourly space velocity (GHSV). (P = 2.7 bar, T = 200 °C, O_2/ethanol = 3.3).

In order to minimise the amount of combustion products formed, a study of the temperature dependence was performed. Measurements were conducted at 175 °C and 165 °C, in order to see if the catalyst remained the high selectivity and conversion even at lower temperatures. The selectivity as well as the activity changed slightly when the temperature was reduced to 175 °C. Even at 165 °C the selectivity towards acetic acid remained above 80 % (73 %) with the conversion staying close to quantitative (98.9 %).

At 165 °C the amount of combustion products were furthermore decreased with the decrease in temperature (Figure 9.5).

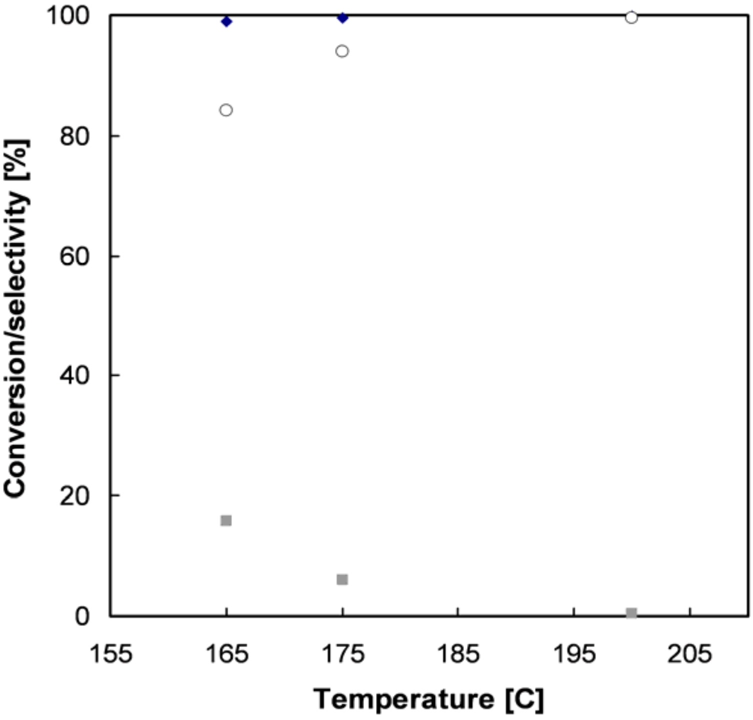

Figure 9.5.: Ethanol conversion (♦) and selectivity of acetaldehyde (■) and acetic acid (○) as a function of the reaction temperature. (P = 2.7 bar, GHSV = 2500 h^{-1}, O_2/ethanol = 3.3).

Finally the oxygen to ethanol molar ratio was investigated. Three ratios were studied one with excess of oxygen, one stoichiometric and one with a deficient amount of oxygen giving molar ratios of 3.3, 1.0, and 0.5. For each ratio measurements were done at three different temperatures (175- 200 °C) but with fixed pressure and space velocity. The overall tendency for all ratios was that the conversion and the selectivity towards acetic acid increased with increasing temperature. The oxygen amount did however play an important role; at the 0.5 ratio the initial conversion was only 37 % however the selectivity towards acetaldehyde was 96% (Figure 9.6 top). When doubling the ratio to 1.0 there was hardly any change in the selectivities compared to the 0.5 ratio. Nevertheless the conversion of ethanol was improved significantly with an initial conversion of 57 %

(Figure 9.6 bottom). For both the 0.5 and the 1.0 ratio the selectivity towards acetic acid remained below 10 %, in addition only a very small amount of CO_2 was formed.

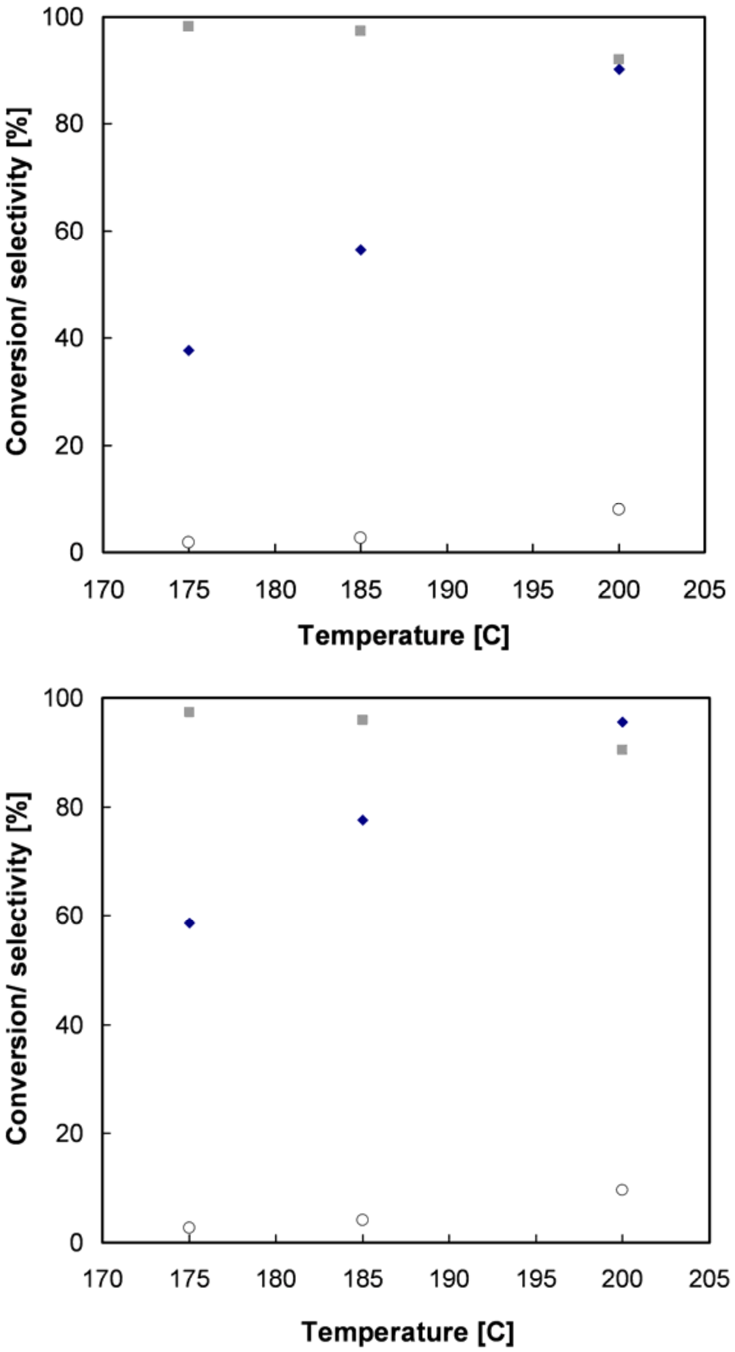

Figure 9.6.: Ethanol conversion (♦) and selectivity of acetaldehyde (■) and acetic acid (○) as a function of the reaction temperature for the O_2/ethanol ratios 0.5 (top) and 1.0 (bottom). (P = 2.7 bar, GHSV = 25000 h^{-1}).

When looking at the synthesis rates, moles of product per gram of catalyst per hour, the picture differed. At 175 °C and 185 °C the tendency for al three series were similar, but at 200 °C the 3.3 ratio series deviated. For the 1.0 and the 0.5 ratio series the synthesis rates for all acetyl products as well as the total synthesis rate increased with the increase in temperature. The 3.3 series however showed a drop in the synthesis rate of acetaldehyde when the temperature was increased to 200 °C, the synthesis rate of acetic acid increased significantly but the increase did not counteract the drop in acetaldehyde, which lead to an overall drop in the total synthesis rate of acetyl products. In Figure 9.7 the three series are depicted with the synthesis rate as a function of temperature and O_2/ethanol ratio.

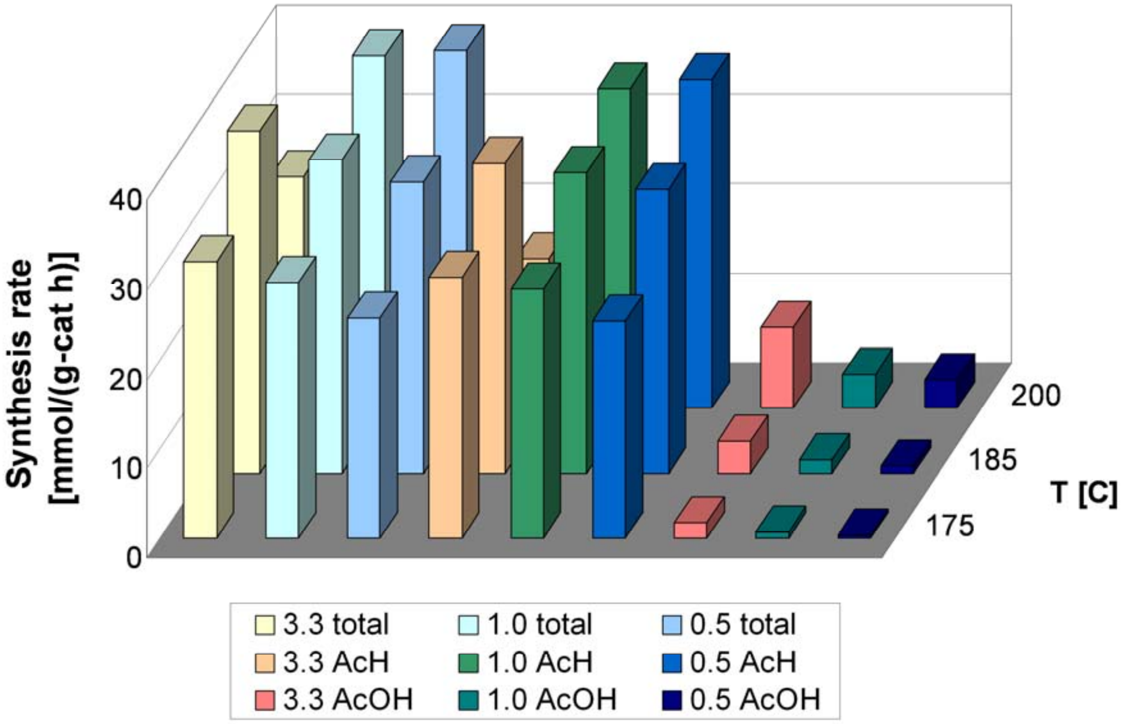

Figure 9.7.: The synthesis rates (mmol/(g-cat * h)) for the three O_2/ethanol ratios 0.5, 1.0, and 3.3 as a function of reaction temperature.

The water content may also play a role in the selectivity of the reaction, this was kept constant trough the measurements at an ethanol to water molar ratio of 0.39. The corresponding ratios for Gubelmann-Bonneau and Iglesia were 0.5 and 0.1 respectively, which could explain the absence of combustion products in the work of Iglesia even though the reaction was carried out at significantly higher pressure [198; 199].

9.2.1. Formation of acetic acid

Based on the investigated conditions the optimal conditions for producing acetic acid is at 200 °C, 2.7 bar, an O_2/EtOH ratio of 3.3 and a space velocity of 2500 h^{-1}. At these reaction conditions the selectivity towards acetic acid reached 81 % with CO_2 being the only significant by-product. If the synthesis rates are compared these conditions do not give the highest value this was achieved with a space velocity of 25000 h^{-1} at 200 °C where a synthesis rate 0.89 g/(g-cat h) were reached. Since acetaldehyde is fairly easy to separate from the acetic acid, and furthermore is a valuable product industrially, it might be feasible to choose reaction conditions that yield a mixture of acetaldehyde and acetic acid. This is the case when running at 2500 h^{-1} at 165 °C, but again the synthesis rate can be improved significantly if the space velocity is increased to 25000 h^{-1} keeping the temperature fairly low at 175 °C hereby repressing the formation of combustion products.

9.2.2. Formation of acetaldehyde

As seen in the previous sections it was possible to tune the reaction so that it produced acetaldehyde in high selectivities with acetic acid being the only other product. In order to favour the formation of the aldehyde the temperature was kept fairly low and the oxygen to ethanol ratio kept at 1.0 or lower. Also the residence time had a significant influence. In general the optimal conditions for acetaldehyde were opposite those proposed for acetic acid, though at lower temperatures it has to be taken in to account that the conversion dropped. From the investigated reaction conditions the optimal seems to be the achieved at 200 °C, 2.7 bars and at a space velocity of 50000 h^{-1}, here the synthesis rate reaches 3.02 g/(g-cat h), however the selectivity is only 85 %. A higher selectivity is reached when the temperature is lowered to 175 °C, here the selectivity reaches 96 % the measurements have however only been performed at 25000 h^{-1} so the synthesis rate is lower. The synthesis rate of 3.02 g/(g-cat h) corresponds to a 92,3% yield of acetaldehyde, which is to be considered as a good yield. For the run at 175 °C the yield reached 92.4 %, the conversion was though lower but it should be possible to recycle the ethanol.

9.3. Summary

It has been shown that a novel high surface area vanadium based catalyst selectively with high activities can be used for the partial oxidation of ethanol to form acetaldehyde or acetic acid. The change in selectivity only requires simple alterations to the reaction conditions.

Yields of acetaldehyde above 90 % were achieved at moderate temperatures and pressures (175-200 °C and 2.7 bar). It was found that the space velocity had a great influence on the composition of the product stream, but even at high velocities the conversion remained above 95 %. At a space velocity of 2500 h^{-1} even at temperature as low as 165 °C a selectivity towards acetic acid above 80 % was achieved. When increasing the reaction pressure an unwanted effect emerged, instead of increasing the amount of acetic acid formed a large amount of CO_2 was formed, the ratio between acetic acid and acetaldehyde was nevertheless improved.

When altering the oxygen to ethanol ratio it was found that an excess of oxygen were needed in order to form significant amounts of acetic acid. On the other hand in order to produce acetaldehyde in high yields an O_2/ethanol ratio of 0.5 gave good yields but with a ratio of 1.0 the conversion was improved significantly.

All in all the catalyst was found to be useful for the gas-phase partial oxidation of aqueous ethanol at moderate temperature and pressure. The long term stability of the catalyst is obvious as the next step of investigation, but the preliminary experiments have not exhibit any signs of significant deactivation.

10. Concluding remarks

This present thesis should have given the reader an insight into the possibility of using biomass as a feedstock for chemicals, more particularly applicability of the catalytic conversions of bioethanol to form more valuable products such as hydrogen and acetic acid. It should furthermore have provided a comprehensive description of the work done within the catalytic steam reforming of ethanol to form hydrogen. Furthermore two new processes for producing acetic acid has been found, both of which utilises bioethanol as the feedstock.

The liquid-phase gold catalysed partial oxidation of aqueous ethanol with air performed in a batch reactor gave very promising results. It was found that the reaction at moderate temperature and pressure (180 °C and 35 bar) gave yields of acetic acid above 90 %. The effect of temperature, pressure, reaction time, were investigated showing that the activity increased with both increasing temperature and pressure, the latter though having a much smaller effect. Two different gold catalysts were studied namely 1 % Au/$MgAl_2O_4$ and 1.5 % Au/TiO_2, the change in support material did not seem to make any significant difference.

