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Production of hydrogen for fuel cells by reformation of biomass-derived ethanol

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Abstract

The reformation of biomass-derived ethanol to a hydrogen-rich gas stream suitable for feeding fuel cells is investigated as an efficient and environmentally friendly process for the production of electricity for mobile and stationary applications. Steam reforming of ethanol is investigated over Ni catalysts supported on La_2O_3, Al_2O_3, YSZ and MgO. The influence of several parameters on the catalytic activity and selectivity is examined including reaction temperature, water-to-ethanol ratio and space velocity. Results reveal that the Ni/La_2O_3 catalyst exhibits high activity and selectivity toward hydrogen production and, most important, long term stability for steam reforming of ethanol. The enhanced stability of this catalyst may be due to scavenging of coke deposition on the Ni surface by lanthanum oxycarbonate species which exist on top of the Ni particles under reaction conditions. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fuel cells; Reformation; Nickel; Lanthanum oxide; Ethanol; Hydrogen production

1. Introduction

The commercial processes for hydrogen production which are presently used include steam reforming of natural gas, partial oxidation of heavy oil residues (followed by water–gas shift (WGS) conversion) and electrolysis of water. Hydrogen is mainly used as feedstock for the chemical industry and as liquid fuel for space applications. However, recent developments in the area of fuel cells dictate that, in the near future, hydrogen will be used, to a large extent, as a secondary energy carrier for the production of electricity for mobile and small-to-medium scale stationary applications. The expected increased demand for hydrogen for fuel cell applications, in combination with environmental concerns related to reducing atmospheric pollution and global greenhouse gas emissions, dictate the development of new methods for hydrogen production, especially from renewable sources, such as biomass.

Hydrogen can be produced in a renewable manner from lignocellulosic biomass with the use of several methods, including pyrolysis, gasification and steam reforming [1–3]. Of special interest are methods in which biomass is converted to intermediate liquid bio-fuels, such as pyrolysis oil or ethanol. The main advantage of liquid bio-fuels is their high energy density and ease of handling, and the fact that they can be used for the on-demand production of hydrogen for fuel cells, with applications in mobile and stationary grid-independent power systems.

Among the various processes and primary fuels that have been proposed for the production of hydrogen for such applications, steam reforming of ethanol is very attractive. The stoichiometry of the reaction for maximum hydrogen production is described by Eq. (1):

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \tag{1}$$

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In addition to advantages related to natural availability, storage and handling safety, ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agroindustries or forestry residue materials, organic fraction of municipal solid waste, etc. In contrast to other, fossil-fuel-based, systems which have been proposed for the same application, namely methanol and gasoline, the bioethanol-to-hydrogen system has the significant advantage of being nearly CO_2 neutral, since the produced carbon dioxide is consumed for biomass growth, thus offering a nearly closed carbon loop.

The proposed overall process for the production of hydrogen and electricity from biomass, is schematically shown in Fig. 1. According to this process, biomass originating from plant cultivation (1) and/or residues of agroindustries and cultivation (2) is used for the production of bioethanol by saccharification/fermentation processes (3). The aqueous mixture is then distilled to the level of 45–55% ethanol (4). The solid residue remaining after fermentation is fed

