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Oxidative reforming of biomass derived ethanol for hydrogen production in fuel cell applications

V. Fierro, V. Klouz, O. Akdim, C. Mirodatos*

Institut de Recherches sur la Catalyse, 2 av. A. Einstein, F-69626 Villeurbanne Cedex, France

Abstract

Oxidative reforming of biomass derived ethanol over an inexpensive Ni–Cu/SiO_2 catalyst has been carried out with respect to solid polymer fuel cell (SPFC) applications. Two types of runs were performed, either under diluted conditions (with helium as diluent) or under conditions corresponding to an on-board reformer. Selectivities of ethanol reforming have been analyzed as a function of operating parameters: reaction temperature, H_2O/EtOH molar ratio and O_2/EtOH molar ratio of the feed to the reformer. The hydrogen content and the CO_2/CO_x molar ratio in the outlet gases were used as parameters to optimize the operating conditions in the reforming reactor. The tests carried out at on-board reformer conditions evidenced that an H_2O/EtOH molar ratio $= 1.6$ and an O_2/EtOH molar ratio $= 0.68$ at 973 K allow a hydrogen rich mixture (33%) that can be considered of high interest for SPFC. Furthermore, the use of oxygen decreases the production of methane and coke which increases in turn the lifetime of the catalyst. The stability of this catalyst has been fully demonstrated by long time runs. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Ethanol; Hydrogen; Fuel cell

1. Introduction

Among the various fuels which can be converted to hydrogen to be used in fuel cells for mobile and stationary applications, alcohols are very promising candidates because they are easily decomposed in the presence of water and generate an H_2-rich mixture suitable for feeding fuel cells. Methanol has been thoroughly studied in recent years but the main drawbacks are its high toxicity and its production based essentially on non-renewable fossil fuels. In contrast, ethanol, which could be produced in large quantities from biomass, can be considered as a renewable motor fuel. Furthermore, the use of bio-ethanol does not increase the greenhouse effect since the oxidative reforming of ethanol releases the same amount of CO_2 as the one absorbed by the biomass within a life cycle of few years.

The catalytic properties of supported transition metal catalysts for ethanol reforming, especially cobalt, and the effect of the particle size and the nature of the support were investigated by Haga et al. [1–4]. Although they concluded that selectivity for the reaction was in the order: Co > Ni > Rh > Pt, Ru, Cu, most of the catalysts investigated for the reforming of ethanol are Ni-based catalysts with additions of Cu, Cr, Zn or K [5–8]. It is generally accepted that nickel promotes C–C bond rupture whereas the role played by the additives is still under discussion. Luengo et al. [6] suggested that Cu and Cr are responsible for the subsequent oxidation of methanol into CO and H_2 whereas Mariño et al. [8] concluded that Cu is the active agent. In a recent work, Freni [9] has studied the reforming of a water/ethanol

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* Corresponding author. Tel.: +33-472-44-5366;
fax: +33-472-44-5399.
E-mail address: mirodato@catalyse.univ-lyon1.fr (C. Mirodatos).

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mixture on a Rh based catalyst as an alternative fuel for molten carbonate fuel. Despite the high H_2 concentration (about 30% at 923 K) in the outlet gases the cost of this catalyst appears to be the main drawback.

Concerning the operating temperature and H_2O/EtOH ratio, Fishtik et al. [10] carried out a thermodynamic analysis of hydrogen production from ethanol steam reforming. They found that for temperatures at or above 700–800 K and for high water/ethanol ratios the desired reaction of ethanol steam reforming is predominant and the amount of undesired products, CO and CH_4, is minimized. A more recent thermodynamic analysis by Ioannides [11] has concluded that an H_2O/EtOH molar ratio higher than stoichometry results in reduced efficiency in hydrogen production, because of increased enthalpy needs for water evaporation. When air is co-fed with ethanol, optimal operating conditions can be found as a function of the preheat temperature of the feed.

This work focuses on the optimization of the operating conditions of the oxidative reforming of biomass-derived ethanol over an inexpensive Ni–Cu/SiO_2 catalyst studied in our laboratory [12]. The objective is to increase hydrogen selectivity maximizing CO_2/CO_x production and minimizing coke deposition on the catalyst. A high hydrogen content has been found at the reformer outlet that can be even increased by water gas sift (WGS) reactions downstream. Effectively, WGS and selective oxidation reactions must be obligatory used in order to get a hydrogen rich stream containing only trace amounts of CO (∼10 ppm) to avoid poisoning of the solid polymer fuel cell (SPFC) electrocatalysts.