The investigation of the effect of the reaction time revealed the formation of an intermediate, acetaldehyde. An investigation of the kinetics of the reaction was conducted and based on the experimental data a reaction pathway proposed, on which a simple kinetic model was developed.

When altering the concentration of ethanol it was possible to shift the selectivity from acetic to ethyl acetate. It was however necessary to go to ethanol concentration higher than 60 wt % in order for ethyl acetate to be the main product. Beside the increase in concentration of ethanol small alterations to the reaction conditions were needed.

From the experiments with the gas-phase vanadium catalysed oxidation of aqueous ethanol it was clear that the reaction conditions had a profound influence on the selectivity as well as the activity. It was found that at moderate pressure and temperatures (175-200 °C, 2.7 bar) it was possible to produce acetaldehyde or acetic acid with selectivities above 90 %. It was found that the selectivity could be shifted from one product to the other by changing the space velocity by an order of 10, producing acetaldehyde at high space velocities and acetic acid at low space velocities. The effect of O_2/ethanol molar ratio was also investigated and as expected at ratios of 1.0 and lower the acetaldehyde were favoured, furthermore the conversion dropped with decreasing O_2/ethanol ratio. The effect of the water to ethanol ratio has yet to be investigated.

The work presented in this thesis has hopefully proven the applicability of bioethanol as a renewable feedstock for production of acetic acid, acetaldehyde and ethyl acetate. There is obviously a lot of optimisation to be done in order to implement the processes industrially, and the present work has not used “real” bioethanol, which most likely contains impurities that could affect the processes.

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Sustainable Chemistry

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Formation of Acetic Acid by Aqueous-Phase Oxidation of Ethanol with Air in the Presence of a Heterogeneous Gold Catalyst**

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Bioethanol is produced by fermentation of biomass in increasing amounts to meet the growing demands for CO_2-neutral transportation fuels and to eventually remove the dependence on fossil fuels. However, bioethanol could also find use as a versatile, sustainable chemical feedstock. Herein, it is shown that it is possible to selectively oxidize ethanol into acetic acid in aqueous solution using air as the oxidant with a heterogeneous gold catalyst at temperatures of about 423 K and O_2 pressures of 0.6 MPa. This reaction proceeds readily in aqueous acidic media and yields of up to 90% are achieved, with CO_2 as the only major by-product. Thus, it constitutes a very simple, green route to acetic acid.

The oxidation of ethanol by air into acetic acid over platinum was among the first heterogeneously catalyzed reactions to be reported. The initial discovery was made by Döbereiner about two centuries ago, even before the term catalysis was coined.[1] So far, the reaction has not been used for large-scale production of acetic acid. Instead, three other routes to acetic acid have found industrial application: fermentation (vinegar), catalytic liquid-phase oxidation of butane, naphtha, or acetaldehyde, and the carbonylation of methanol, which has recently become the most important.[2]

In the most widely used industrial processes today, the feedstock is almost exclusively derived from fossil fuels. Thus, the production of acetic acid consumes fossil fuels and therefore contributes slightly to increasing CO_2 levels in the atmosphere, and, more importantly, the cost of acetic acid is strongly dependent on the price of the fossil fuels. Therefore, it is interesting that the cost of renewable feedstocks has decreased dramatically relative to fossil fuel feedstocks over the last four decades. Specifically, the cost of corn relative to oil has decreased fivefold from 1950 to 2005. Today, bioethanol is mostly produced by fermentation of starch-containing crops, such as corn or sugar cane, but it seems likely that cellulose-rich agricultural waste will gain importance as a feedstock in the future.[3] Therefore, and also because of the continuing technological improvements of the production process, the cost of bioethanol is expected to decrease.[4] Thus, with increasing fossil fuel prices, the production of acetic acid from bioethanol will become increasingly favorable compared to current fossil fuel-based methods. Clearly, this development requires that an active and selective catalyst for oxidation of ethanol with dioxygen to form acetic acid [Eq. (1)] is available.

$$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O \qquad (1)$$

So far, primarily palladium and platinum catalysts have received attention as catalysts for ethanol oxidation.[5] However, with these catalysts it has proven difficult to reach sufficient selectivities at high conversions.

Here, it is reported for the first time that gold catalysts are both very active and selective catalysts for aqueous-phase oxidation of ethanol with air into acetic acid at 373–473 K with O_2 pressures of 0.5–1 MPa. Interestingly, metallic gold was for many years considered too unreactive to be useful as a catalyst.[6] However, this view was challenged in the seminal studies of Haruta and co-workers,[7,8] who showed that gold very efficiently catalyzed the room-temperature oxidation of CO with O_2 to form CO_2, and by Hutchings, who studied acetylene hydrochlorination with gold catalysts.[9] Since then, numerous reports of different gold-catalyzed reactions have appeared and the field has recently been reviewed and highlighted.[10–12]

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The catalytic oxidation of alcohols with air has also attracted significant attention as a "green" reaction.[13] Among the heterogeneous catalysts, mainly Pd and Pt have shown promising result.[14,15] Rossi and co-workers were the first to show that alcohols, specifically diols and sugars, can be oxidized to the corresponding acids with gold catalysts but only when a base is present.[16,17] Later, the oxidation of glycerol to glycerate using Au/C was similarly demonstrated.[18] Recently, it was shown that heterogeneous ceria-supported gold catalysts are able to oxidize several higher alcohols into the corresponding carboxylic acids using air as oxidant.[19] In these experiments, the support played an active role in the catalytic cycle. However, it has also been shown that solvent-free oxidations of primary alcohols can selectively yield aldehydes.[20] Thus, it is noteworthy that the gold-catalyzed aqueous-phase oxidation of ethanol with air into acetic acid reported here proceeds readily in acidic aqueous solution.

Bioethanol is typically produced in a series of steps, namely fermentation in a batch process (yielding 3–15 vol% aqueous ethanol), distillation to obtain the azeotrope (containing 96 vol% ethanol), and further distillation to achieve the anhydrous ethanol that is required as a fuel additive.[21] Therefore, we decided to study the oxidation of ethanol in a batch process with ethanol concentrations corresponding to those obtained during fermentation, as this is expected to represent the easiest scheme for acetic acid production from bioethanol. All catalysts were prepared on a porous support of $MgAl_2O_4$ ($65\,m^2g^{-1}$) using $HAuCl_4{\cdot}3H_2O$, $PtCl_4$, and $PdCl_2$ as metal precursors. The catalytic experiments were conducted in stirred reactors (50 mL, Parr Autoclaves, stainless steel). Liquid samples were drawn from the reactor periodically using the sampling system and analyzed by gas chromatography (GC). Similarly, gas samples were also analyzed by GC. No reaction was observed in the absence of catalyst or when using the pure supports without gold. The metal content of all catalysts was analyzed by atomic absorption spectroscopy (AAS). The gold catalysts were also characterized by transmission electron microscopy (TEM) before and after testing. Typically, 20 images were recorded for each catalyst sample.

Initially, we studied whether gold could catalyze the selective oxidation of ethanol into acetic acid with air in aqueous solution, and how such a catalyst would compare with previously reported systems based on platinum and palladium. Table 1 compares the performance of Au, Pt, and Pd catalysts on a $MgAl_2O_4$ support. Previously, the nature of the support has been shown to be critically important for gold catalysts.[19,22] $MgAl_2O_4$ was chosen as the support material here since it is stable at high water pressures and because it can be considered completely inactive in redox processes. Thus, the observed activity can be attributed solely to the metal nanoparticles, and no synergistic effect with the support is expected. Other supports might be found to affect the catalytic performance.

Table 1: Comparison of $MgAl_2O_4$-supported Au, Pt, and Pd catalysts for oxidation of aqueous ethanol to acetic acid with air.[a]

Cat.	*T* [K]	*p* [MPa]	*t* [h]	Conv. [%]	Yield [%]	STY[b] [$mol\,h^{-1}\,L^{-1}$]
Au[c]	453	3	4	97	83	0.21
Pt	453	3	4	82	16	0.047
Pd	453	3	4	93	60	0.15

[a] Conditions: 150 mg catalyst, 1 wt% of metal, 10 mL of 5 wt% aqueous ethanol, [b] Space-time yield. [c] Corresponding to 0.07 mol% Au.

Remarkably, the gold catalyst not only exhibits similar or higher catalytic activity than palladium or platinum but, in particular, a significantly higher selectivity towards acetic acid than both of these well-known catalysts. The major by-product for the gold catalyst is CO_2, whereas the Pd and Pt catalysts also produce significant amounts of acetaldehyde. Thus, we decided to further investigate the performance of gold catalysts for ethanol oxidation to gain a more detailed insight into this reaction and to identify suitable reaction conditions.

Figure 1 shows representative TEM images of the 1 wt% $Au/MgAl_2O_4$ catalyst used in this study. Generally, gold particle sizes of 3–6 nm are observed both before and after testing, with no sign of sintering. Figure 1 also illustrates how the ethanol conversion and the acetic acid yield depend on the reaction time. The reaction is conducted with only a slight excess of oxygen and therefore the reaction rate does not obey pseudo-first-order kinetics.

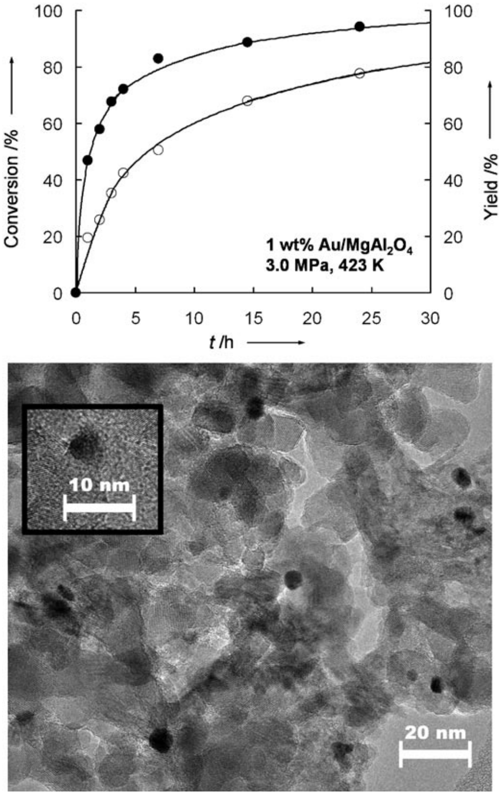

Figure 1. Top: Performance of 150 mg of 1 wt% $Au/MgAl_2O_4$ catalyst in the oxidation of 10 mL of aqueous 5 wt% ethanol with air at 423 K and 3.0 MPa (● ethanol conversion, ○ acetic acid yield). Bottom: TEM images of the 1 wt% $Au/MgAl_2O_4$ catalyst used for ethanol oxidation. The inset shows a high-resolution image of a gold particle with a diameter of about 5 nm.

Figure 2 shows how the performance of the catalyst depends on temperature and pressure. It is noteworthy that yields above 80% are obtained without any special effort to optimize the reaction conditions or catalyst composition. It can also be seen that the reaction rate and selectivity are only slightly influenced by the total pressure when oxygen is present in excess.

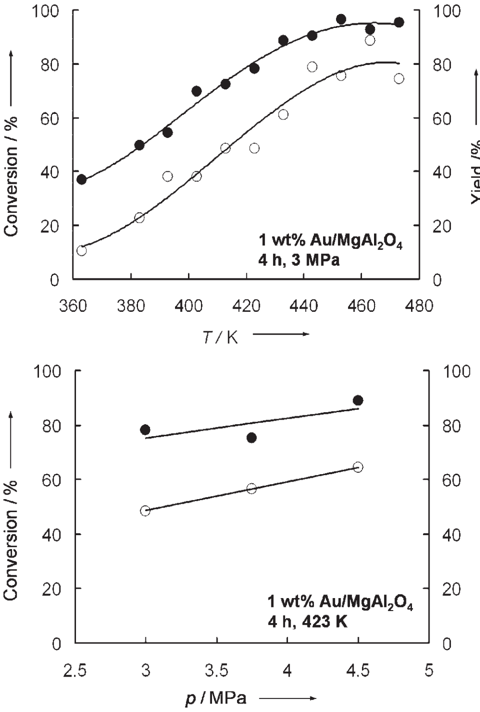

Figure 2. Ethanol conversion (●) and acetic acid yield (○) with 10 mL of 5 wt% aqueous ethanol after 4 h in the presence of 150 mg of 1 wt% Au/MgAl$_2$O$_4$ catalyst. Top: temperatures of 363–473 K and an air pressure of 3 MPa. Bottom: pressures of 3–4.5 MPa and a temperature of 423 K.

As the reaction progresses, the solution becomes more and more acidic, but this does not influence the catalyst's performance. By more careful selection of reaction conditions, for example by increasing the reaction time at 423 K or at 453 K and 3.5 MPa, it is possible to achieve acetic acid yields of over 90% (e.g., 92% yield after 8 h at 453 K and 3.5 MPa). The spinel is found to be quite stable under the present reaction conditions. After a typical reaction run, less than 1% is lost according to ICP-MS. Additionally, only phase-pure spinel is found by powder X-ray diffraction. This is in agreement with the previous finding that magnesium aluminum hydroxide (Al/Mg = 2) transforms into spinel under hydrothermal conditions.[23]

Thus, it is seen that gold catalysts are indeed able to selectively oxidize ethanol to acetic acid in air at moderate temperatures and dioxygen pressures with very high yields. This suggests that it might prove viable to produce aqueous acetic acid in a gold-catalyzed process using aqueous bioethanol as the feedstock. Acetic acid can also be obtained directly by fermentation, however this also represents a challenge since the bacteria do not thrive under the highly acidic reaction conditions.[2] Here, the very high stability of the gold-on-MgAl$_2$O$_4$ catalyst allows the use of high temperatures and pressures, which results in high rates. Recently, bioethanol has also received attention as a feedstock for renewable dihydrogen by steam-reforming[24] or autothermal reforming.[25] Figure 3 illustrates some proven possibilities for using bioethanol, including both fuel and feedstock applications.

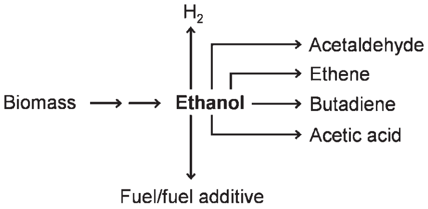

Figure 3. Possible uses of bioethanol as a fuel or as a feedstock for important bulk chemicals.[26]

A future challenge for chemists could be to find efficient routes from bioethanol to fuels and chemicals. Such processes will also compete with other new processes that allow direct conversion of carbohydrates into, for example, dihydrogen[27,28] or synfuels,[28,29] which are currently being explored. Here, we have focused on synthesizing acetic acid from ethanol in a simple, green process since acetic acid has a significantly higher value than fuels (including dihydrogen) and also than ethene, acetaldehyde, and butadiene, for example. Therefore, this might represent the currently most efficient use of part of the available bioethanol.

