Hydrogen Production by Bio-ethanol reforming for Small-scale Fuel Cell Applications

Mika Huuhtanen[1]*, Prem Kumar Seelam[1], Esa Turpeinen[1], Krisztian Kordás[2] and Riitta Liisa Keiski[1]

[1]*University of Oulu, Department of Process and Environmental Engineering, Mass and Heat Transfer Process Laboratory, FI-90014 University of Oulu, P.O.Box 4300*

[2]*University of Oulu, Department of Electrical and Information Engineering, Microelectronics and Material Physics Laboratories, FI-90014 University of Oulu, P.O.Box 4500*

1 Introduction

The depletion of fossil fuels in the future and availability of crude oil are serious concerns around the globe. Moreover, the green house gas (GHG) emissions, which have influence on the climate change and environmental problems on the earth, have to be reduced. In order to have a CO2 neutral energy production, renewable energy sources will be one of the solutions to cut-off GHG emissions and to gain energy security [1]. Various biofuels, which can be produced sustainably from renewable raw materials, can be used and they are benign renewable energy carriers. Bio-ethanol as a raw material for H_2 generation is a good alternative because of its non-toxicity, high energy density and easy delivery. Bio-ethanol can be produced from biomass like cellulosic materials, e.g. lignin or hemicelluloses, wood residuals, food industry side streams, etc., for example via fermentation. Production of bio-ethanol from these resources is in focus in research and the most sustainable way to produce it is studied widely. Bio-ethanol produced from sugar or corn based raw materials are of less interest due to the need of plants suitable for food production. [1, 2].

The hydrogen production via bio-ethanol reforming for fuel cell applications has attracted significant interest both in academic and industrial research [3]. Bio-ethanol reforming process can be done by three alternative ways as follows:

1. Steam reforming using water (SR) (Endothermic)
2. Dry reforming using CO_2 (DR) (Endothermic)
3. Autothermal steam reforming using partial oxidation (OSR+POX) (Exothermic)

Steam reforming and autothermal reforming are reported to be effective routes for producing hydrogen from ethanol [3]. The catalyst plays a crucial role for the production of hydrogen through ethanol reforming. In the present study, several catalytic materials, mainly CNT (carbon nanotube) support based catalysts but also conventional reforming catalysts were tested and reported.

2 Aim of the research work

In this study, the feasibility of carbon nanotube (CNT) based catalyst materials are investigated in ethanol reforming. Catalysts for the bio-ethanol reformer operating at low temperatures, i.e. below 400ºC, are needed. The research is focused on developing new and sustainable ways

* *Corresponding author, E-mail: mika.huuhtanen@oulu.fi*

to produce hydrogen by ethanol reforming for e.g. small-scale fuel cell systems having electric output power below 10 kW. The technologies will cover low temperature bio-ethanol reforming, study of hydrogen selective membranes for produced gas stream purification as well as the combinations of these two; catalytic membrane reactors to produce pure hydrogen streams suitable for fuel cells. Pd based hydrogen selective catalytic membranes were studied to obtain high hydrogen gas selectivity and purity with good hydrogen permeability. Further, theoretical and experimental research works were done to find and optimise appropriate operating pressures and temperatures for a micro-reactor performance to achieve a good hydrogen gas yield in reforming. CFD will be used as one of the tools when designing an optimal micro reactor structure for reforming. This project is in cooperation with COST Action 543 "Research and Development of Bio-ethanol Processing for Fuel Cells, BIOETHANOL" (2006–2010).

3 Experimental method

Ni, Co, Pt, and Rh nanoparticles are deposited on CNTs by impregnating the corresponding metal-acetates/acetylacetonates followed by calcination and activation of catalysts at elevated temperatures. To achieve porous and gas permeable electrodes which are suitable for hydrogen fuel cell applications, films of aligned CNTs decorated with Pt nanoparticles (Pt/CNTs) were synthesized. In order to extend the active area of the proton exchange membrane, composites of Pt/CNT electrodes with proton conductive materials are also investigated. Catalysts for reforming and fuel cell studies are made in the Microelectronic and Material Physics Laboratories at the University of Oulu.

The reforming experiments were carried out in a tubular reactor system (Fig 1). A series of experiments for catalyst activity tests were performed. The complete setup consists of a reactor system with a furnace (Fig 1A) and reformer (Fig 1B) with a catalyst bed. The ethanol-water mixture was inserted by a peristaltic pump. Nitrogen was used as the carrier gas. The outlet gas stream was measured by a Gasmet™ FTIR analyzer, while hydrogen content was measured with a specific hydrogen analyzer (XMTC). The reactor system consists of two nested quartz tubes. The catalyst sample was placed into the inner quartz reactor tube with a quartz wool sealing. The complete reactor system was set into the furnace.

The CNT-based catalysts were studied in the ethanol reforming reaction using water:ethanol molar ratio of 3:1 at temperatures between 200 and 550 °C. The catalyst samples contained Ni, Co, Rh and Pt as active metals supported on CNT. The water:ethanol mixture was inserted into the reactor with a feeding ratio of 20 vol-% of the total flow in nitrogen carrier.