2. Experimental

2.1. Catalysts

The catalyst was prepared by impregnating a silica support (Degussa) with a BET surface of 200 $m^2\,g^{-1}$ and by using $Ni(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ as precursors. The catalyst has a $Cu/(Ni + Cu)$ weight ratio of approximately 10 and a total metal content of 18.4%. Prior to catalytic testing, the catalyst was placed in a fixed bed reactor and reduced under flowing hydrogen (30 ml min^{-1}) at 650 °C for 8 h with a heating rate of 2 °C min^{-1}. After reduction the catalyst was cooled down to reaction temperature.

2.2. Apparatus and test conditions

The catalytic tests were carried out in a conventional fixed-bed micro-reactor system. Two types of runs were performed, either under diluted conditions (with helium as diluent) or under conditions corresponding to an on-board reformer (with ethanol, water and air as the only reactants). For the former runs, 15–50 mg of the catalyst were used, while for the latter on-board-like conditions, about 500 mg of the catalyst are introduced in the reactor. Operating temperature was measured by a thermocouple placed inside the oven and close to the reactor wall and catalyst was dispersed with SiC to minimize hot spot effects.

Runs under helium diluted conditions were carried out at atmospheric pressure in a fixed bed reactor ($\phi_{\text{int}} = 4$ mm and $H_{\text{bed}} = 7$ mm). A saturator-condenser kept at 18 °C was used to saturate the inert gas flow with ethanol ensuring a partial pressure of 5085 Pa. Water was synthesized in situ, with helium as diluent and Pt/Al_2O_3 (Aldrich) as catalyst. The total flow rate was maintained at 50 ml min^{-1}. The reactants and the products in the effluent gases are analyzed by gas chromatography (Carbosieve column—thermal conductivity detector and HayeSep D column—flame ionization detector). Additional gas analyses are performed by on line mass spectrometry (VG Quadrupole).

Runs under on-board-like conditions were performed in a set up providing an ethanol/water/air mixture from a gaseous N_2/O_2 mixture and a liquid H_2O/EtOH mixture regulated by an HPLC pump (Gilson 307). The liquid was vaporized at 175 °C and then mixed with the air before being fed to the fixed bed reactor. Non-converted water was trapped at the reactor outlet before gas analysis by gas chromatography (Porapak Q column and molecular sieve—thermal conductivity detector).

Carbon deposits were quantified by temperature-programmed oxidation (TPO). After being cooled to room temperature under inert atmosphere, the used catalyst was heated at linearly increasing temperature (10 °C min^{-1}), up to 900 °C under oxygen (20 vol.% in He). The formation of carbon was followed by on-line mass spectrometry and the amount of carbon deposited determined from the integration of the CO_2 production curves as a function of time/temperature.

3. Results and discussion

Fig. 1 shows the effect of the reaction temperature on the selectivity of reforming reaction. Ethanol is totally converted in the temperature range of 300–600 °C.

At low temperatures, 300–400 °C, the main reactions that take place are dehydrogenation of ethanol to acetaldehyde and methanation due to reaction of CO and CO_2 with hydrogen. By increasing temperature reaction, selectivities to methane, coke and acetaldehyde decrease and hydrogen production is favored.

Temperature around or slightly higher than 600 °C seems to be appropriate for reforming reaction because hydrogen production is important and CO_2/CO_x is high enough for the rest of the process. Thus, selectivity, conversion and coke production were studied at 600 °C as a function of the H_2O/EtOH molar ratio and in the absence of oxygen and results are shown in Fig. 2. Ethanol is totally converted independently of the H_2O/EtOH molar ratio and the selectivity to oxygenated products (aldehydes, acids) is negligible. Selectivity to hydrogen decreases and water conversion, selectivity to methane and coke formation increase as H_2O/EtOH ratio decreases. The most important effect was observed in CO_2/CO_x ratio that decreases dramatically as H_2O/EtOH ratio decreases, this effect corresponds to a higher content of CO.

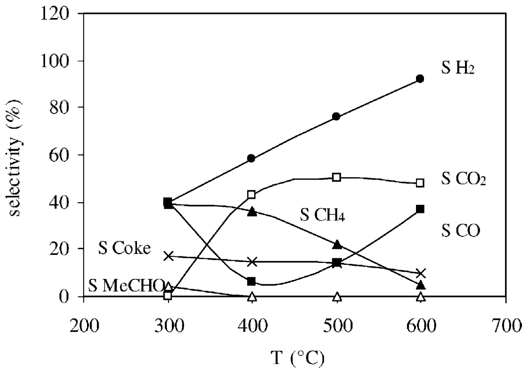

Fig. 1. Selectivities of ethanol reforming as a function of temperature (H_2O/EtOH = 3.7).