Experimental Section

The gold catalysts were prepared by deposition-precipitation[30] of HAuCl$_4$·3H$_2$O (supplied by Aldrich) on MgAl$_2$O$_4$. Stoichiometric MgAl$_2$O$_4$, calcined at 1000 °C,[31] was tabletized, crushed, and sieved to a particle size of 100–250 μm prior to use. For comparative purposes, Pd and Pt catalysts supported on MgAl$_2$O$_4$ were prepared by incipient-wetness impregnation of hydrochloric acid solutions of PdCl$_2$ and PtCl$_4$, respectively. The resulting catalyst precursors were dried at 120 °C for 6 h and calcined at 773 K for 2 h. The pure, stoichiometric, and calcined spinel used here is neutral and causes essentially no change of pH (less than ±0.05) when suspended in water or treated hydrothermally in water.

The reactor (total free volume of 55 mL) was charged with 5 wt% aqueous ethanol (10 mL), and the catalyst (150 mg) was added. After closing the autoclave, it was charged with technical air (80 vol% N$_2$, 20 vol% O$_2$) at the required pressure (2.5–5.0 MPa) and sealed. No dioxygen was added to replace that consumed by the reaction and consequently only a limited excess of oxygen is present after reaction. The reactor was then heated to a reaction temperature between 373 and 473 K where it was kept for the desired time period (4 to 45 h). The time required to reach the reaction temperature varied slightly. The pressure was monitored during the reaction and the pH was determined in the product. After the reaction, the autoclave was cooled to about 278 K. After each run, the reactor and internal components were cleaned by polishing and washing with water. The catalyst was separated by ultrafiltration and used up to three times. At this point it had lost most of its activity, which corresponds to TONs of more than 10000. The content of Al, Mg, and Au in solution after each run was measured by ICP-MS. In a separate experiment, pure spinel was treated under hydrothermal conditions (150 °C, 3.0 MPa) with 5 wt% acetic acid. No acetic acid was found to be lost onto the support.

The GC apparatus was equipped with both FID and TCD detectors to allow identification of all liquid and gaseous products present in amounts above about 1 vol%. Product compositions and concentrations were determined using standard solutions. In some cases, the entire reaction mixture was also titrated with aqueous sodium hydroxide after the reaction run to validate the GC results. In all cases, the analyses gave identical results within the experimental uncertainties.

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Keywords: acetic acid · bioethanol · gold · heterogeneous catalysis · oxidation

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Perspective

Bioethanol: fuel or feedstock?

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Abstract: Increasing amounts of bioethanol are being produced from fermentation of biomass, mainly to counteract the continuing depletion of fossil resources and the consequential escalation of oil prices. Today, bioethanol is mainly utilized as a fuel or fuel additive in motor vehicles, but it could also be used as a versatile feedstock in the chemical industry. Currently the production of carbon-containing commodity chemicals is dependent on fossil resources, and more than 95% of these chemicals are produced from non-renewable carbon resources. The question is: what will be the optimal use of bioethanol in a longer perspective?

Keywords: bioethanol; fuel; feedstock

SETTING A NEW SCENE

Growing demands for CO_2-neutral transportation fuels and the desire to achieve a reduced dependence on fossil resources have been the major driving forces for the substantial increase in the amounts of bioethanol produced by fermentation of biomass. An interesting question is whether the optimal use of bioethanol is as a fuel, or as a feedstock for producing higher-value chemical products.

The vast majority of all fuels and carbon-containing chemicals are produced from fossil resources. Studies predict that most kinds of fossil resources will be depleted within the next century.[1] Furthermore the combustion of fossil fuels causes elevated levels of greenhouse gases (GHG) in the atmosphere, which could possibly lead to global warming.[2,3] As a consequence, society must gradually change from an economy based on fossil resources to one based on sustainable resources. Here, biomass could have a significant role to play. In Fig. 1, the price for a range of selected fuels and chemicals produced from fossil or renewable resources are indicated. Obviously, the costs of the raw materials, both fossil and renewable, depend on many factors and therefore the scale is only approximate. From these raw materials it is possible to produce all the chemicals needed in society. The relevant transformations are typically catalytic reactions, and the cost of the various fuels and chemicals is largely governed by the cost of the raw material and the efficiency of the involved processes. It is noteworthy that with the proper technology it is possible to convert biomass to essentially all the high-value commodity chemicals and fuels currently available from fossil resources. There could even be some advantages using biomass compared to fossil fuels as a feedstock, e.g., for production of certain oxygenated chemicals since introduction of oxygen functionalities into hydrocarbons can be rather difficult, whereas many products derived from biomass already contain some oxygen.[4] However, this also entails an increase in production costs for some of the non-oxygen-containing products, such as gasoline.

Figure 1 illustrates that, in relative terms, it is possible to produce some chemicals more easily and in fewer steps from biomass than from fossil resources, whereas others are less readily available.[5] Thus, fossil and renewable resources are not necessarily equally useful starting materials for all possible products. In this context, it is particularly important to note that

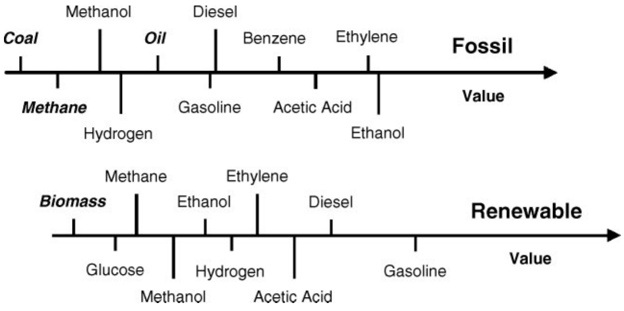

Figure 1. Indication of relative prices for a range of selected chemicals produced from either renewable or fossil resources. The raw materials are shown in italics and the remaining fuels and chemicals are typically produced in one or more process steps starting from fossil or renewable resources.

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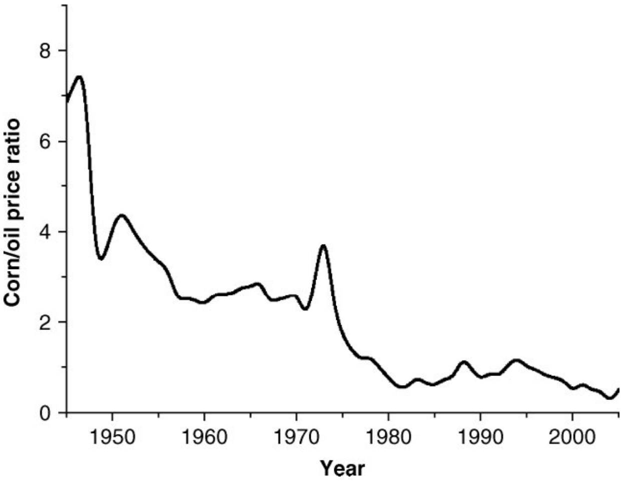

Figure 2. Corn/oil price ratio during in the last part of the 20th century (data from www.eia.doe.gov or www.lefflercom.com).

the figure does not show the amount of each chemical produced. For instance, it is not currently possible to produce the world's need for ethylene from biomass, because the production of ethylene is about three times as high as the production of bioethanol, which would be the most likely feedstock for ethylene production in a renewable economy.

In an evaluation of the usefulness of renewable resources compared to fossil resources as possible sources of fuels and chemicals, the cost of the feedstocks plays a central role. Therefore, it is very interesting to note that the price of biomass relative to oil has decreased more than 10 times over the last 60 years, as shown in Fig. 2 (data from www.eia.doe.gov or www.lefflercom.com). The prices of the products derived from renewable resources are sensitive to technological improvements of the production process, probably more so than those in the fossil economy, since here the involved processes have been improved through significant efforts over many years. One key improvement would be to find more efficient routes for conversion of biomass to fuels or chemicals. If the decrease in the corn/oil price ratio continues and the technology improves, the relative cost for biomass-derived chemicals and fuels will decrease, making it more feasible to switch to biomass.

In addition, it could be important that the use of biomass as a sustainable resource for production of fuels and commodity chemicals should offer improved security in supply, since biomass can be grown in most parts of the world. This is in contrast to oil resources, which are limited by being located in few and, for some, unstable areas of the world.

Ethanol is one chemical that can be readily obtained from biomass by fermentation. The total world production of bioethanol is constantly increasing and was estimated to reach more than 46 billion liters per year in 2005.[6]

RENEWABLE FUELS

In many countries, ethanol is used as an additive to gasoline. In particular, Brazil and the United States have invested significant resources in using blends of ethanol and gasoline as a fuel for motor vehicles (with internal combustion engines). Today, around 2% of the total transportation fuels are covered by bioethanol in the United States.[7] The US Department of Energy has set a goal of replacing 30% of transportation fuels with bioethanol and biodiesel by 2025.[7] Many other countries are also producing or planning to produce ethanol from biomass for use as a motor fuel. The European Union has established a goal of 5.75% biomass-derived transportation fuels by December 2010.[7] The use of fuel ethanol has been quite successful in Brazil, where it is produced at a very low cost by fermentation of sugarcane. In the United States corn is the dominant biomass feedstock for production of ethanol, and in the EU straw and other agricultural wastes are the preferred types of biomass for ethanol production. It is, however, somewhat more difficult to obtain a high conversion to ethanol from these types of biomass, resulting in much higher production costs of bioethanol in Europe.

The renewable energy content for production of bioethanol from corn with current technology was recently estimated to be between 5% and 26%, where the non-renewable energy used in the production was mainly contributed by coal and natural gas.[8] However, currently the energy balance for bioethanol production is quite controversial. Anyhow, an increase in the renewable energy content and a significant reduction in GHG emissions can be expected by use of gene-modified starch-rich non-food biomass and/or second-generation fermentation plants with improved conversion of lignocellulose. First-generation plants use only the sugar and the starch in the biomass material and are therefore only highly effective with starch-rich materials like sugarcane. On the other hand, second-generation fermentation plants can also convert most of the lignocellulose (cellulose, hemicellulose and lignin) to useful chemicals, which is necessary when, for instance, straw is the biomass feedstock.[9] Thus these new improved technologies for biomass conversion uses less non-renewable energy and give both a higher CO_2 reduction and a higher ethanol yield than first-generation plants due to a higher utilization of the feedstock.[10,11] Moreover, the feedstocks for second-generation plants are cheaper (agricultural waste etc.) and do not give the same ethical concerns when using potential food resources for energy production. In the second-generation biorefinery, the highest CO_2 reduction is reached by co-producing other valuable products. In the Danish bioenergy concept this is achieved by co-producing methane and hydrogen.[12] Another significant issue is that abundant coal resources are the primary source of non-renewable energy in conversion of biomass into ethanol. In that way, a premium liquid transportation fuel is produced from a less valuable energy resource, which further reduces the need for import of petroleum.[13]

The environmental impact of using blends of ethanol–gasoline depends on the actual fraction of ethanol in the blend. A recent review by Niven questions whether the use of ethanol as a fuel additive has any environmental advantage compared to using pure gasoline.[15] A fuel blend of 10 vol% ethanol offers little reduction in GHG emissions or improvement in energy efficiency, with the drawback of increasing risk and severity of soil and groundwater contamination. Increasing the ethanol fraction to 85 vol% decreases emissions of GHG, but may cause significant air pollution in the form of NO_x and organic compounds.[14] However, if 85 vol% ethanol is the goal, alterations to existing combustion engines are necessary, and different car exhaust catalysts could probably reduce the emissions of NO_x and organic compounds. When 10 vol% mixtures are used, ethanol works as an octane enhancer and improves combustion, which reduces CO and ground-level ozone emissions.[13] Ethanol is also less poisonous to the environment than other octane boosters such as lead and methyl *tert*-butyl ether (MTBE).

Another possible future use of bioethanol to supply a sustainable/green transportation fuel is catalytic steam reforming for production of H_2. Many consider hydrogen to be a future energy source, especially for the transportation sector and mobile devices.[15] Today most hydrogen is produced from steam reforming of natural gas. However, this is not a solution to substantially decrease emissions of GHG to the atmosphere. There are two primary reasons as to why conversion of bioethanol to hydrogen is promising. First, direct combustion of ethanol used for transportation is estimated to have an energy efficiency of approximately 20%, whereas utilizing hydrogen in a fuel cell has an energy efficiency of up to 60%.[16] Therefore, even though the conversion of ethanol to hydrogen requires some energy input, it may be possible to capture more than 50% of the energy from photosynthesis as electricity from autothermal reforming of ethanol.[17] Secondly, the most expensive step in using bioethanol directly as a fuel is removal of the water. With steam reforming of ethanol to hydrogen, it is not necessary to remove water, making the process considerably cheaper. Ethanol can also be used directly in a fuel cell. However, the efficiency of the current direct ethanol fuel cell is quite inadequate.[18] The catalytic chemical reactions for steam reforming of bioresources are very complex. Specific information about the intermediates can, however, be provided by computational methods and thereby help pinpoint where to set in catalytic modifications to improve this viable route to large-scale hydrogen production.[19]

FEEDSTOCK

More than 95% of all carbonaceous chemicals are produced from fossil resources. The only existing alternative to produce these chemicals is to use biomass and biomass-derived molecules as feedstocks. The chemical industry is enormous, and a significant reduction in GHG emissions could therefore be achieved by a change to renewable CO_2-neutral resources. Bioethanol production is already implemented in many places around the world and in progress in many other places. This means that the amount of bioethanol available most likely will keep increasing for several years. Studies suggest a yearly increase of approximately 6.5% until 2020, leading to an annual production of more than 120 billion liters in 2020.[20] With this amount of bioethanol available, there is great promise in partly converting the chemical industry to one based on renewable resources.

Instead of using bioethanol for transportation fuel purposes where it has a relatively low value, it could instead be used as feedstock for other important chemical products with a much higher value. Figure 3 illustrates some possible uses of biomass-derived ethanol. Besides its use for hydrogen production by steam reforming or the direct use as a fuel or fuel additive, it could be utilized for producing acetaldehyde, ethylene, butadiene and acetic acid, among others. The annual amount of these chemicals produced worldwide is around 1.4, 120, 7.5 and 8.5 million tons, respectively.[21] Today, the annual production of bioethanol is around 45 million tons, which means that it could replace a significant amount of these petrochemical products. For this to be economically viable, the products produced from bioethanol must obviously be more valuable than the bioethanol itself. Moreover, it is necessary to keep the conversion processes inexpensive.