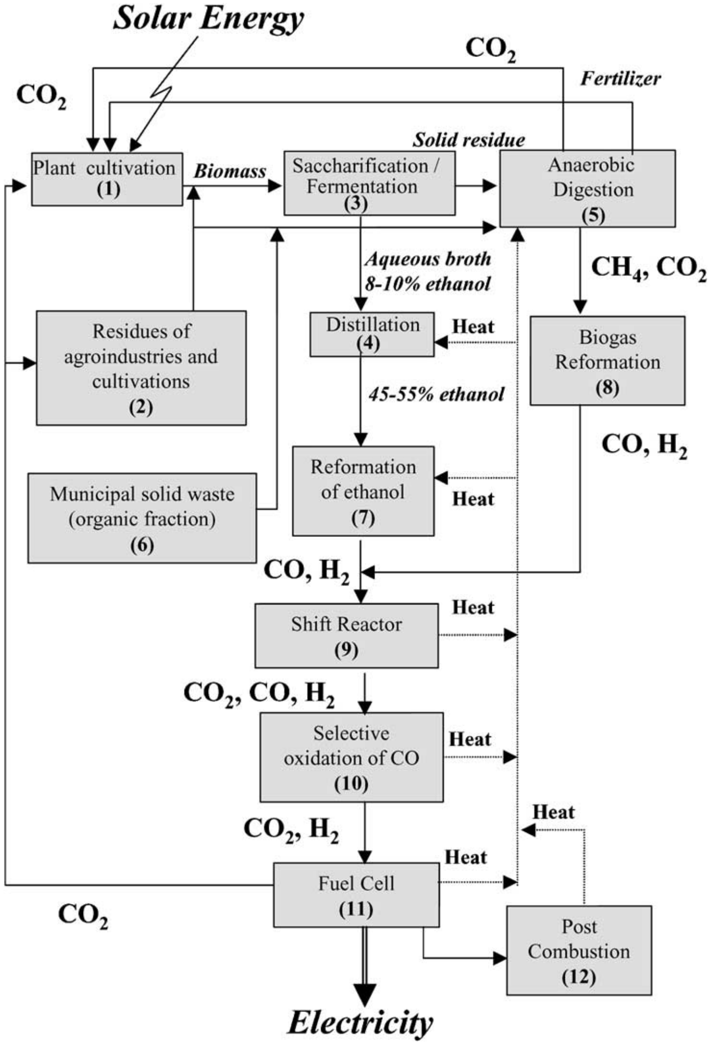

Fig. 1. Overall process for the renewable production of hydrogen and electricity from biomass-derived ethanol with high efficiency and zero emissions.

to an anaerobic digestion unit (5) where biogas, a mixture of CH_4 and CO_2, is produced. In the same unit, the organic fraction of municipal solid waste (6) may be added. A H_2-rich process gas is produced by reformation of bioethanol (7) and biogas (8). A WGS reactor is then used for the transformation of CO into H_2 and CO_2 (9). The process gas may then be further purified by selective oxidation of residual CO (10) before fed to a fuel cell (11) to produce electricity. A post combustion reactor (12) may be used (where necessary) to clean up the effluent of the fuel cell.

The proposed process has the significant advantage of being heat integrated since necessary heat for the reformation processes and distillation is supplied by combustion of a small amount of biogas (stationary applications) or partial oxidation of ethanol (mobile applications). In addition, the highest possible overall efficiency is obtained, which is attributed to the fact that a very large fraction of biomass is utilized, via the integration of the fermentation and anaerobic digestion steps, and also to the use of fuel cells whose efficiency for the production of electricity is more than twice that of conventional thermal engines. It has been estimated that the efficiency of the proposed process is nearly twice the efficiency of burning biomass and producing electricity by conventional means. The zero emissions of the process is due to the fact that hydrogen is used as fuel, the combustion of which produces only water.

The steam reforming of ethanol for hydrogen production has been shown to be entirely feasible from a thermodynamic point of view [4–7]. 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 few papers appear in the open literature dealing with the conversion of ethanol to hydrogen [7–10].

The present work reports results obtained over Ni catalysts supported on several carriers and is focusing on the Ni/La_2O_3 catalyst, which has been found to exhibit high activity and excellent stability for the reaction of carbon dioxide reforming of methane to synthesis gas [11] and the reaction of steam reforming of ethanol [12]. The study was carried out by varying operating conditions such as reaction temperature, steam-to-ethanol ratio and space velocity, in order to examine the effect of these parameters on the catalytic activity, selectivity and stability. It is shown that under selected experimental conditions, the Ni/La_2O_3 catalyst is very active and stable for the steam reforming of ethanol and is characterized by high selectivity toward hydrogen production.

2. Experimental

2.1. Apparatus

Catalytic performance tests have been carried out using an apparatus which consists of a flow system, the reactor unit and the analysis system. The flow system is equipped with a set of mass-flow controllers (MFCs), which accurately control the flow of the inlet gases (He, Ar, H_2, O_2, air, calibration mixtures, etc.), and a set of valves which allow selection of gas feed composition and introduction of the gas mixture to the reactor or to a by-pass stream. An HPLC pump (Marathon) is used for feeding the liquid reagents. The liquid feed consists of a water/ethanol mixture of known composition, which is premixed in a separate container. The liquid is pumped to a vaporizer where the reagents are heated to $150\,^{\circ}C$ and mixed (when desired) with the gas stream coming from the MFCs. The resulting gas mixture is then fed to the reactor through stainless steel tubing, which is heated at $150\,^{\circ}C$ by means of heating tapes.

