Steam reforming of biomass-derived ethanol for the production of hydrogen for fuel cell applications

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Ni/La$_2$O$_3$ catalyst exhibits high activity and good long term stability for steam reforming of ethanol to hydrogen production and is a good candidate for ethanol reforming processors for fuel cell applications.

Fuel cells may be a promising alternative means of electricity generation for stationary decentralized applications. They offer significant advantages which include absence of pollutant emission, since they use hydrogen as the fuel, and high conversion efficiency, which may be even higher when they operate on the co-generation mode. In recent years, fuel cells have been seriously considered for electric vehicle operation, making possible so-called Zero Emission Vehicles.

An important source of hydrogen for stationary fuel cell applications is natural gas, while for transportation, methanol and gasoline are being considered. These fossil fuels do not address the issue of carbon dioxide emissions, however, which may only be addressed by the use of a renewable fuel as the hydrogen source. Ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agroindustries or forestry residue materials, or even organic fractions of municipal solid waste. Thus, in contrast to the fossil-fuel-based systems, the bioethanol-to-hydrogen-system has the significant advantage of being nearly CO$_2$ neutral, since the carbon dioxide produced is consumed for biomass growth, thus offering a nearly closed carbon loop. In addition, the use of ethanol offers important storage and handling safety advantages.

In the present communication, the catalytic steam reforming of ethanol for hydrogen production is discussed, with respect to catalyst performance characteristics. The steam reforming of ethanol for hydrogen production has been shown to be entirely feasible from a thermodynamic point of view.[1–3] An issue of major importance is then to develop highly active, selective and durable catalysts for the reaction. Although much work has been carried out on methanol reforming, only a limited number of reports have appeared in the literature dealing with the reforming of ethanol.[4–6] Here, we report results obtained over a Ni/La$_2$O$_3$ catalyst, which has been previously found to exhibit good performance characteristics under conditions of carbon dioxide reforming of methane to synthesis gas.[7] It is shown that under certain operating conditions, the Ni/La$_2$O$_3$ catalyst is very active and stable for the steam reforming of ethanol and is characterized by high selectivity toward hydrogen production.

The 17% Ni/La$_2$O$_3$ catalyst employed in the present study was prepared by the wet impregnation method using Ni(NO$_3$)$_2$ and La$_2$O$_3$ (Alfa Products) as starting materials, following a procedure that has been described in detail elsewhere.[7] Catalytic performance tests have been conducted in the temperature range 300–800 °C, over catalyst samples previously reduced *in situ* with hydrogen (500 °C, 2 h). In a typical experiment, a water–ethanol mixture (molar ratio 3:1) is pumped into a heated chamber and vaporized. The water–ethanol gas stream (160 cm^3 min^{-1}) is then fed to a quartz micro-reactor containing 100 mg of catalyst. The composition of the reactor effluent is analyzed by means of two gas chromatographs, connected in series: the first is equipped with

two packed columns (Porapak, Carbosieve) and two detectors (TCD, FID) and uses He as carrier gas. Porapak is used for the separation of C$_2$H$_5$OH, H$_2$O, CH$_3$CHO, CH$_4$, C$_2$H$_4$ and C$_2$H$_6$. Carbosieve is used for the separation of CO, CO$_2$ and CH$_4$. The second gas chromatograph, which uses N$_2$ as carrier gas, is equipped with a Carbosieve column and a TCD detector and is solely used for the analysis of the produced hydrogen.