The production costs for bioethanol is on average around 250 US $ per ton, for ethylene it is around 700 US $ per ton, and for acetic acid it is around 650 US $ per ton.[5] Looking into the amounts and production costs of the respective chemicals, it seems realistic to produce, for example, acetic acid from bioethanol with the proper catalytic reaction pathway. Such a reaction was recently proposed, where ethanol is oxidized with air in an aqueous-phase reaction over a gold catalyst.[22] Moreover, analysis of the reaction indicates that it is competitive both economically and environmentally to the conventional petrochemical production of acetic acid by the Monsanto process. With regard to CO_2 emission, the Monsanto process produces around 0.7

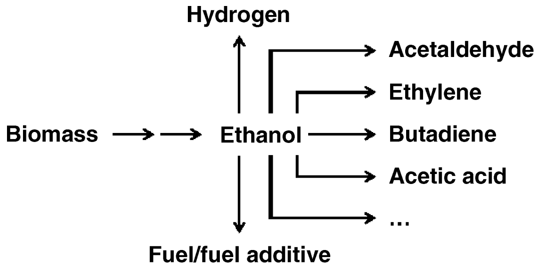

Figure 3. Possible uses of bioethanol as a fuel or as a feedstock for important bulk chemicals.

tons of CO_2 for every ton of acetic acid, whereas production from bioethanol is almost CO_2 neutral. Thus, production of chemicals from bioethanol can actually lead to higher CO_2 savings than by using it as a fuel. At the moment, it is not possible to produce all the required ethylene from bioethanol, because ethylene is produced in much greater amounts than bioethanol. This, though, is likely to change in the future with increasing production capacity of bioethanol and eventually with increasing oil prices. However, in the foreseeable future, the production of bioethanol will most likely be smaller than the production of the most important carbon-containing commodity chemicals, and therefore it could easily be an important feedstock for several of these.

THE FUTURE

During the previous century, petroleum became an essential source for energy and commodity chemicals. One future goal is to convert biomass into products that can compete with corresponding products derived from fossil resources with a focus on sustainability, resource availability and supply reliability. The aim for the US Department of Energy is to replace 25% of carbonaceous chemicals with biomass-derived chemicals by 2025.[7] To achieve this goal, there is a need for some manageable oxygenated molecules. With its large-scale production ethanol is an obvious choice for such a molecule, but other easily available molecules from biomass, like glucose and fructose, could also be very important for attaining this and further ambitions.

The most energy-efficient utilization of dry biomass is to use it in a combined heat and power plant, where it directly substitutes fossil fuels on a 1:1 basis, and yields energy efficiencies above 90%. Furthermore, a 50% increased CO_2 reduction can be achieved if biomass is used for combined heat and power production instead of production of bioethanol using first-generation technologies.[23]

Recently, it was estimated for the European Union that around 20% of the total energy consumption in the future could be covered from the use of biomass, without compromising the need for food. Thus, biomass cannot alone cover the energy demands.[24]

The main motivation for producing ethanol has so far been the need for transportation fuels. The consumption of transportation fuels alone in the United States is over 530 billion liters per year, whereas US bioethanol production was only about 15 billion liters in 2005.[25] Bioethanol will most certainly have some positive influence on CO_2 emissions from the transportation sector, but it might prove possible to achieve an even better environmental effect by using it as a feedstock for the chemical industry. Finding effective catalytic reaction pathways for producing commodity or specialty chemicals from bioethanol rather than using it to substitute the least expensive fossil products, such as the fuels, will most likely hold the greatest economic promise. Thus, the optimal use of bioethanol, in terms of efficiency, could well be to incorporate it into high-value materials otherwise produced from fossil resources and eventually burn the resulting waste in a thermal power station for heat generation.

The central point is that all available resources, both fossil and renewable, are limited and it is essential that we carefully consider how each is best used. This is a future key challenge for chemical research and development.

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Review

Maximizing renewable hydrogen production from biomass in a bio/catalytic refinery

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Abstract

Biological production of hydrogen from biomass by fermentative or photofermentative microorganisms has been described in numerous research articles and reviews. The major challenge of these techniques is the low yield from fermentative production, and the large reactor volumes necessary for photofermentative production. Due to these constraints biological hydrogen production from biomass has so far not been considered a significant source in most scenarios of a future hydrogen-based economy.

In this review we briefly summarize the current state of art of biomass-based hydrogen production and suggest a combination of a biorefinery for the production of multiple fuels (hydrogen, ethanol, and methane) and chemical catalytic technologies which could lead to a yield of 10–12 mol hydrogen per mol glucose derived from biological waste products. Besides the high hydrogen yield, the advantage of the suggested concept is the high versatility with respect to input of different types of biological wastes, which are abundant and cheap residues from agricultural production. Also the concept leaves the opportunity to optimize the microbiological and catalytic processes to meet specific needs for fuel flexibility.

Keywords: Fermentative hydrogen production; Biorefinery; Chemical catalysis; Ethanol; Methane

Contents

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1. Introduction

The world energy demand has tripled since 1949 and is still increasing mainly due to the industrial development in China and India but also due to the globally fast growing transport sector. Today, 86% of the world energy consumption and almost 100% of the energy used in the transportation sector is constituted by fossil fuels [1]. Within this centennial it is assumed that the world's accessible oil reservoirs will be close to depletion and it is, therefore very important to develop suitable long-term technologies based upon renewable energy that gradually can substitute the declining fossil fuel production.

Also fossil fuels have had a major impact on the CO_2 concentration in the atmosphere. At present, the CO_2 concentration is the highest ever recorded, exceeding pre-industrial concentrations by almost 100 ppm and are far above concentrations measured in gas pockets of ice cores, reaching back 400.000 years [2].

One possible successor to the fossil fuel era is the establishment of a hydrogen society, where hydrogen produced from renewable sources is the primary energy carrier (Fig. 1). The two most important challenges are to generate enough hydrogen from renewable sources and to lower the production cost of hydrogen. Other problems concerned are the storage, distribution and utilization of hydrogen. Currently, most hydrogen is produced from fossil fuels, since this is the most cost-effective [3]. However, several ways of producing hydrogen by other technologies and from renewable resources are emerging.

An obvious source of hydrogen is seawater, which can be split by electrolysis, and splitting of water into hydrogen and oxygen on metal surfaces has been the focus of several recent studies, e.g., [4]. The electricity needed for this can be produced from renewable sources such as sun, wind and geothermal energy [5]. Also biomass can be used as a source for hydrogen production [6]. To minimize conflicts with global food supply, however, agricultural and municipal waste should be the preferred biomass for energy production. This is possible but more difficult compared to the conversion of crops such as corn and sugarcane that are rich in starch and sugar [7]. Using waste as an energy source, both reduces the CO_2 emission and exploits an otherwise unused product.

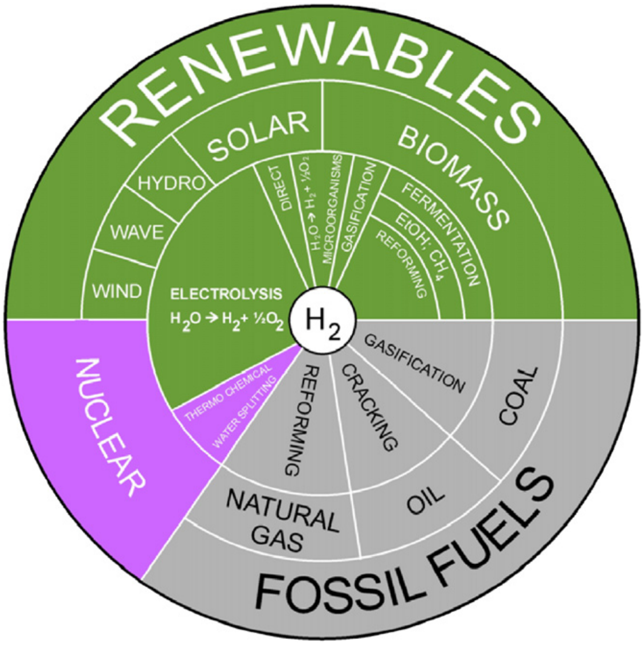

Fig. 1. Potential sources of hydrogen.

2. Biological hydrogen production from biomass

Biological production of hydrogen from biomass proceeds through either dark fermentation or photofermentation. Biophotolytic production of hydrogen is carried out by some algae and cyanobacteria, but since this is not a biomass converting process, it will not be considered in this review.

2.1. Dark fermentation

Dark fermentation of organic matter is an obligate series of microbial processes occurring under anaerobic conditions when no electron acceptors (O_2, NO_3^-, SO_4^{2-}, Fe^{3+}, etc.) are present. A part of the substrate carbon is oxidized and another part is reduced leading to the formation of products that are more or less oxidized than the original substrate. Electrons derived from this process are used for the reduction of protons to molecular hydrogen. In all thermodynamically feasible dark fermentation processes exploited by known microorganisms, hydrogen is only produced in combination with volatile fatty acids (VFA) and/or alcohols—never as the single reduced compound. Therefore, the maximum theoretical hydrogen yield of 12 mol/mol (Table 1), from complete conversion of glucose to hydrogen and carbon dioxide is never attained in known biological *in vivo* systems. Due to these thermodynamic constraints, the maximum attainable hydrogen yield from hexose fermentation is considered to be 4 mol/mol and can be performed by numerous species belonging to bacterial genera such as *Enterobacter* and *Clostridium* (reaction 3, Fig. 2) [8]. The production of larger amounts of H_2 would happen at the expense of cell growth, which would cause evolutionary elimination. In practical fermentation processes the yield is even lower (Table 2) since a very low hydrogen partial pressure is required to avoid that competing intracellular H_2 consuming reactions leading to smaller H_2 yields are favored [9]. To circumvent this, purging with N_2 or Ar has been attempted [10]. This increases the hydrogen yield closer to the attainable maximum, but also demands subsequent gas separation. Since the H_2 yield is a function of the equilibrium of the reactions in Table 1, temperature, substrate and product concentrations as well as pH influence the maximum H_2 outcome.

A major problem in direct fermentation of agricultural and municipal wastes is the activity of hydrogen utilizing acetogenic bacteria and methanogenic archaea present in the substrate, which rapidly will convert hydrogen to acetate and methane (Table 1). Several other hydrogen utilizing processes can occur in open systems and it is, therefore, necessary to sterilize the substrate and inoculate with specific organisms. Decreasing the hydraulic retention time and lowering of pH has been

Table 1
Energy yield from hydrogen producing and consuming microbial reactions

Process	$\Delta G'_0$ (kJ/mol)
Production	
$C_6H_{12}O_6 + 12H_2O \rightarrow 12H_2 + 6HCO_3^- + 6H^+$	+3.2
$C_6H_{12}O_6 + 4H_2O \rightarrow 4H_2 + 2HCO_3^- + 2CH_3COO^- + 4H^+$	−206
$C_6H_{12}O_6 + 2H_2O \rightarrow 2H_2 + CH_3CH_2CH_2COO^- + 2HCO_3^- + 3H^+$	−254.3
Consumption	
$4H_2 + HCO_3^- + H^+ \rightarrow 2CH_4 + 3H_2O$	−135.6
$4H_2 + 2HCO_3^- + H^+ \rightarrow CH_3COO^- + 4H_2O$	−104.5

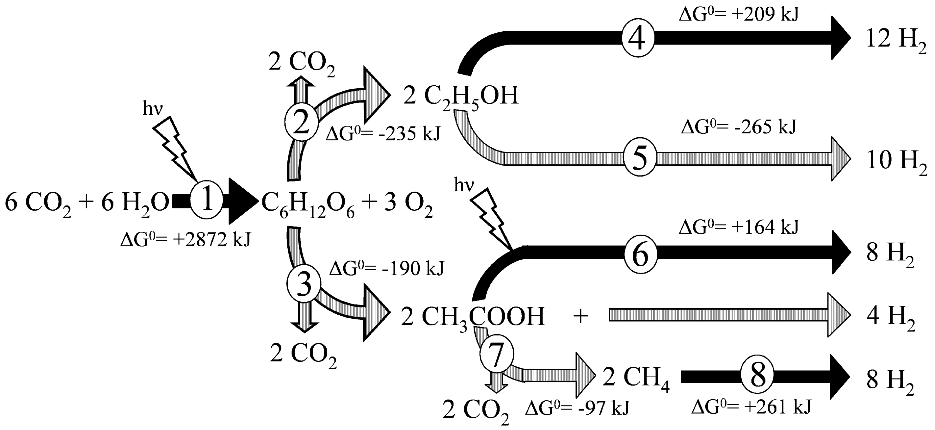

Fig. 2. Overview of biological and catalytic processes leading to the formation of hydrogen. Arrows in black represent endergonic processes, while hatched arrows represent exergonic processes. A lightning indicates photo-processes driven by light energy. Reaction 1: photosynthesis as carried out by plants and algae. Reaction 2: ethanol fermentation as carried out by yeast. Reaction 3: anaerobic fermentation to acetate, carbon dioxide and hydrogen. Reaction 4: hypothetical hydrogen production from ethanol. Reaction 5: autothermal reforming [36]. Reaction 6: photofermentative hydrogen production. Reaction 7: methanogenesis. Reaction 8: steam-reforming of methane.

Table 2
Hydrogen yield from microbial fermentative in vivo experiments

Organisms	Substrates	Process	Maximum yield (mol H_2/mol hexose)	Reference
Enterobacter cloacae	Glucose	Batch	2.2	[41]
	Sucrose		3.0	
Enterobacter aerogenes	Molasses	Batch	0.52	[42]
		Batch, Ar purging	1.58	
Rhodopseudomonas palustris	Glucose	Batch, intermittent purging with Ar	2.76	[43]
Clostridium butyricum	Glucose	Continuous culture, N_2 purging	1.4–2.3	[44]
Mixed microbiota	Starch	Chemostat	1.7	[45]
Mixed microbiota	Sucrose and sugarbeet extract	Continuous culture	1.0	[46]
		Continuous culture, N_2 purging	1.7	

shown to inhibit hydrogen consuming microbes since most of these grow relatively slowly and at neutral pH [11,12]. Also, a high-temperature pretreatment step is often included if lignocellulosic material is used as substrate. This will sterilize the material.

To go beyond the border of 4 mol hydrogen/mol hexose and approach the theoretical maximum of 12 mol of hydrogen it might be possible to engineer suitable organisms since potentially usable biochemical pathways are known. This has to our knowledge not been practiced in living cells, but Woodward et al. [13] have demonstrated that it was possible to generate 11.6 mol H_2 per mol glucose-6-phosphate by combining the enzymes of the oxidative pentose phosphate cycle under optimized *in vitro* conditions.

The ongoing intensive genome sequencing of microorganisms will result in a further understanding of pathways leading to hydrogen formation and might also elucidate potential means to modify these pathways, combining pathways from organisms of ecological niches and taxonomic groups which do not meet in nature.

2.2. *Integrated photofermentative hydrogen production*

The low hydrogen yield attained in dark fermentation reactions and the residual VFA in the fermentation liquor has led to the obvious combination of the dark fermentation process with a bacterial photosynthetic hydrogen production process converting VFA to H_2 and CO_2. Purple non-sulfur bacteria can utilize VFA such as acetate as electron donors in a hydrogen producing light driven process catalyzed by nitrogenase under nitrogen deficient conditions. The theoretical yield of this process is 8 mol H_2 per mol of acetate (reaction 3, Fig. 2). Numerous experiments have been carried out on photofermentative H_2 production either with different wastes as direct substrate or in series following a dark fermentation reactor [14,15]. A major challenge in this process is the demand for anaerobic photobioreactors taking up large areas. Claasen et al. calculated that the required area of a photobioreactor converting the effluent of a 450 m^3 dark fermentation reactor would be 12 ha since the solar conversion efficiency and the production rates are very low [15]. In a recent analysis of practical application of biohydrogen production, Levin et al. [16] calculated the reactor volume necessary to power a 1 kW PEM fuel cell. The necessary volume of a mesophilic dark fermentation reactor was 0.2–1.14 m^3, while a photobioreactor yielding the same amount of H_2 would have a volume of 149 m^3. Similar to the dark fermentation processes, genome sequencing and analysis might also lead to improvement of photofermentative processes, which so far only have been improved by unspecific mutagenesis. Photofermentative hydrogen production using current state of the art organisms and technology has, however, been considered economically unrealistic by many authors [16,17].