The continuous flow microreactor consists of two 4.0 mm i.d. sections of quartz tube, which serve as inlet and outlet to and from a quartz cell of 6.0 mm i.d. The catalyst is placed in the cell and kept in place by means of quartz wool. The temperature of the catalyst is measured along the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well, which runs through the bed. Heating of the reactor is provided by an electric furnace controlled by a programmable controller, which is connected with a thermocouple placed in the middle of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed.

The analysis system used for the determination of reactants and products consists of two gas chromatographs (Shimadzu). The first one is equipped with two packed columns (Porapak-Q and Carbosieve) and two detectors (TCD, FID) and operates with He as the carrier gas. Injection of the gas mixture and column selection is achieved by the use of two six-port valves. Porapak-Q is used for the separation of C_2H_5OH, H_2O, CH_3CHO, CH_4, C_2H_4 and C_2H_6, while Carbosieve is used for the separation of CO, CO_2 and CH_4. Since the presence of large amounts of water hinders analysis in the Carbosieve column, a condenser is placed before its inlet, in order to condense and remove H_2O from the gas stream. The condenser consists of a pyrex tube (length ∼8 cm, i.d. ∼3 cm) filled with glass beads (3 mm) and is placed in a water bath filled with crushed ice. Apart from H_2O, other substances such as CH_3CHO and unreacted C_2H_5OH are also condensed and removed from the stream. The second gas chromatograph is equipped with a Carbosieve column, connected at the exit of the condenser, and a TCD detector. This chromatograph uses N_2 as the carrier gas and is solely used for the determination of the concentration of H_2 in the reformate.

Determination of the response factors of the TCD and FID detectors has been achieved with the use of gas streams of known composition (Scott specialty gas mixtures, self prepared EtOH/H_2O/CH_3CHO mixtures, etc.). Since several substances (CO, CO_2, O_2, H_2) can only be analyzed after the condenser, an internal standard (Ar added in the feed and/or CH_4 produced during the reaction) is used to account for the volume change. Reaction gases are supplied from high-pressure gas cylinders (Air Liquid) and are of ultrahigh purity. Analytic grade ethanol was obtained by Merck.

2.2. Catalyst preparation

Nickel catalysts supported on La_2O_3, Al_2O_3, YSZ and MgO were prepared by the wet impregnation method using nickel nitrate (Alfa) as the metal precursor. A known amount of $Ni(NO_3)_2$ was dissolved in water and the oxide was added to the solution under continuous stirring. The slurry was heated slowly to 70 °C and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and then calcined in air at 500 °C for 2 h for complete decomposition of nickel nitrate. After this treatment the catalyst samples were reduced at 500 °C in H_2 flow for 5 h. In all cases, the metal loading was 17 wt.%.

Certain experiments were conducted over catalysts where the active component (Ni/La_2O_3) was deposited on γ-Al_2O_3 pellets (Engelhard) with a specific surface area of 180 m^2/g. 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 subsequently impregnated with $Ni(NO_3)_2$, dried at 110 °C for 24 h, reduced in H_2 at 500 °C for 5 h and crashed to particles of 0.25–0.50 mm in diameter. The Ni content of this catalyst was 20 wt.%.

In addition to nickel-based materials, 20% Co/Al_2O_3, 0.5% Rh/Al_2O_3 and 3% Ru/TiO_2 catalysts were also prepared by the wet impregnation technique, employing the corresponding oxides and metal nitrates as starting materials.

2.3. Steam reforming experiments

In a typical experiment, 100 mg of catalyst are placed in the reactor and held in place by means of quartz wool. Prior to each experiment, the fresh sample is reduced in situ at $T = 750$ °C, for 2 h, under a hydrogen flow of 50 cc/min. The feed is then switched to He and the reactor is heated at the desired reaction temperature. A liquid water–ethanol mixture (molar ratio of 3:1 or 2:1) is pumped into the heated chamber and vaporized. The water–ethanol gas stream (diluted in He if desired) is then fed to the reactor and the conversion of reactants and selectivities toward reaction products are determined by the analysis system described above.