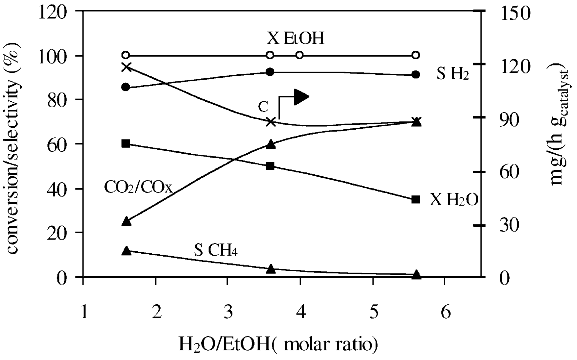

Fig. 2. Conversion and selectivities of ethanol reforming and coke production as a function of H_2O/EtOH molar ratio (600 °C, O_2/EtOH = 0).

In order to decrease CO content O_2 was also feed in the reactor with an O_2/EtOH molar ratio ranging from 0 to 1.8. Fig. 3 shows conversion of the reactants, product selectivities and coke formation at 600 °C with an H_2O/EtOH molar ratio of 3.6.

Ethanol and oxygen are totally converted independently of O_2/EtOH molar ratio whereas water conversion decreases very rapidly as O_2 increases. Decreasing water content in the feed gas is found to markedly reduce the CO_2/CO_x ratio. Addition of oxygen is expected to compensate this detrimental effect, while keeping a high selectivity to hydrogen and a low formation of carbon on the catalyst. Effectively, the introduction of low amounts of oxygen (O_2/EtOH $\sim$ 0.5) practically restores S_{H_2} to values obtained with twice the amount of added water and maintains the CO_2/CO_x ratio to an acceptable level.

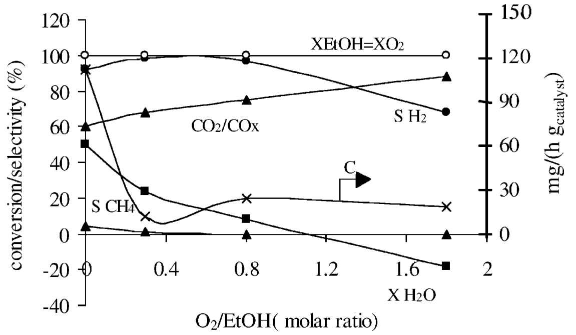

Fig. 3. Conversions and selectivities of ethanol reforming and coke production as a function of O_2/EtOH molar ratio (600 °C, H_2O/EtOH = 3.6).

Table 1
Comparison of the ethanol reforming selectivities to H_2, CO_2, CO and CH_4 at diluted and at on-board conditions

	S_{H_2} (%)	S_{CO_2} (%)	S_{CO} (%)	S_{CH_4} (%)
Diluted conditions: $H_2O/EtOH = 3.7$ and $O_2/EtOH = 0$, $T = 600\,^{\circ}C$	96.1	37.6	57.3	5.6
On-board conditions: $H_2O/EtOH = 1.6$ and $O_2/EtOH = 0$, $T = 600\,^{\circ}C$	61.6	45.3	20.4	24.4
On-board conditions: $H_2O/EtOH = 1.6$ and $O_2/EtOH = 0.5$, $T = 700\,^{\circ}C$	96.8	40.3	56.9	6.1

Under on-board-like reforming conditions (no inert gas dilution except nitrogen from air), the conversions and selectivities are changed (see Table 1). These changes probably indicate a complex kinetic law with positive and negative partial reaction orders that are changed due to the higher partial pressures of the reactants at on-board-like reforming conditions. It was found that the reaction temperature has to be increased in order to recover an important hydrogen production. This may come from a shift in the thermodynamic equilibrium, which especially improves methane steam reforming. The introduction of a larger amount of oxygen also improves the oxidative properties of the system by consuming methane at the benefit of carbon oxides. Under these more realistic conditions the optimized experimental conditions involve a reforming temperature close to 700 °C, a molar ratio of $H_2O/EtOH$ equal to 1.6, a molar ratio of $O_2/EtOH$ equal to 0.68 and a contact time close to 0.2 min kg mol^{-1} [12].

Since the commercial development of oxidative reforming of ethanol requires a good stability of the catalyst, the latter was tested for 140 h at the optimized operating conditions. The catalyst exhibited a constant selectivity to the reaction products and the ethanol was totally converted during this time. The outlet composition presents a percentage of hydrogen of 33.0%, lower concentrations of CO and CO_2 (12.9 and 9.2%, respectively) and a much smaller concentration of methane (1.4 %).

4. Conclusion

The performance of an inexpensive Ni–Cu based catalyst in the reforming of ethanol has been evaluated. This catalyst exhibits high activity and, most important, good long term stability for steam reforming of ethanol to hydrogen production and therefore it is a very good candidate to be used in ethanol reforming processors for fuel cell applications. Performance tests conducted under various experimental conditions show that, in general, the selectivity toward hydrogen increases with increasing reaction temperature and decreases with decreasing the ratio of H_2O:EtOH in the feed. Moreover, the introduction of oxygen in the feed gas favors the production of hydrogen, while limiting the formation of methane and carbon deposition.

Acknowledgements

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