3. Chemical conversion of biomass to hydrogen

Presently, most hydrogen is manufactured from fossil resources and is immediately, and without separation, utilized at the same industrial site as a feedstock for large-scale commodity chemicals, e.g., for production of ammonia and methanol [18]. The most important processes for hydrogen production are coal gasification and catalytic steam-reforming of alkanes, primarily methane. By use of the steam-reforming technology, which is the most energy-efficient process for hydrogen production today, it is possible to construct plants with production capacities in excess of 250 000 m^3 H_2 (STP) per hour [19]. Ideally, four molecules of hydrogen are formed for each molecule of methane when it reacts with water according to reaction 8 (Fig. 2). However, in practice about $\frac{1}{3}$ of the methane must be combusted to supply the energy needed for the endothermic steam-reforming reaction which is typically conducted at temperatures about 800 °C [20]. The cost of hydrogen supplied by either coal gasification or catalytic steam-reforming is very dependent on the cost of the fossil feedstock and on the need for transportation. Relatively modest improvements in these mature, and energy-efficient technologies are expected but currently there are significant efforts to design and construct plants with increasing production capacities to benefit from the economy-of-scale. This development is largely driven by the desire to produce liquid transportation fuels from natural gas (and possibly at some point from coal) in the Fischer–Tropsch process [21].

The degradation of biomass into hydrogen requires rupture of C–C, C–O, C–H and O–H bonds, and formation of H–H and new C–O and O–H bonds. This can be achieved in biomass gasification which, in principle, is analogous to coal gasification in an essentially thermal process [22]. However, recently it has been shown that biomass monomers, such as glucose, can be steam-reformed at relatively mild conditions, e.g., 200 °C, into hydrogen [23] in the presence of suitable catalysts [24]. In principle, one molecule of glucose could be reacted with water to produce 12 molecules of hydrogen (Table 1). So far it has, however, only been possible to achieve about six molecules of hydrogen since methane is formed simultaneously by catalytic CO or CO_2 hydrogenation.

4. Biomass conversion in biorefineries

Traditionally, the development of biological processes to transform biomass to more versatile energy carriers has focused on the production of one energy carrier, either hydrogen, methane, or ethanol. During the last decade, however, several studies have been carried out on the production of methane and hydrogen in two-step processes [25–27]. Among the energy carriers, only methane is released from the conversion of organic matter in nature; both hydrogen and ethanol are intermediates during anaerobic degradation and are further metabolized to methane in nature [28]. The production of these two energy carriers, therefore, demands a physical separation of individual processes in the anaerobic degradation chain, or the use of defined microbial cultures under controlled conditions. This can be carried out in a biorefinery, which is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass [29]. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum. Industrial biorefineries have been identified as the most promising route to the creation of a new biobased industry [30].

By producing multiple products, a biorefinery can take advantage of the differences in biomass components and intermediates and maximize the value derived from the biomass feedstock. A biorefinery might, for example, produce one or several low-volume, but high-value, chemical products and a low-value, but high-volume liquid transportation fuel, while generating electricity and process heat for its own use and perhaps enough for sale of electricity. The high-value products enhance profitability, the high-volume fuel helps meet national energy needs, and the power production reduces costs and avoids greenhouse-gas emissions.

An example of a biorefinery for production of several products by the biochemical route is now under construction in Tennessee in a joint venture between the companies Dupont and Tate and Lyle. The plant will produce a mixture of compounds including a bio-polymer (1,3 propandiol) with the same properties as polyester in addition to other products including ethanol using corn as raw material. Production of the new biopolymer Bio-PDO ™ uses 40% less energy than would be needed to produce a petroleum-based equivalent. The new plant will save the equivalent of 10 million gallons of gasoline per year, or enough to fuel 22,000 cars annually [http://npe.dupont.com/pr-npe-renew-rsrcs.html].

4.1. Energy production in biorefineries

There is currently a tremendous world-wide interest in the production of ethanol from biomass, and in countries like USA and China, major national biofuel programs have been initiated to produce cost-efficient ethanol and other fuels from agricultural and forestry lignocellulosic biomasses. Technologically, lignocellulosic biomass is pre-treated by acid hydrolysis or other physical or/and chemical methods, followed by enzymatic hydrolysis to open the plant fibers and to convert the polymers of cellulose and hemicellulose to sugars accessible to fermenting microorganisms such as bakers yeast (*Saccharomyces cerevisiae*). The hydrolysis processes are, however, costly and *S. cerevisiae* is unable to ferment pentoses released from hemicelluloses. Yeast strains carrying out this process have, however, been constructed, but the rates and yields are still low [31,32]. Therefore, several new types of fermentations are currently being developed using different species of bacteria instead of, or as a supplement to, yeast fermentation. The use of extremophilic bacteria growing at temperatures close to the boiling temperature of ethanol has been appealing since a continuous stripping of ethanol can be performed reducing product inhibition problems caused by high ethanol concentrations [33]. Similar to the dark fermentative production of hydrogen, bacterial ethanol production often results in other products such as hydrogen and organic acids to maintain the electron balance and the thermodynamic efficiency. To yield the maximum available energy from biomass conversion, therefore, a combination of two or more biological processes in biorefinery concepts is obvious.

The Danish Bioenergy Concept is such a combinatory system approach (Fig. 3) [34]: Briefly biomass is pre-treated by wet oxidation to convert lignocellulosic compounds and to increase the availability of fermentable sugars, which are subsequently fermented to ethanol by yeast cells. Pentoses, which are not converted by yeasts, are then fermented to ethanol and hydrogen in a thermophilic fermentation process. Manure can be mixed in as a cheap source of water and as a way to increase production of methane from the effluent from the ethanol/hydrogen process. Process water can be partly re-circulated after purification in the methane step.

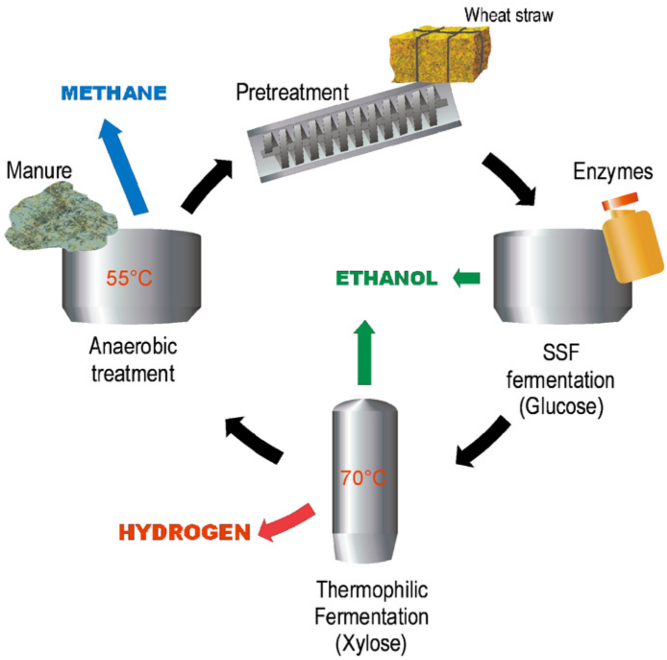

Fig. 3. The Danish Bioenergy Concept. See text for detailed description.

Instead of concentrating on the biological production of only one energy carrier, the simultaneous production of hydrogen, methane, and ethanol leaves the possibility to optimize the exploitation of the specific energy carriers to suit specific needs corresponding to the current use of specific fossil fuels for specific purposes. Hydrogen can for instance be used in fuel cells for urban transportation. Ethanol can be used in fuel cells in rural areas, and methane can be used for local electricity and heat production in fuel cells or microturbines. Despite the obvious advantages of combining the production of different energy carriers, only few concepts have been published. Common to the known concepts is a much better exploitation of the biomass by suiting specific microbiological processes to the conversion of different fractions of the substrates to different fuels. The different processes are thereby exploited in an additive sequential fermentation transforming most of the energy available in the substrate to usable energy carriers. The production of several energy carriers leaves the possibility to optimize the production of one energy carrier at the expense of the other carriers by choice of microorganisms and operation conditions, and by genetic modification of the microorganisms. Currently the Danish Bioenergy Concept is optimized with respect to ethanol production.

Furthermore, biorefineries might be considered as more environmentally friendly processes since process water and nutrients from the different processes can be recirculated, and waste production can be kept minimal.

4.2. Bio/catalytic conversion of biomass to bioenergy

A further development of the biorefinery, and a promising alternative to specialized fermentative hydrogen production is the use of hybrid techniques combining biological conversion with catalytic down-stream processing (Fig. 4). This might

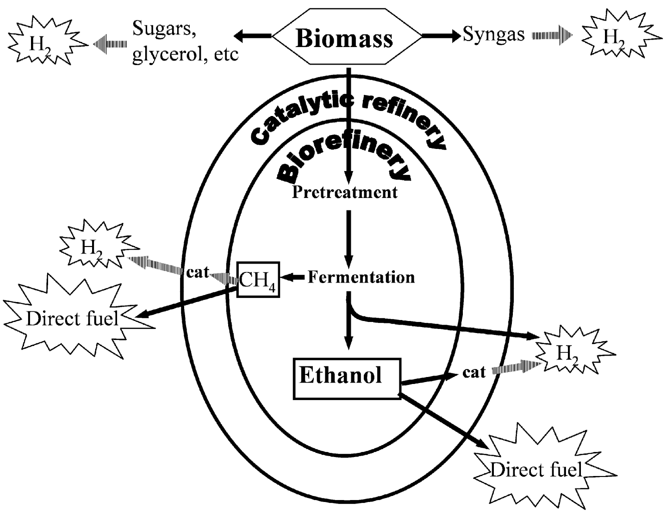

Fig. 4. Bio/catalytic conversion of biomass to hydrogen and other fuels. Hatched arrows indicate catalytic conversion.

particularly be relevant in the replacement of gasoline with hydrogen in the automobile sector where the storage technology of sufficient amounts of hydrogen has still not been satisfactorily solved [35]. Highly efficient autothermal reformers capable of converting 1 mol ethanol to 5 mol hydrogen have recently been demonstrated [36]. Since 2 mol of ethanol can be achieved for each sugar molecule, the hydrogen yield of this two-step process is 83% of the theoretical maximum compared to the 10–20% achieved by direct hydrogen fermentation. So far, however, the only known catalyst for the autothermal process is an extremely expensive supported rhodium catalyst [37].

As described in Section 3, it is possible to convert various carbohydrates and lower alcohols directly into a mixture of hydrogen and carbon oxides by aqueous phase reforming conducted at about 200 °C. In principle, the low-temperature aqueous phase reforming process can supply even more hydrogen than the autothermal reforming process, but this process is endothermic and thus requires continuous heating. Therefore, both of these processes hold potential for integration with a biorefinery designed to co-produce hydrogen. In scenarios, where stand-alone hydrogen facilities are desired, the autothermal reforming process would be preferred, especially if cheaper catalysts were developed. In scenarios where process integration is extensive, the low-temperature aqueous reforming process might represent the best choice, since other process streams, such as methane, can be used to provide the required heating. For both reforming processes, further developments are required before they can be implemented into large-scale applications. Particularly, more stable and less-expensive catalysts are required, and additionally, the preferred catalyst systems need to be tested with relevant feedstocks from a biorefinery.

The introduction of downstream catalytic conversion of biofuels leaves the possibility to combine a less complex fuel handling technology (ethanol instead of hydrogen) for transportation purposes with all the benefits of the fuel cell technology. In the transition period before a hydrogen-based energy economy has been realized, a gradual change to the use of renewable energy can be facilitated by the use of suitable biofuels in existing internal combustion engines. Acidic zeolite catalysts have attracted considerable attention as a possible means of converting fossil resources such as coal or natural gas into transportable liquid fuels *via* synthesis gas. In fact, for a significant period of time, the so-called methanol-to-gasoline (MTG) process was performed on an industrial scale to supply the majority of all gasoline consumed in New Zealand [38]. Since then Gayobo et al. and Aguayo et al. have demonstrated the conversion of ethanol into liquid fuels (biogasoline) [39,40]. Although compressed methane, and ethanol in even high ethanol:gasoline mixtures can be used with few modifications of the engines, biogasoline produced by catalytic conversion of methane and bioethanol will have fewer implications with respect to logistics and end use. If aviation and air transport are sustained in future transportation scenarios, the availability of safe liquid fuels with high energy content storable under ambient conditions is a prerequisite. Neither hydrogen, methane nor ethanol fulfill these requirements while hydrocarbons produced catalytically from refined biomass might constitute a satisfactory solution.

A current environmental concern regarding bioethanol: gasoline mixtures is the increase in vapor pressure in the mixture caused by ethanol. We suggest that catalytic conversion of ethanol to gasoline could solve this problem in the transition period towards a hydrogen-based society.

Acknowledgments

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Aerobic oxidation of aqueous ethanol using heterogeneous gold catalysts: Efficient routes to acetic acid and ethyl acetate

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Abstract

The aerobic oxidation of aqueous ethanol to produce acetic acid and ethyl acetate was studied using heterogeneous gold catalysts. Comparing the performance of Au/$MgAl_2O_4$ and Au/TiO_2 showed that these two catalysts exhibited similar performance in the reaction. By proper selection of the reaction conditions, yields of 90–95% of acetic acid could be achieved at moderate temperatures and pressures. Based on our findings, a reaction pathway for the catalytic oxidation of ethanol via acetaldehyde to acetic acid is proposed, and the rate-determining step (RDS) in the mechanism is found to be the (possibly oxygen-assisted) dehydrogenation of ethanol to produce acetaldehyde. It also is concluded that most of the CO_2 formed as a byproduct in the reaction results from the absorbed intermediate in the dehydrogenation of ethanol to produce acetaldehyde. By varying the amount of water in the reaction mixture, the possibilities for producing ethyl acetate by the aerobic oxidation of ethanol is also studied. At low ethanol concentrations, the main product is acetic acid; at concentrations >60 wt%, it is ethyl acetate.