The variable operation parameters for the present experimental investigation are the reaction temperature, the steam-to-ethanol ratio and the total flow rate. All experiments have been performed under atmospheric pressure.

3. Results and discussion

3.1. Effect of operating conditions on the performance of supported Ni catalysts

The nature of the carrier is known to influence the catalytic performance of supported metal catalysts. For this reason, preliminary catalytic performance and stability tests were conducted over Ni catalysts supported on La_2O_3, Al_2O_3, YSZ and MgO under various experimental conditions in order to select the best performing and stable catalyst for the steam

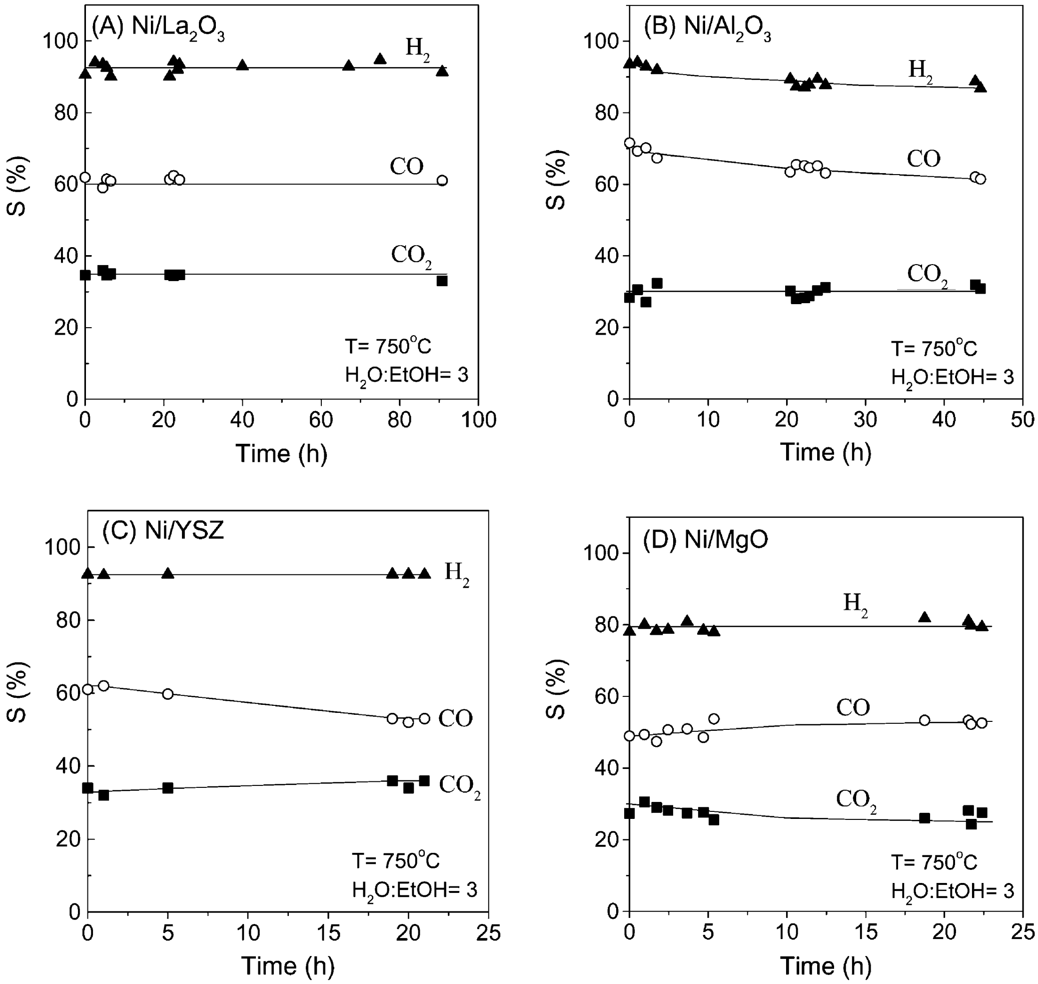

Fig. 2. Alteration of the selectivities of H_2, CO and CO_2 with time-on-stream over Ni catalysts (17 wt.%) supported on: (A) La_2O_3; (B) Al_2O_3; (C) YSZ; (D) MgO. Experimental conditions: $T = 750\,°C$; mass of catalyst, 100 mg; particle diameter, $0.09 < d_p < 0.18$ mm; H_2O:EtOH = 3:1; flow rate, 160 cc/min (EtOH: 15 cc/min, H_2O: 45 cc/min, balance: He); $X_{EtOH} = 100\%$.

reforming of ethanol. In this series of experiments, the ethanol–water mixture was diluted in He.