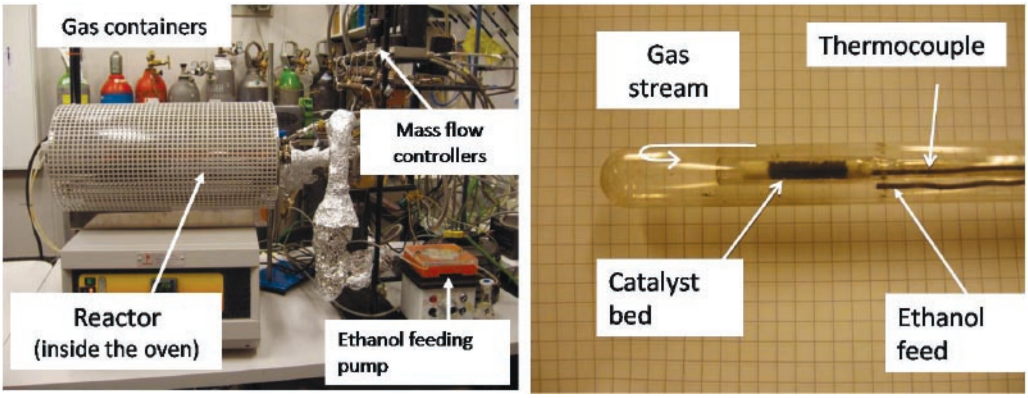

Figure 1 Reactor setup for bio-ethanol reforming: A. reactor system B. reformer with a catalyst bed.

4 Results and discussion

In the preliminary study, catalytic materials, e.g. Ni on alumina support, have been tested in ethanol reforming at 700 °C and at atmospheric pressure with ethanol/water molar ratio of 1:3 and 1:13. The effect of metal loading has also been tested with 12, 17 and 27 wt-% of Ni. The effect of feed ratios were also tested and found that the feed ratio with 1:13 (ethanol/steam) gives better ethanol conversion and higher hydrogen yield per ethanol mol than feed ratio 1:3. The co-fed oxygen makes catalyst more stable by diminishing carbon formation but also enhances the CO formation. In the case of dry reforming, it enhances the solid carbon formation and diminishes the hydrogen yield. Finally, ethanol conversion and hydrogen formation increase linearly as a function of temperature.

CNT based catalysts tested in the steam reforming reaction showed good performance in activity and hydrogen formation. Over the Ni and Co based CNTs the ethanol conversion reached over 90% at low temperatures (325 °C and 375 °C, respectively). The hydrogen formation was over 6 vol-% over both catalysts at 400 °C, reaching the maxima (>12 vol-%) at around 520 °C. Over Pt and Rh impregnated CNT catalysts the formation of H2 was significantly lower. The addition of Pt/CNT to Ni and Co based CNT catalysts did not have any effect on the hydrogen yield; Rh/CNT addition lowered the yield. Both Pt and Rh increased the CO formation with Co/CNTs, but decreased it with Ni/CNT catalysts.

5 Conclusions

Based on the results gained it shows that nickel based catalysts are the most promising catalytic materials for the ethanol steam reforming process. Ni and Co as active metals on CNT support are found to be the best ones. Rh/CNT with Co- or Ni-based CNT catalysts lowered H_2 yield, but also CO formation diminished. Pt/CNT with Co- or Ni-based CNTs increases slightly temperatures in which the formation of H_2 started. In addition, gas purification and processing is still needed to remove the impurities in order to get product gas appropriate e.g. for fuel cell applications.

In the next step, the work will be focused to find and modify the catalysts for alcohol reforming at low temperatures. In addition, the research work will be done on micro-reactor design and catalytic membrane utilisation for hydrogen production.

References

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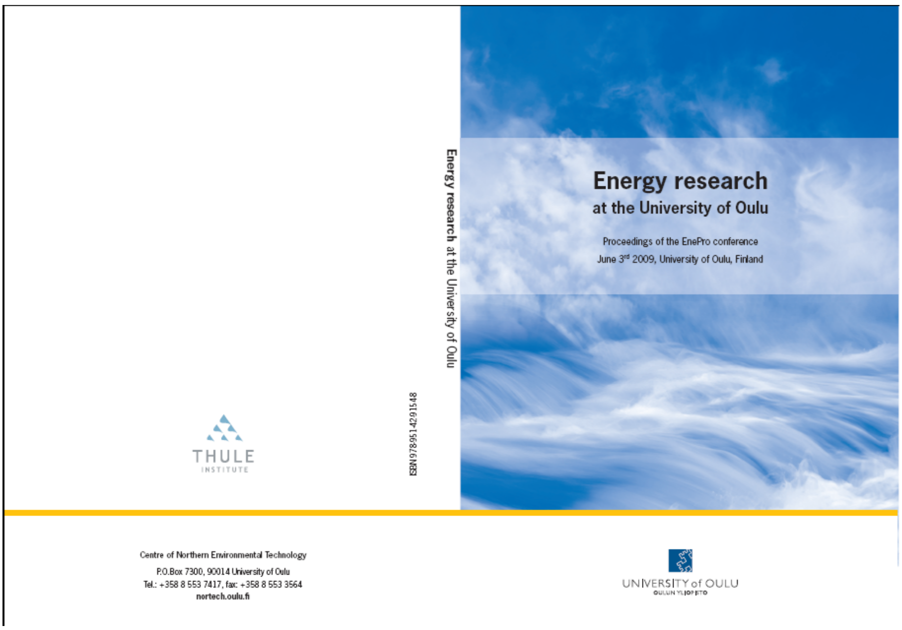

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