Keywords: Heterogeneous catalysis; Gold; Aerobic oxidation; Acetic acid; Ethyl acetate; Bioethanol

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1. Introduction

Gold catalysis has attracted significant attention over the last two decades [1–4]. This increasing interest can be traced back primarily to two pioneering discoveries: the aerobic oxidation of CO and the addition of HCl to acetylene by Haruta et al. [5] and Hutchings et al. [6], respectively. Initially, it was primarily the possibility of performing preferential oxidation of carbon monoxide to carbon dioxide with dioxygen in the presence of dihydrogen that led to the growing interest in the special reactivity of supported nanosized gold particles [7,8]; however, most recently, the selective oxidation of alcohols to carbonyl compounds with dioxygen/air over gold catalysts has become of interest. Both supported gold particles and polymer-stabilized clusters have been investigated as possible catalysts for the selective oxidation of alcohols [9,10]. The substrates investigated to date include aromatic, aliphatic, and allylic alcohols; both primary and secondary alcohols; and some polyols. It has been suggested that aliphatic alcohols can be more difficult to oxidize than benzyllic alcohols [11]. For the polyols, gold catalysts have been reported to exhibit a higher chemoselectivity than the analogous supported palladium and ruthenium catalysts [12–14], thereby making it possible to control the alcohol group in the polyol that is preferentially oxidized. For the oxidation of aliphatic diols containing both a primary and a secondary alcohol group, the regioselectivity is highly shifted toward oxidation of the primary alcohol group [15]. In addition, the effect of the solvent is noteworthy, because in aqueous solution, the carboxylic acid is favored over the aldehyde, but in solvent-free experiments, aldehyde is favored [12]. Moreover, the use of Fe_2O_3 or C as a support material seems, in contrast to CeO_2-, TiO_2-, or SiO_2-supported catalyst, more active toward the formation of esters [16]. The group of Prati and Rossi investigated the oxidation of both simple alcohols and more complex polyols such as glucose [17–21]. They also studied in more detail the reactivity of various diols, particularly ethylene glycol

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and phenylethane-1,2-diol [15,22–25]. In these studies, it was found that the activity of gold on metal oxides increased with decreasing particle size, whereas for gold on carbon catalysts, the activity apparently reached a maximum at a mean diameter of 7–8 nm [22]. Hutchings et al. worked with both pure supported gold catalysts and Au/Pd alloys for the oxidation of alcohols and aldehydes [15,26]. Carrettin et al. studied the oxidation of glycerol in aqueous solution and found that oxidation occurred only in the presence of a base but still at moderate temperature (333 K) and with high selectivity [27,28]. Similarly, others also have conducted oxidation of glycerol with dioxygen using gold catalysts and found that the selectivity varied significantly with conversion [29]. Recently, Corma et al. used supported gold catalysts for the solvent-free oxidation of various alcohols and concluded that nanocrystalline CeO_2 acts as a co-catalyst, improving the catalytic activity of the gold [30]. They demonstrated that the gold catalyst is superior to palladium catalysts in the selective oxidation of secondary alcohols to form ketones [12], and also investigated the oxidation of allylic alcohols in detail [31]. In the case of the allylic alcohols, the gold catalyst was found to have significantly greater chemoselectivity than the Pd catalyst; moreover, gold makes it possible to form mainly the α,β-unsaturated carbonyl compound. Idriss et al. investigated the gas-phase oxidation of ethanol over an Au/CeO_2 catalyst in the temperature range of 373–1073 K and found that the product composition changed significantly with temperature [32]; at low temperatures, acetaldehyde was the main product, whereas at higher temperatures, the selectivity switched toward acetone and finally to methane.

Here we report the aerobic oxidation of one of the simplest alcohols, ethanol, using heterogeneous gold catalysts. Previously, we reported that using a $Au/MgAl_2O_4$ catalyst, high yields of acetic acid can be achieved when ethanol is oxidized in aqueous phase at moderate temperatures and pressures [33]. In this work, the influence of the support was been investigated and the reaction pathway clarified, with the origin of CO_2 as a side product in the reaction and the RDS identified. This could be important in improving the catalyst performance or for identifying completely new catalysts. Furthermore, we found that ethyl acetate also can be formed from ethanol solutions by aerobic oxidation.

The reason for specifically studying the oxidation of ethanol is that ethanol could be one of the future feedstocks of the chemical industry. Ethanol can be easily produced from agricultural products by fermentation and thus can be considered a renewable resource. The annual amount of bioethanol produced currently exceeds 50 million tons per year and is increasing. In comparison, the total amount of acetic acid produced annually is around 10 million tons. Thus, a sufficient amount of bioethanol is produced to have a significant impact, even if only part of it is used as a chemical feedstock rather than a fuel additive [34].

Crude bioethanol contains only 8–10 vol% ethanol [35], and thus purification of ethanol by distillation to produce a useful fuel is a very costly process. Consequently, an investigation aimed at determining whether crude bioethanol can be directly converted to acetic acid or ethyl ester, which could be less expensive to isolate industrially, is of great interest.

2. Experimental

All experiments were conducted in stirred Parr mini-reactor batch autoclaves, made of either T316 steel or titanium, with a total volume of 56 mL. First, 10 mL of the reagent mixture was transferred to the autoclave with 150 mg of the catalyst, after which the desired pressure of technical air was applied in the autoclave. The autoclave was heated under stirring and kept at the reaction temperature for the desired reaction time, then cooled in an ice bath to below 278 K. The liquid reaction mixture was analyzed on a Shimadzu GC-9A gas chromatograph equipped with a Nukol capillary column (15 m × 0.53 mm i.d., Supelco) and a flame ionization detector. The gas was collected in a gas sample bag and led into the sample loop of the Perkin–Elmer PE AutoSystem XL gas chromatograph equipped with a Porapak 80/100 mesh Supelco column and a thermal conductivity detector. The gas analyses were only done qualitatively, but the only gas-phase product detected was CO_2. Thus, the amount of CO_2 was calculated based on the carbon mass balance, because this was the only gaseous product of the reaction. The catalyst used for all experimental work (1.5% Au/TiO_2) was purchased from the World Gold Council and is a reference catalyst [36]. The catalyst was characterized by XRD, which showed that the TiO_2 support was phase-pure anatase. The pore volume and surface area were determined to be 0.507 and 45.6 m^2/g, respectively. The $Au/MgAl_2O_4$ catalyst was prepared as described previously [33]. A series of experiments with a 5 wt% solution of ethanol (1.09 M) was conducted to investigate both the time dependence and the temperature dependence of the formation of acetic acid and side products. Measurements were conducted in the temperature range of 363–473 K for time spans ranging from 15 min to 24 h. Furthermore, the catalyst was recycled several times to investigate the catalyst's lifetime/reusability.

To investigate which step in the oxidation of ethanol to acetic acid could be rate-limiting, experiments were conducted with a 5 wt% acetaldehyde solution at reaction times of 0.5–4 h. To further clarify the mechanism, experiments with aqueous solution of acetic acid also were conducted. All of the experiments designed to investigate the kinetics were conducted at 423 K and 3.5 MPa pressure.

For the ethyl ester formation, the reactions were run in several steps to achieve a sufficiently high oxygen content without going to pressures >3.5 MPa (at room temperature). This was done by first conducting one step as for the acetic acid formation and then quenching the autoclave to 273 K, with the depleted air let out. Then the autoclave was refilled with a new batch of air and the reaction was restarted. Several combinations of reaction times were investigated, but the best results were achieved when the reaction time of the first step was kept at 2 h and the second for four hours. The temperature was kept constant at 423 K for all of the experiments aimed at producing ethyl acetate. The ethanol concentration varied between 15 and 96 wt%.

Transmission electron microscopy images were obtained using a JEOL 3000 electron microscope. About 30 images were recorded for each catalyst sample.

3. Results and discussion

3.1. Acetic acid

Acetic acid is a commodity chemical that demonstrates relatively rapid growth in production volume and is used in several areas, including the production of vinyl acetate monomer, which is used for the manufacture of the polymer polyvinyl acetate. At present, the main route of acetic acid production is carbonylation of methanol [37]. This route uses fossil resources exclusively, with two separate steam-reforming steps usually involved in the process. We have previously shown that heterogeneous gold catalyst effectively facilitates the oxidation of ethanol to form acetic acid, which obviously represents a potential renewable route to acetic acid. In the present work, we studied this reaction in more detail.

We investigated the time dependency and temperature dependency of the reaction using the Au/TiO_2 catalyst under the same reaction conditions as reported for the Au/$MgAl_2O_4$ catalyst [33]. Our results show that the analogous experiments with the Au/TiO_2 catalyst gave very similar results. Fig. 1 shows temperature-dependent findings. When compared to our previous findings for Au/$MgAl_2O_4$ [33], the present results illustrate the catalysts' similar behaviors. Clearly, both the conversion and yield increased with increasing temperature; however, the two curves do not exhibit exactly the same form, providing a first indication that the reaction proceeds via an intermediate. For both catalysts, the yield of acetic acid reached >90% at high conversion; the level was slightly higher (95%) for the Au/TiO_2 catalyst than for the Au/$MgAl_2O_4$ catalyst, but the difference is close to the experimental uncertainty. This value corresponds to a space-time yield of about 0.24 mol/h/L.

Fig. 2 shows TEM images of the two catalysts demonstrating similar gold particle sizes (3–6 nm). However, on average, Au/TiO_2 has a slightly smaller particle size. Fig. 3 illustrates the effect of the reaction time on conversion and yield; it can be seen that at the given conditions, ethanol conversion increased with increased reaction time and finally reached >99%. The yield of acetic acid followed the same trend found for the Au/$MgAl_2O_4$ catalyst. Overall, the results demonstrate no significant difference between the two metal oxide supports; they do not exclude a possible influence of the support material on the catalyst activity, however. In particular, if the support were shifted to a non-metal oxide compound, the effect could be very different; this has been reported for the selective oxida-

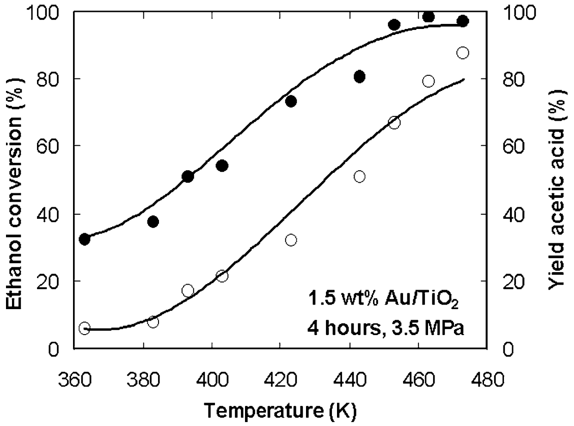


Fig. 1. Yield of acetic acid (○) and conversion of ethanol (●) as a function of temperature.

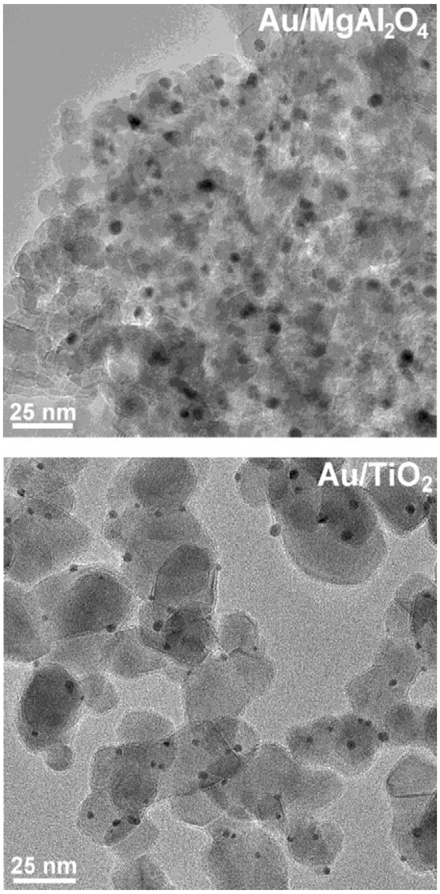


Fig. 2. TEM images of Au/$MgAl_2O_4$ (top) and Au/TiO_2 (bottom).

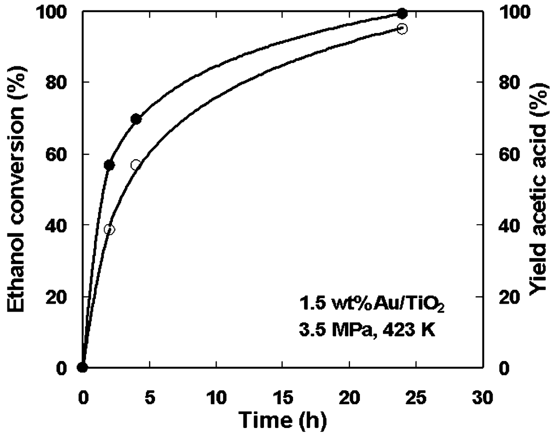


Fig. 3. Yield of acetic acid (○) and conversion of ethanol (●) as a function of time.

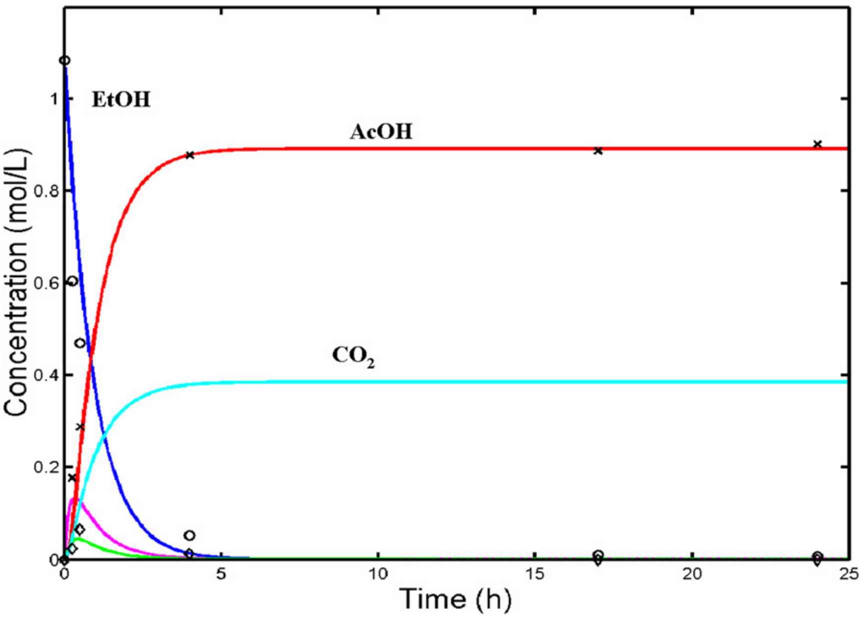


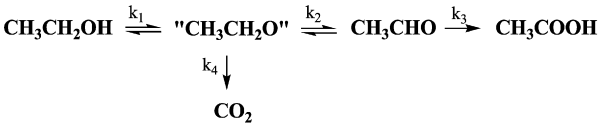
Fig. 4. Simple kinetic modeling of the reaction, solid lines theoretical values based on the reaction scheme in Fig. 5; (○, ×, ◇) experimental values (EtOH, AcOH, AcH). The green line represents acetaldehyde and the mauve the surface intermediate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

tion of glucose [38]. Preliminary experiments using carbon as a support material have not demonstrated nearly as high conversion of ethanol or selectivity toward acetic acid as found for the present metal oxide supports. Experiments conducted with the pure support materials (TiO_2 and $MgAl_2O_4$) gave acetic acid yields $<2\%$.