Experimental results obtained at 750 °C using a stoichiometric H_2O:EtOH ratio of 3:1 are shown in Fig. 2A–D, in which the selectivities (S) toward H_2, CO and CO_2 are plotted as functions of time-on-stream for the catalysts examined. In all cases, conversion of ethanol (X_{EtOH}) was 100%. It is observed that, under the present experimental conditions, the Ni/La_2O_3 catalyst (Fig. 2A) is highly selective towards H_2 ($S_{H_2} > 90\%$) and very stable for almost 100 h on stream. Selectivities toward CO and CO_2 also remain constant at ca. 60 and 35%, respectively. The only byproduct observed under these conditions is CH_4.

The formation of H_2, CO_2 and CO may be described by the reactions of steam reforming (Eq. (2)) and WGS (Eq. (3)) which take place simultaneously in the reformer:

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO,\quad \Delta H = +57\,\text{kcal/mol} \tag{2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2,\quad \Delta H = -10\,\text{kcal/mol} \tag{3}$$

Thermodynamic analysis of the water–ethanol system [4–6] shows that, at equilibrium, the only additional reaction product in the gas-phase is methane, the formation of which is due to the hydrogenation of CO (methanation):

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O, \quad \Delta H = -49\,\text{kcal/mol} \tag{4}$$

Results obtained with time-on-stream over the Ni/Al_2O_3 catalyst (Fig. 2B) are, initially, comparable to those obtained over Ni/La_2O_3, but the selectivities toward reaction products progressively decrease with time-on-stream. This behavior may be attributed to the formation of coke which is accumulated on the catalyst surface, thus leading to deactivation. Carbon formation may take place in several ways, however the lowest values of Gibbs free energy corresponds to the "Boudouard" reaction [4]:

$$2CO \leftrightarrow CO_2 + C, \qquad \Delta H = -41\,\text{kcal/mol} \tag{5}$$

Another possible route for the formation of carbon over the present catalyst is via ethylene produced by dehydration of ethanol on the acidic Al_2O_3 support [13]:

$$C_2H_4 \rightarrow \text{polymers} \rightarrow \text{coke} \tag{6}$$

In the case of Ni/YSZ (Fig. 2C) selectivity toward H_2 remains constant at ca. 92%, but S_{CO} and S_{CO_2} change with time and tend to stabilize after more than 20 h on stream. Finally, the Ni/MgO catalyst seems to be very stable under the present conditions (Fig. 2D), but the selectivity toward hydrogen (ca. 80%) is lower than that observed over the other catalysts.

When the reaction temperature was lowered to 600 °C, the relative catalytic performance of the catalysts was significantly different, under similar experimental conditions. Results obtained from Ni/La_2O_3 are shown in Fig. 3A. It is observed that selectivities toward H_2, CO and CO_2 initially change with time-on-stream and stabilize after ca. 20 h, at values of 77, 50 and 35%, respectively. Selectivity toward hydrogen is lower than that observed at 750 °C mainly due to the formation of appreciable amounts of CH_3CHO and CH_4 (see below). The behavior of Ni/Al_2O_3 was found to be qualitatively similar to that of Ni/La_2O_3. In contrast, Ni/YSZ and Ni/MgO catalysts were found to deactivate to a significant extend, possibly due to the formation of coke.