Typical experimental results obtained are presented in Fig. 1, in which the conversion of ethanol and the selectivities to various reaction products are shown as a functions of reaction temperature. At temperatures below 300 °C, steam reforming of ethanol does not occur appreciably. Instead, dehydrogenation of ethanol occurs to an appreciable extent producing acetaldehyde and hydrogen. Increasing reaction temperature results in a progressive decrease of selectivity toward acetaldehyde, which drops to zero at temperatures above 550 °C. In this temperature range the reforming reactions of both acetaldehyde and ethanol prevail. It is interesting to observe that no ethylene is detected in the reaction products, indicating that no dehydration of ethanol is taking place, as might be expected. This is due to the fact that this particular catalyst, which utilizes La$_2$O$_3$ as the carrier material, does not possess any acidic sites, which are required for the dehydration route. Steam reforming of ethanol takes place to a significant extent at temperatures above 400 °C, as evidenced by the sharp increase of ethanol conversion and by the increase of selectivities toward CO and H$_2$ (Fig. 1). By-products of the reaction are CO$_2$ and CH$_4$, which are formed by reaction of CO with water (shift reaction) and with hydrogen (methanation), respectively. Selectivities toward CO$_2$ and CH$_4$
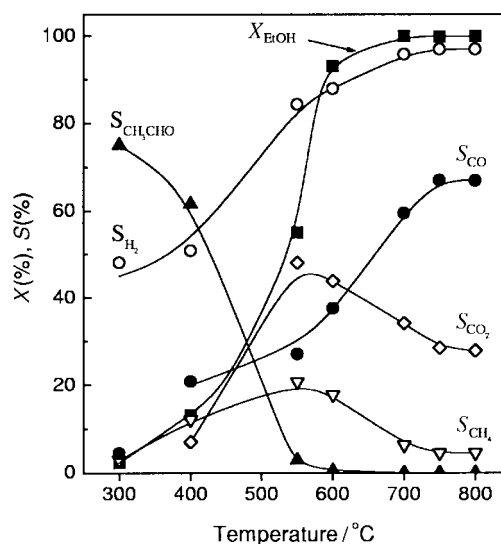

Fig. 1 Effect of reaction temperature on the conversion of ethanol (X_{EtOH}) and on selectivities toward acetaldehyde (S_{CH_3CHO}), carbon monoxide (S_{CO}), carbon dioxide (S_{CO_2}), methane (S_{CH_4}) and hydrogen (S_{H_2}), obtained over the 17% Ni/La$_2$O$_3$ catalyst. *Experimental conditions*: mass of catalyst: 100 mg; particle size: 0.25–0.50 mm; H$_2$O:EtOH molar ratio: 3:1; flow rate: 160 cm^3 min^{-1} (W/F = 0.0375 g s cm^{-3}); P = 1 atm.

increase with increasing temperature and go through maxima at *ca.* 550 °C. Above this temperature, the reformation of methane with CO_2 and with H_2O becomes thermodynamically feasible, resulting in a decrease of the selectivities of both CH_4 and CO_2, since the Ni/La_2O_3 catalyst is known to be very active for these reforming reactions.[7] The observed decrease in the production of CO_2 may be due in part to the inverse shift reaction. At temperatures above 600 °C, the conversion of ethanol reaches 100% and the selectivity toward hydrogen exceeds 90% (Fig. 1). Under these conditions, the only undesirable product is methane, which competes with H_2 for hydrogen atoms. However, from a practical point of view, a small concentration of methane in the reformate may be tolerated since methane present at the exhaust of the fuel cell can be burned, along with unreacted hydrogen, to provide the heat necessary for the highly endothermic reforming reaction. In any event, conversion of methane *via* reforming with CO_2 and H_2O proceeds at higher reaction temperatures, resulting in increased yield of H_2 production.

The contact time dependence of the conversion of ethanol and of the selectivity toward reaction products, as well as the stability of the catalyst with time-on-stream were examined over a catalyst in which the active component (Ni/La_2O_3) was deposited on γ-Al_2O_3 pellets (Engelhard) of a surface area of 180 $m^2\,g^{-1}$. This type of catalyst formulation may be necessary for a practical application since La_2O_3 is hydroscopic and pellets made out of this material do not possess the necessary strength in the presence of steam, especially at low temperatures. This problem is avoided if lanthana is dispersed over the surface of materials which have the necessary strength, such as alumina pellets. For the experiment described here, the γ-Al_2O_3 pellets were impregnated with $La(NO_3)_3$ and then calcined in air at 900 °C for 30 h. The resulting material was then impregnated with $Ni(NO_3)_2$, dried at 110 °C for 24 h, reduced in H_2 at 500 °C for 5 h and crushed to particles of 0.25–0.50 mm in diameter.