The long-term stability of the TiO_2-supported catalyst did not seem to be better than that of the $Au/MgAl_2O_4$. A significant decrease in activity was seen when the catalyst was reused, but it remained active even after several runs. The used catalyst showed no signs of coke formation, as supported by its color. TEM images obtained from the catalyst maintained under reaction conditions for 10 days clearly showed that the gold particle size increased significantly but remained <10 nm. Typical particle sizes in the spent catalyst were around 5–7 nm. Small alterations of the catalyst composition might possibly improve the long-term stability. Along these lines, Mirescu et al. [38] recently studied gold catalysts with quite long lifetimes, but under much milder reaction conditions than those that we used, where the catalyst was subjected to hydrothermal conditions.

3.2. Kinetics

Studying the reaction in more detail as a function of the reaction time revealed that not only acetic acid, but also acetaldehyde as well as CO_2 were formed. Moreover, a very small amount of ethyl acetate also was detected when the ethanol concentration was increased slightly. Our results demonstrate that acetaldehyde was formed in higher concentrations when the reaction time was kept short, as shown in Fig. 4. This figure clearly indicates that the reaction proceeded via acetaldehyde before forming acetic acid. To determine the RDS, an aqueous solution of acetaldehyde was used as the reagent instead of the ethanol solution. These experiments showed that the RDS



$$\begin{tikzcd} CH_3CH_2OH \arrow[r, shift left, "k_1"] & \text{"}CH_3CH_2O\text{"} \arrow[l, shift left] \arrow[r, shift left, "k_2"] \arrow[d, "k_4"'] & CH_3CHO \arrow[l, shift left] \arrow[r, "k_3"] & CH_3COOH \\ & CO_2 & & \end{tikzcd}$$

Fig. 5. Reaction pathway, "CH_3CH_2O" is the dehydrogenation intermediate.

most likely was the dehydrogenation of ethanol, because the oxidation of acetaldehyde occurred very rapidly. The CO_2 formation detected can be presumed to originate from full oxidation of an adsorbed reaction intermediate. This supposition is supported by experimental data showing that acetic acid did not decompose to form CO_2; in fact, the acetic acid concentration remained constant after 24 h. Furthermore, experiments with acetaldehyde gave 100% conversion and an acetic acid yield of at least 98%, indicating that the aldehyde was not decomposed exclusively to CO_2. This finding is in agreement with others investigators, who have proposed a similar reaction pathway for the same reaction using another catalyst [39]. The simple kinetic model in Fig. 5 explains all of these observations.

Consequently, we propose the reaction pathway shown in Fig. 5. In this pathway, ethanol is first adsorbed to the catalyst surface, where an activated intermediate species is formed, which then is oxidized/dehydrogenated to the aldehyde. Finally, the aldehyde is further oxidized to the acid. The intermediate, CH_3CH_2O, can undergo C–C bond cleavage to produce CO_2 or can lead to the formation of acetaldehyde.

The given model can be fitted quite well to the experimental data given in Fig. 4, achieving the values for the rate constants displayed in Table 1. The difference in the values for the rate constants k_2 and k_4 can be explained by the fact that the full oxidation of the intermediate (k_4) involves C–C bond-breaking, whereas dehydrogenation (k_2) requires only C–H bond-breaking, which is less demanding. Furthermore, the RDS

Table 1
Fitted values of first-order rate constants (mol/(L h))

Rate constant	k_1	k_2	k_3	k_4
Value	1.1	5.1	14.1	1.1

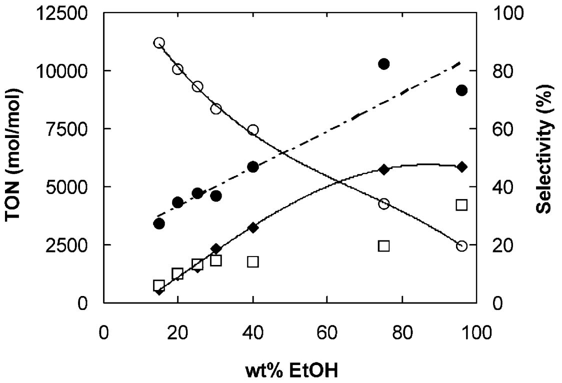


Fig. 6. Selectivity and activity of the gold catalyst as a function of the concentration of ethanol (○, acetic acid; ◆, ethyl acetate; □, acetaldehyde; ●, TON).

for the formation of acetic acid obviously is related to the activation of the ethanol (k_1). This step involves the (possibly oxygen-assisted) dehydrogenation of ethanol to form acetaldehyde.

3.3. *Ethyl acetate*

Ethyl acetate is typically produced by esterfication of acetic acid. It has a wide range of applications in, for instance, the paint industry and also is gaining interest as a substitute for methyl ethyl ketone in, for example, the food industry [40]. Previously, methyl esters have been produced by gold-catalyzed oxidation of a methanolic solution of primary alcohol using oxygen as the oxidant both with and without the presence of base [14,41]. Similarly, Corma et al. [30] reported that aliphatic primary alcohols can be oxidized to the corresponding ester. Nonetheless, ester formation in aqueous solutions has not yet been investigated in detail.

Consequently, we have explored the possibility of forming ethyl ester by making small alterations to the reaction conditions used for the production of acetic acid. Increasing the ethanol concentration increased the selectivity toward ethyl acetate, as expected. However, when the concentration was <60 wt% ethanol, the major product remained acetic acid. Fig. 6 plots the selectivity in the liquid phase as well as the turnover number (TON) as a function of ethanol concentration. The selectivities are based on the mol of products (EtOAc, AcOH, and AcH) in the liquid phase. Fig. 6 clearly shows a decrease in selectivity toward acetic acid and a concomitant increase in selectivity toward the ethyl ester. However, the selectivity toward the ester appeared to reach a maximum at the highest concentrations. The concentration of acetaldehyde, the major remaining product, increased at lower water content. Under the reaction conditions used here, ethanol conversion decreased due to the oxygen deficiency imposed by use of relatively low dioxygen pressure and reaction time, which were kept constant for all concentrations; however, the TON increased with increasing concentration, indicating that the catalyst remained active even at the high ethanol concentrations.

Under the given reaction conditions, the acetic acid-to-ethyl acetate ratio was determined largely by thermodynamic constraints. Thus, ethyl acetate formation was limited by the water content in the reaction mixture, because water obviously participates in the equilibrium for the ester formation. The water content is determined not only by the amount of water present in the feed, but also by the extent of the reaction and by the selectivity. In particular, a significant amount of water is formed when CO_2 is produced. Thus, using crude bioethanol for such an ethyl acetate process requires using a feed with a low water content, which adds to the cost of the feedstock. In addition, the importance of a highly selective catalyst is clear.

4. Conclusion

Aerobic oxidation of ethanol over a heterogeneous gold catalyst has been found to be slightly dependent on whether spinel or titania is used as the support material, with the latter giving the highest yields. Furthermore, a reaction mechanism has been postulated for the conversion of ethanol to acetic acid going through two intermediates, one unknown and the other acetaldehyde, and with only one significant byproduct, CO_2. The RDS was found to be the dehydrogenation of the ethanol to form acetaldehyde; this might be a two-step process, with a supported intermediate converted to acetaldehyde. This simple kinetic model was supported by the experimental data.

The reaction conditions were modified to seek a higher selectivity toward the ethyl ester. This was achieved by altering the ethanol concentration. At low ethanol concentration, the major product was acetic acid, but at higher concentrations, the selectivity was shifted toward ethyl acetate, as expected. However, concentrations >60 wt% were needed, indicating that water had a significant limiting effect.

Acknowledgments

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Selective gas-phase oxidation of aqueous ethanol with dioxygen using nanoparticle vanadia/anatase catalyst

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Abstract

The gas-phase oxidation of aqueous ethanol with dioxygen has been examined with a new nanoparticle V_2O_5/TiO_2 catalyst. Product selectivity could to a large extent be controlled by small alterations of reaction parameters, allowing optimization to produce acetaldehyde at selectivity higher than 90 % near quantitative conversion. Furthermore, selectivity above 80 % for acetic acid could be achieved at low gas hourly space velocity at temperatures as low as 165 °C.

Keywords: Bioethanol, acetaldehyde, acetic acid, heterogeneous catalysis, gas-phase oxidation, nanoparticle V_2O_5/TiO_2

Introduction

The continuing depletion of the available fossil resources implies new challenges to the future chemical industry, as more than 90 percent of all carbonaceous chemicals presently are produced from oil [1]. In this respect, biomass - as a renewable source - is a natural choice of alternative carbon feedstock, and actually prior to the advent of the fossil resources biomass was the primary feedstock of the chemical industry.

One of the biochemicals already produced on an industrially scale is bioethanol which reached a production of 46 billion liters in 2005 [2], primarily from fermentation. Bioethanol has found main usage as at fuel or fuel additive in the transportation sector, though at present it is impossible to produce enough bioethanol to replace gasoline. Moreover, it is required that all water, which typically accounts for up to 95 wt%, is removed from crude bioethanol prior to its use in combustion engines to reach satisfying fuel utilization. Initial flash distillation will generally provide a fraction with about 50 wt% water remaining, while further water removal is a very energy demanding and costly process, particularly due to azeotrope formation. Alternatively it has therefore been suggested that ethanol is further converted into higher value-added chemicals via reactions that are not as sensitive to the water content [3]. In this context an interesting possibility is to oxidize the ethanol whereby commodity acetyl derivatives such as, e.g. acetaldehyde, acetic acid and ethyl acetate can be formed.

The catalytic oxidation of (aqueous) ethanol using air or pure dioxygen as the oxidant has been known for many years, but has not attracted continued interest. Recently, however, we have shown that aqueous ethanol with concentrations comparable to those obtained by fermentation (ca. 5 wt% aqueous ethanol) selectively is oxidized to acetic acid in high yields (92 %) by a supported $Au/MgAl_2O_4$ catalyst in liquid phase reactions at 180 °C and 35 bar air pressure [4]. At higher ethanol concentrations (above 60%), the same catalytic reaction leads primarily to formation of ethyl acetate [5] and the reaction was shown to proceed via acetaldehyde as intermediate.

Gas-phase oxidation reactions using catalytic systems based on molybdenum oxide [6] and tin oxide-molybdenum oxide catalysts [7] (the latter with 80 % aqueous ethanol feed) have also previously been reported to selectively yield acetic acid though at much higher oxygen pressures and temperatures of 250-320 °C. Very recently a more complex catalyst composed of mixed Nb-Mo-V oxides dispersed on titania has also been applied at elevated pressure and temperature (16 bar, 237 °C) with a feed of aqueous ethanol and oxygen [8]. Also here a high selectivity towards acetic acid (95%) was found along with minor amounts of acetone, and a thoroughly kinetic investigation elucidated the importance of the presence of water in order to selectively form the acid.

Pure vanadia catalysts based on titania-modified MCM-41 or MCM-41 support have also been applied in gas-phase ethanol oxidation at ambient pressure [9]. Here reactions were found to favor formation of acetaldehyde and minor amounts of ethene at reaction temperatures below 200 °C while CO_2 predominated at higher temperatures. Only with the titania-modified catalyst was minor amount of acetic acid also observed. For the MCM-41 supported catalyst a promoting effect of sodium was further revealed with a maximum in reactivity at sodium to vanadium molar ratios of 0.5 [10]. In contrast, a V_2O_5 catalyst supported on TiO_2 and immobilized on clay was found to provide very high selectivity of 97 % towards acetic acid even at relatively moderate temperatures and pressures (180 °C and 1.7 bar) with the only byproduct being CO_2 [11], suggesting an undisclosed support effect on reaction progression.

In the present work we have investigated the gas-phase oxidation of 50 wt% aqueous ethanol at moderate temperatures of 165-215 °C and ambient oxygen pressures using a new nanoparticle V_2O_5/anatase catalyst.

Experimental

Catalyst preparation and characteristics

The oxidation catalyst used in the study was a 15 wt% V_2O_5 catalyst supported on crystalline TiO_2 as anatase. The catalyst was prepared by a novel sol-gel, co-precipitation procedure involving concomitant hydrolysis of Ti(IV)- and V(V)-alkoxides in presence of decomposable ammonium chloride crystallization germ, as recently described [12]. This synthetic procedure yielded nano-sized catalyst particles with a narrow size distribution around 12 nm (determined by TEM), and a well defined pore size distribution with pore diameters in the range 3-5 nm (calculated from nitrogen physisorption isotherms). Notable, a relative high-surface area of 127 m^2/g of the anatase support allowed loading of up to 15 wt% vanadia without exceeding monolayer coverage of V_2O_5 (surface density of vanadium atoms estimated to 7.7 V atoms/nm^2).

Catalytic gas-phase oxidations

Oxidation reactions were conducted in an all-heated stainless steel continuous, fixed-bed flow system using 200 mg of fractionized (180-300 μm) catalyst diluted with 800 mg of pre-calcined (400 °C, 3 h) SiO_2 (silica gel 100, Merck) and 50 wt% ethanol solution (prepared with 99.99 % ethanol, Aldrich) as feedstock. The liquid was continuously evaporated and mixed with oxygen (10 % O_2 in He, Strandmoellen Lab) in a Controlled Evaporator Mixer (Hi-Tec CEM unit, Bronkhorst) heated to 180 °C. The reaction pressure was kept constant during the experiments by a regulation loop consisting of a pneumatic back-pressure regulator valve (Microvalve 3510, Samson), an electronic controller (Trovis 6493) and a pressure transducer (Wika S-11). The reaction temperature was measured inside the reactor (± 0.1 ºC) by an internally positioned thermocouple (Inconel® 600, Omega) placed in the catalyst bed. During the catalytic runs gas samples (1.0 ml) were analyzed periodically every 16 min by an integrated on-line FID-GC (Perkin Elmer Autosystem XL, Nukol capillary column, 15 m × 0.53 mm ID, Supelco Inc.) using auto gas sampling until steady state was reached. The FID-GC analysis allowed determination of ethanol conversion and selectivity to acetyl products by comparison to authentic samples. The amount of carbon dioxide formed was determined from the molar balance, but was only significant (i.e. ≥ 2 %) at the highest pressures and temperatures examined.

Several reaction parameters were investigated independently by keeping all other parameters constant, including gas hourly space velocity (GHSV = 2500-50000 h^{-1}), temperature (165-215 °C), total pressure (2-10 bars) and O_2/ethanol molar feed ratio (0.5-3.3). Initial reaction conditions (i.e. standard conditions) were adjusted to a total gas flow of 100 ml/min of 10 % O_2 in helium and a liquid flow of 0.684 g/h of 50 wt% aqueous ethanol (i.e. ethanol/water molar ratio of 0.39), corresponding to an O_2/ethanol molar ratio of 3.3 and a GHSV of 25000 h^{-1}. The reaction temperature was set to 200 °C and the total pressure to 2.7 bar, which resulted in full conversion of the ethanol. At standard conditions a control experiment with pure SiO_2 (1.0 g) allowed to exclude the effect of the dilutant (10 % conversion with 96 % selectivity towards acetaldehyde) on the catalyst performance.