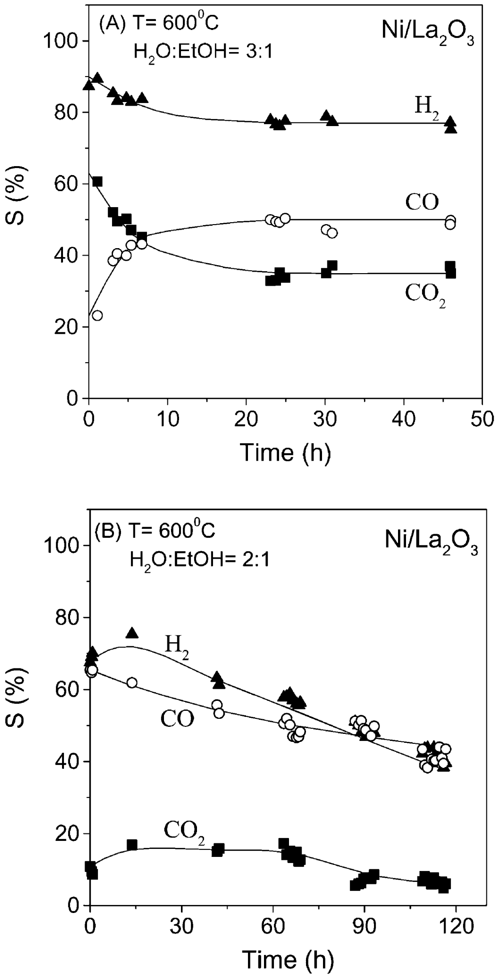

Fig. 3. Alteration of the selectivities of H_2, CO and CO_2 with time-on-stream over Ni/La_2O_3 obtained at $T = 600\,^\circ C$. Experimental conditions: (A) H_2O:EtOH = 3:1; (B) H_2O:EtOH = 2:1, others as in Fig. 2.

The effect of water-to-ethanol ratio was also examined over the same catalysts. Results obtained from the Ni/La_2O_3 catalyst using a molar ratio of H_2O:EtOH = 2:1, at the reaction temperature of 600 °C are shown in Fig. 3B. It is observed that decreasing the water-to-ethanol ratio results in rapid deactivation of the catalyst at 600 °C, which continuous even after more than 100 h on stream. At the reaction temperature of 700 °C, deactivation was found to be slower. Similar results obtained over Ni/Al_2O_3, Ni/YSZ and Ni/MgO (not presented) showed that all catalysts exhibit severe deactivation which is more pronounced at lower reaction temperatures and lower steam-to-ethanol ratios, as would be expected.

The lose of stability observed with decreasing reaction temperature and/or water-to-ethanol ratio in the feed is in accordance with thermodynamic predictions regarding the formation of coke. Garcia and Laborde [4] performed a thermodynamic analysis in the pressure range of 1–9 atm and water-to-ethanol feed ratios of 0:1–10:1. They concluded that optimal conditions for hydrogen production are at $T > 650\,\mathrm{K}$, atmospheric pressure and excess water in the feed. Under these conditions methane production is minimized and carbon formation is thermodynamically inhibited. At water-to-ethanol feed ratios <1, solid carbon will appear at any temperature and any pressure, while at a feed steam-to-ethanol ratio of 10:1 solid carbon will not appear at any temperature and pressure. At water-to-ethanol ratios of 2:1 used in the present set of experiments, formation of carbon is expected to occur to an extend that depends on reaction temperature [4].

Experimental results presented in Figs. 2 and 3 clearly show that catalytic performance and stability of Ni is enhanced when supported on La_2O_3, compared to Al_2O_3, YSZ and MgO. Therefore, the Ni/La_2O_3 catalyst was further tested in order to examine in detail the effect of reaction temperature on catalytic activity and selectivity. Typical experimental results obtained are presented in Fig. 4, in which conversion of ethanol and selectivities to reaction products are plotted as functions of reaction temperature. It is observed that at temperatures below 300 °C, the conversion of ethanol is very small. In this temperature region, the reaction is highly selective toward acetaldehyde, which is formed by dehydrogenation of ethanol:

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \qquad (7)$$

Increasing reaction temperature results in a progressive decrease of the selectivity toward acetaldehyde, which drops to zero at temperatures above 550 °C. Steam reforming of ethanol (and acetaldehyde) takes place to a significant extend at temperatures above 400 °C, as evidenced by the sharp increase of ethanol conversion and by the increase of the selectivities toward CO and H_2 (Fig. 4). Byproducts of the reaction are CO_2 and CH_4, which are mainly formed by reaction of CO with water (Eq. (3)) or hydrogen (Eq. (4)), respectively. It is interesting to observe that no ethylene is detected under these conditions, indicating that no dehydration of ethanol is taking place, as might be expected. This is due to the fact that this particular catalyst does not possess any acidic function, which is required for the dehydration route.