The effect of contact time on the catalytic performance of the (Ni/La_2O_3)/Al_2O_3 catalyst at the reaction temperature of 750 °C is shown in Fig. 2, in which the conversion of ethanol and the selectivities towards various reaction products are plotted as functions of *W/F*. It is observed that for contact times > 0.1 g s cm^3 the conversion of ethanol is 100% and the reaction is highly selective toward hydrogen ($> 95\%$), the only unwanted by-product being methane ($< 5\%$). As the contact time decreases, the conversion of ethanol progressively drops, accompanied by a decrease of the selectivity toward the
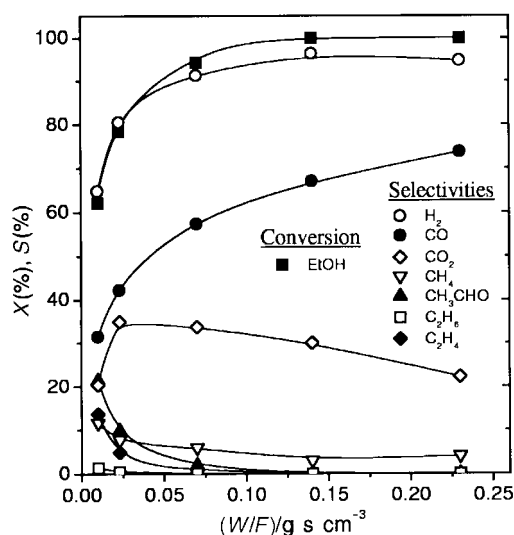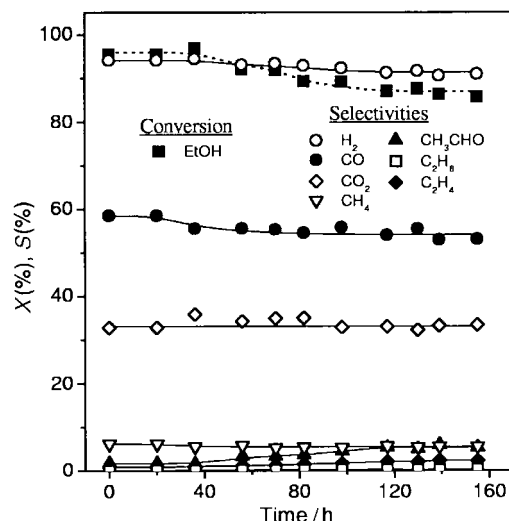
Fig. 3 Conversion of ethanol and selectivities toward reaction products as functions of time-on-stream, obtained over the (Ni/La_2O_3)/Al_2O_3 catalyst. *Experimental conditions*: mass of catalyst: 100 mg; particle size: 0.25–0.50 mm; H_2O:EtOH molar ratio: 3:1; flow rate: 87 cm^3 min^{-1} (*W/F* = 0.0690 g s cm^{-3}); $T = 750$ °C; $P = 1$ atm.

reformation products (CO and H_2) and by an increase of the selectivity toward CO_2 and by-products, such as CH_3CHO, C_2H_4 and C_2H_6. It is interesting to observe that at low contact times (low ethanol conversion) appreciable amounts of ethylene are formed, obviously by dehydration of ethanol over acidic Al_2O_3 sites. This reaction did not occur measurably over the Ni/La_2O_3 catalyst which does not possess acidic sites.

The stability of the (Ni/La_2O_3)/Al_2O_3 catalyst has been examined at 750 °C and the results are shown in Fig. 3, in which the alterations of activity and selectivity are plotted as functions of time-on-stream. Under the experimental conditions employed (see legend of Fig. 3), a small deactivation of the catalyst is observed during the first 80–100 h on stream, where conversion of ethanol drops from 95 to 88%, while further exposure of the catalyst to the reaction mixture does not result in further deactivation. It is interesting to observe that selectivity toward hydrogen does not change significantly and slightly decreases from the initial value of 94 to 91% after 155 h on stream. Selectivities toward the formation of other products, such as CO, CO_2, CH_4, CH_3CHO, C_2H_4 and C_2H_6 also stabilize after 100–120 h.

Summarizing, the present results reveal that the Ni/La_2O_3 catalyst, or the (Ni/La_2O_3)/Al_2O_3 pelleted form, exhibits high activity and, most importantly, good long term stability for steam reforming of ethanol to hydrogen production and is a good candidate to be used in ethanol reforming processors for fuel cell applications.

Fig. 2 Effect of space time (*W/F*) on the conversion of ethanol and on the selectivities toward reaction products, over the (Ni/La_2O_3)/Al_2O_3 catalyst. *Experimental conditions*: mass of catalyst: 100 mg; particle size: 0.25–0.50 mm; H_2O:EtOH molar ratio: 3:1; $T = 750$ °C; $P = 1$ atm.

Notes and references

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