Results and discussion

The ethanol conversion and the selectivity towards acetaldehyde and acetic acid products was measured as a function of reaction temperature for a series of experiments performed with an O_2/ethanol mole ratio of 3.3, as depicted in Figure 1. The conversion increased with increasing temperature (as expected), reaching nearly full conversion (>99 %) at 200 °C. Moreover, the selectivity changed significantly with temperature allowing acetaldehyde to be formed at a yield above 80 % at 175 °C along with only a small amount of acetic acid and traces (≤ 1 %) of carbon dioxides. At higher temperatures the selectivity towards acetic acid increased reaching a selectivity of 55 % at 215 °C, clearly signifying the importance of the reaction temperature on product formation.

((Figure 1))

In Figure 2 the conversion of ethanol and the selectivity towards acetaldehyde and acetic acid are shown as a function of four space velocities examined (GHSV = 2500, 12500, 25000, and 50000 h^{-1}). When the residence time was increased (i.e. GHSV decreased) the reaction shifted towards formation of acid while acetaldehyde predominantly formed at short residence times, as expected if the acid is formed via the aldehyde. Notable, the conversion of ethanol remained close to 100 % in all reactions thus allowing acetic acid to be produced preferentially at lower temperatures and low space velocity, though the amount of acetic acid produced per gram of catalyst per hour (i.e. synthesis rate) of course was smaller at low space velocity. The synthesis rate of acetic acid was, for example, 0.89 g/(g cat h) at 215 °C with GHSV = 25000 h^{-1} and only 0.48 g/(g cat h) at 200 °C with a lower space velocity of 12500 h^{-}

[1]. A maximum selectivity of 99 % acetic acid with respect to acetyl products (81 % based on ethanol conversion) was reached at full ethanol conversion when the reaction was performed at GHSV = 2500 h^{-1} and 200 °C. Additionally, the selectivity and conversion changed only slightly when the temperature was reduced to 175 °C, and even at a temperature as low as 165 °C the selectivity towards acetic acid remained above 80% (73 % based on ethanol) with the conversion close to quantitative (99 %).

((Figure 2))

When reactions were conducted at different reaction pressures a significant change in the product composition was observed while conversion remained near 100 % at all pressures, as shown in Figure 3. Hence, a gradually decrease in the selectivity toward acetaldehyde from 60 to 25 % occurred when the reaction pressure was changed from 2.0 to 10 bar, while the selectivity towards acetic acid remained essentially constant at 20 %. The products accounting for the loss in acetyl selectivity was most likely mainly CO_2 formed by full oxidation and a minor amount of acetone, as also previously encountered with vanadia catalysts [11] but not observed in the presence of niobium and molybdenum which appeared to inhibit full oxidation [8].

((Figure 3))

Examination of the effect of the oxygen-to-ethanol molar ratio on the reaction using the three O_2/ethanol molar ratios of 3.3, 1.0 and 0.5 at 2.7 bars and GHSV = 25000 h^{-1}, clearly revealed a correlation between the conversions reached at analogous temperatures and the oxygen content of the feed, as shown in Figure 1 and 4. Thus, with a low O_2/ethanol molar ratio of 0.5 the conversion was 37 % at 175 °C and 91 % at 200 °C, respectively, while the analogous conversions reached 59 % and 83 % (at 175 °C) and 95 % and > 99 % (at 200 °C) for the higher O_2/ethanol molar ratios of 1.0 and 3.3. In contrast, the reaction selectivity towards acetaldehyde remained high at all temperatures (> 90 %) for the lower O_2/ethanol molar ratios, and only with presence of an excess of oxygen, i.e. with a ratio of 3.3, was acetic acid predominantly formed. Importantly, no significant amount of combustion products were detected for either of the examined O_2/ethanol molar ratios.

((Figure 4))

The synthesis rates of acetaldehyde and acetic acid for the 0.5 and 1.0 O_2/ethanol molar ratio-series increased gradually, and in an identical manner, in the temperature interval 175-200 °C to a maximum of 36 mmol acetaldehyde/(g cat h) and 4 mmol acetic acid/(g cat h), respectively (Figure 5). The same tendency was also observed for the series with a molar ratio of 3.3 at the lower temperatures, although the values were higher than for the two other series. However, at 200 °C the synthesis rate of acetaldehyde decreased considerably for the 3.3 series with an amount that did not correspond entirely to the observed increase in the synthesis rate of acetic acid, as shown in Figure 5. This overall decrease in total synthesis rate is most likely due to preferential formation of combustion products in the presence of a relative large excess of O_2. However, it could also be related to the water content which were kept constant throughout the reactions here at an ethanol to water molar ratio of 0.39. In previous vanadia-catalyzed gas-phase oxidations of aqueous ethanol with a corresponding ratio of 0.1

combustion products were absent, even though the reactions were carried out at significantly higher oxygen pressure [8].

((Figure 5))

Conclusion

In this work it has been shown how reaction conditions can be optimized in gas-phase oxidation of 50 wt% aqueous ethanol with dioxygen using a novel supported V_2O_5/TiO_2 catalyst based on nano-sized anatase support to produce either acetaldehyde or acetic acid in high selectivities at near full conversion. Acetaldehyde was the prevailing reaction product in oxidations performed at 175-200 °C, 2.7 bar and at space velocities above 25000 h^{-1} reaching yields above 90 %. In contrast, acetic acid was the predominant reaction product at low space velocity where selectivity above 80 %, even at temperatures as low as 165 °C, could be reached.

Acknowledgments

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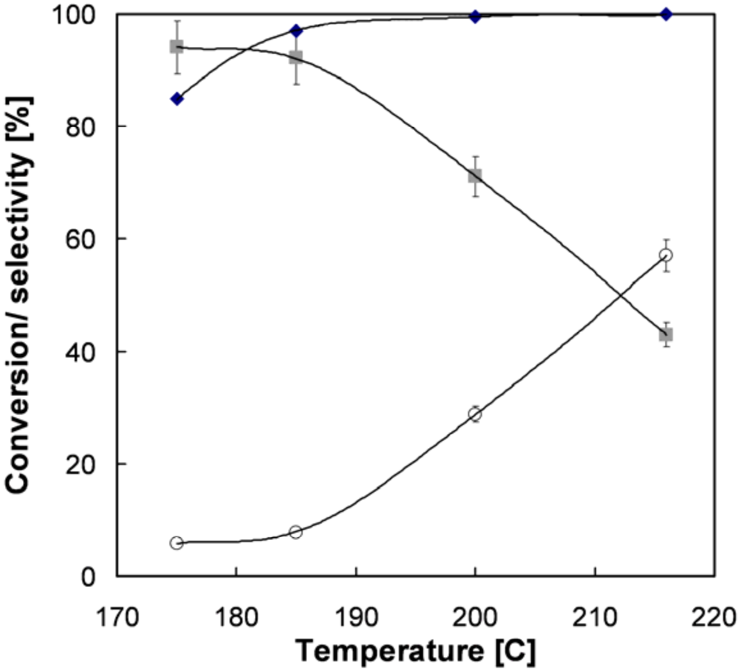

Figure 1: Ethanol conversion (♦) and selectivity towards acetaldehyde (□) and acetic acid (○) as a function of reaction temperature (*P* = 2.7 bar, GHSV = 25000 h^{-1}, O_2/ethanol mole ratio = 3.3).

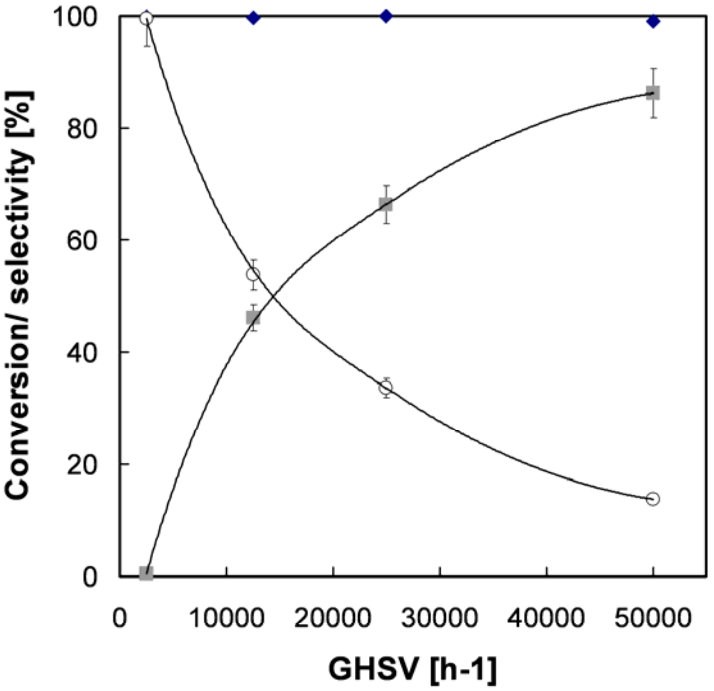

Figure 2: The effect of gas hourly space velocity (or the residence time) on ethanol conversion (♦) and selectivity towards acetaldehyde (□) and acetic acid (○) (*P* = 2.7 bar, *T* = 200 °C, O_2/ethanol mole ratio = 3.3).

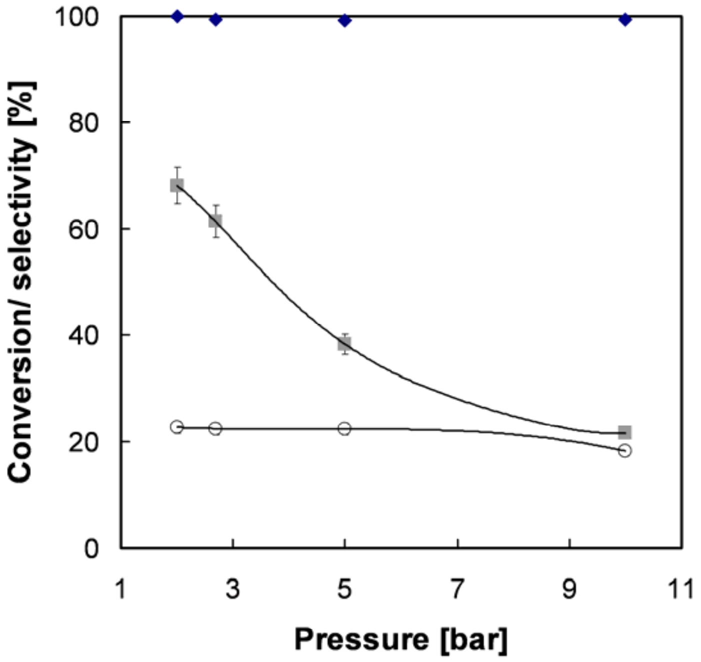

Figure 3: Ethanol conversion (♦) and selectivity towards acetaldehyde (□) and acetic acid (○) versus reaction pressure (T = 200 °C, GHSV = 25000 h^{-1}, O_2/ethanol mole ratio = 3.3).

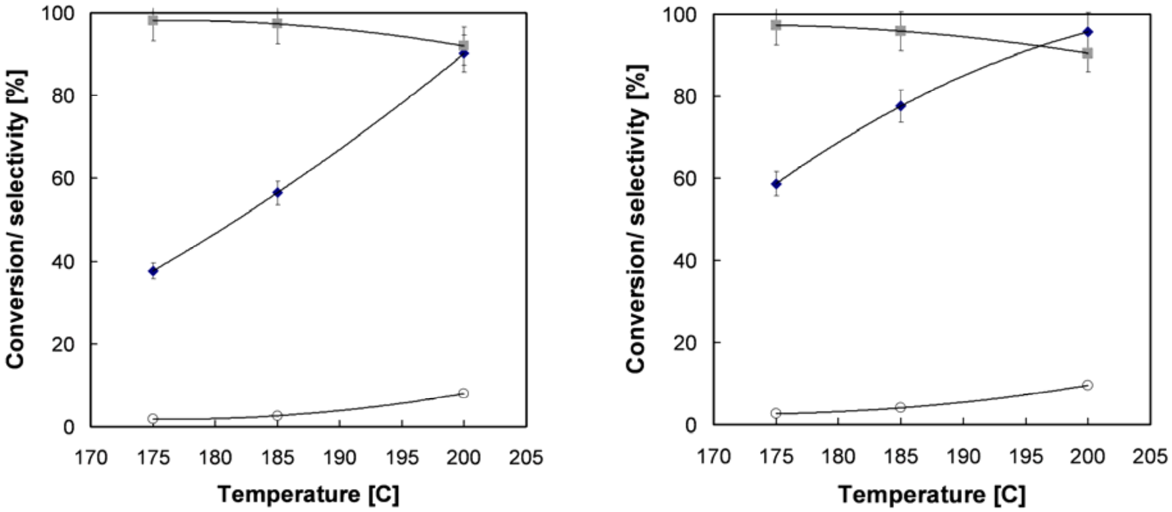

Figure 4: Ethanol conversion (♦) and selectivity towards acetaldehyde (□) and acetic acid (○) as a function of reaction temperature for the 0.5 O_2/ethanol mole ratio series (left) and the 1.0 O_2/ethanol mole ratio series (right) (P = 2.7 bar, GHSV = 25000 h^{-1}).

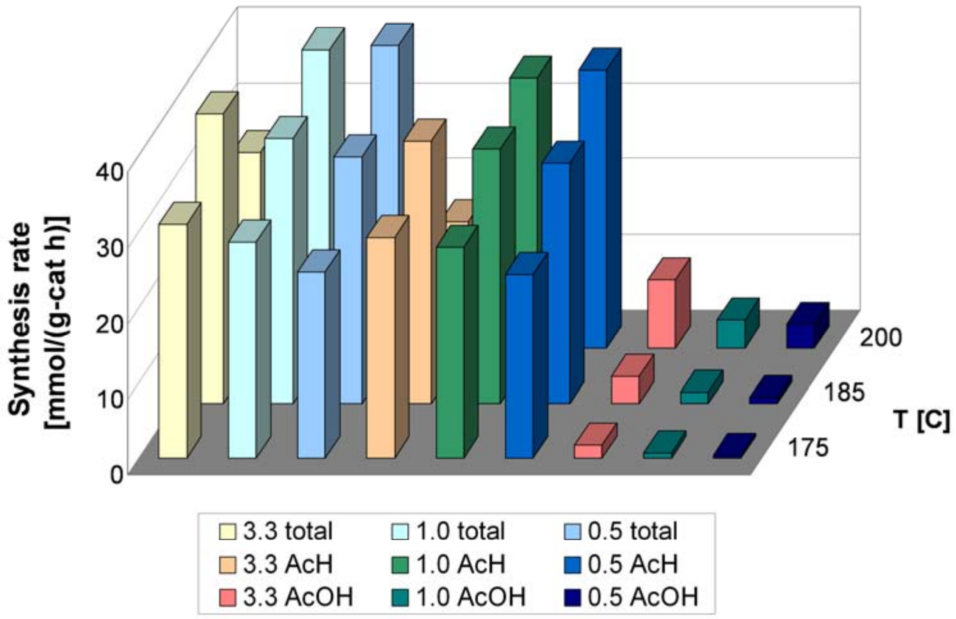

Figure 5: Molar synthesis rates of acetaldehyde and acetic acid as a function of reaction temperature and O_2/ethanol ratio (P = 2.7 bar, GHSV = 25000 h^{-1}).