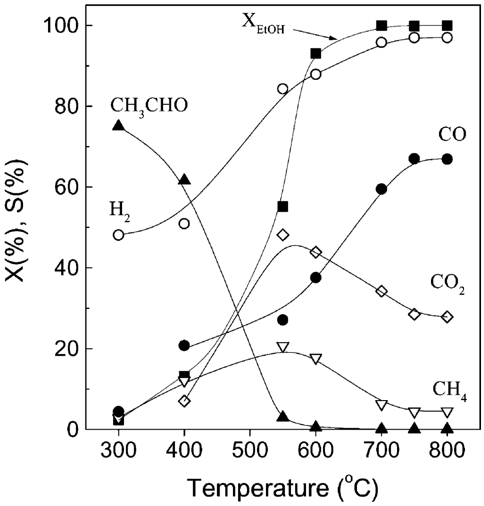

Fig. 4. Effect of reaction temperature on the conversion of ethanol (X_{EtOH}) and on the selectivities (S) toward reaction products obtained over the Ni/La_2O_3 catalyst. Experimental conditions are same as in Fig. 2.

Selectivities toward CO_2 and CH_4 increase with increasing temperature, go through maxima at ca. 550 °C and then decrease at higher temperatures. This behavior may be attributed to the reformation of CH_4 with CO_2 (Eq. (8)) and/or H_2O (Eq. (9)), which become thermodynamically feasible at these temperatures:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H = +59\,\mathrm{kcal/mol} \qquad (8)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H = +49\,\mathrm{kcal/mol} \qquad (9)$$

Indeed, the Ni/La_2O_3 catalyst is known to be very active for these reforming reactions [11]. The observed decrease in the production of CO_2 may be partly due to the inverse shift reaction (Eq. (3)).

At temperatures above 600 °C, the conversion of ethanol reaches 100% and the selectivity toward hydrogen exceeds 95% (Fig. 4). Under these conditions, the only undesirable product is methane. 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.

3.2. Catalytic performance of $Ni/(La_2O_3/Al_2O_3)$ catalyst under realistic reaction conditions

Lanthanum oxide is hygroscopic and pellets made out of this material do not possess the necessary strength in the presence of high concentrations of steam, especially at low temperatures. This problem may be avoided if lanthana is dispersed over materials that exhibit the necessary strength, such as alumina pellets. In order to examine this possibility, additional experiments were conducted over samples in which the active component (Ni/La_2O_3) was deposited on γ-Al_2O_3 pellets. These experiments were conducted using concentrated water–ethanol mixtures in the feed.

Catalytic performance results obtained from $Ni/(La_2O_3/Al_2O_3)$ are shown in Fig. 5A where conversion of ethanol and selectivities to reaction products are plotted as functions of reaction temperature. It is observed that the temperature-dependence of conversion of ethanol and of selectivities to reaction products is qualitatively similar to the corresponding obtained over the Ni/La_2O_3 catalyst (compare with Fig. 4). However, under the experimental conditions employed, X_{EtOH} reaches 100% at higher temperatures (>800 °C). Selectivity toward H_2 is relatively low at temperatures below 600 °C, due to the formation of ethylene, which is promoted by the presence of Al_2O_3 in the supporting material. At higher temperatures, S_{H_2} exceeds 95% and at 840 °C only small amounts of byproducts (mainly CH_4) are observed in the reformate gas.

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. 5B, where the conversion of ethanol and the selectivities to reaction products are plotted as functions of *W*/*F*. It is observed that for contact times higher than ca. 0.1 g s cm^{-3} the conversion of ethanol is complete and the reaction is highly selective toward hydrogen (ca. 95%), the only unwanted byproduct being methane (less than 5%). As the contact time decreases, the conversion of ethanol progressively drops, accompanied by a decrease of the selectivity toward the reformation products (CO and

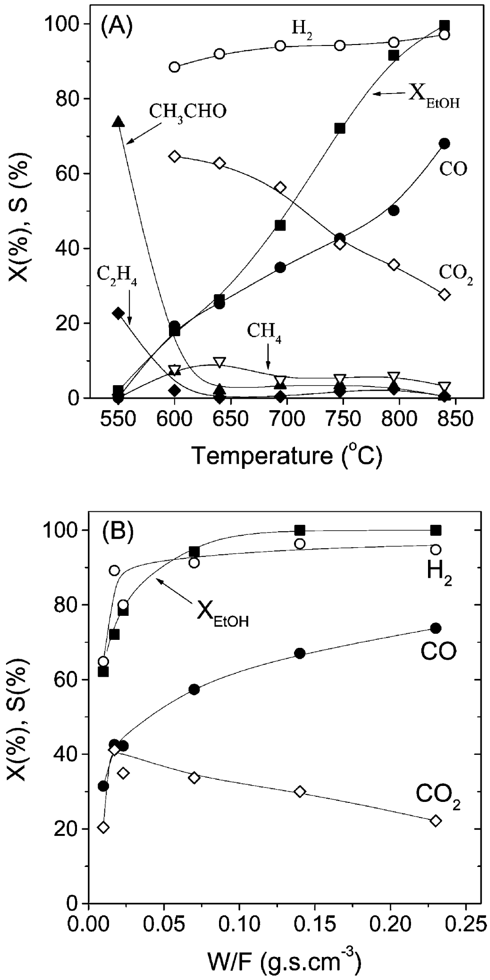

Fig. 5. (A) Effect of reaction temperature on the conversion of ethanol (X_{EtOH}) and on the selectivities toward products obtained over the 20% $Ni/(La_2O_3/Al_2O_3)$ catalyst. Experimental conditions: mass of catalyst, 100 mg; particle diameter, $0.25 < d_p < 0.50$ mm; H_2O:EtOH = 3:1; flow rate, 350 cc/min (EtOH: 87 cc/min, H_2O: 263 cc/min). (B) 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: $T = 750$ °C, others as in (A).

H_2) and by an increase of the selectivity toward CO_2 and byproducts, such as CH_3CHO, C_2H_4 and C_2H_6 (not shown). 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 performance of other catalytic materials, such as Co, Rh and Ru was also examined under conditions of steam reforming of ethanol and is compared with that of Ni catalyst in Fig. 6A and B, in which conversion of ethanol and selectivity toward hydrogen are plotted as functions of reaction temperature. For comparison, the corresponding results obtained in the absence of catalyst in the reactor (homogeneous reactions) are also shown. It is observed that the homogeneous conversion of ethanol becomes significant at temperatures above 750 °C and reaches 80% at 850 °C (Fig. 6A). However, selectivity toward hydrogen is very small under these conditions and increases from ca. 35 to 55% upon increasing reaction temperature from 650 to 850 °C (Fig. 6B).

The 20% Co/Al_2O_3 catalyst is almost inactive under the experimental conditions employed. The 3% Ru/TiO_2 catalyst exhibits better performance but both X_{EtOH} and S_{H_2} are significantly lower than the corresponding values obtained over $Ni/(La_2O_3/Al_2O_3)$. In contrast, the 0.5% Rh/Al_2O_3 catalyst exhibits comparable activity with the $Ni/(La_2O_3/Al_2O_3)$. However, selectivity towards hydrogen is poor over the rhodium catalyst, especially at temperature below 750 °C (Fig. 6B). In addition, preliminary experiments conducted under steam reforming conditions (not presented here) showed that the 0.5% Rh/Al_2O_3 catalyst suffers from appreciable deactivation with time-on-stream.

The stability of the $Ni/(La_2O_3/Al_2O_3)$ catalyst was examined at 750 °C employing an undiluted feed stream of 3:1 steam-to-ethanol ratio, for a time-on-stream of over 150 h. Under the experimental conditions employed, a small deactivation of the catalyst was observed during the first 80–100 h on stream, when conversion of ethanol dropped from ~95 to ~90% [12]. Further exposure of the catalyst to the reaction mixture did not result in further deactivation. Selectivity toward hydrogen did not significantly change with time-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 stabilized after more than ca. 100 h on stream [12].

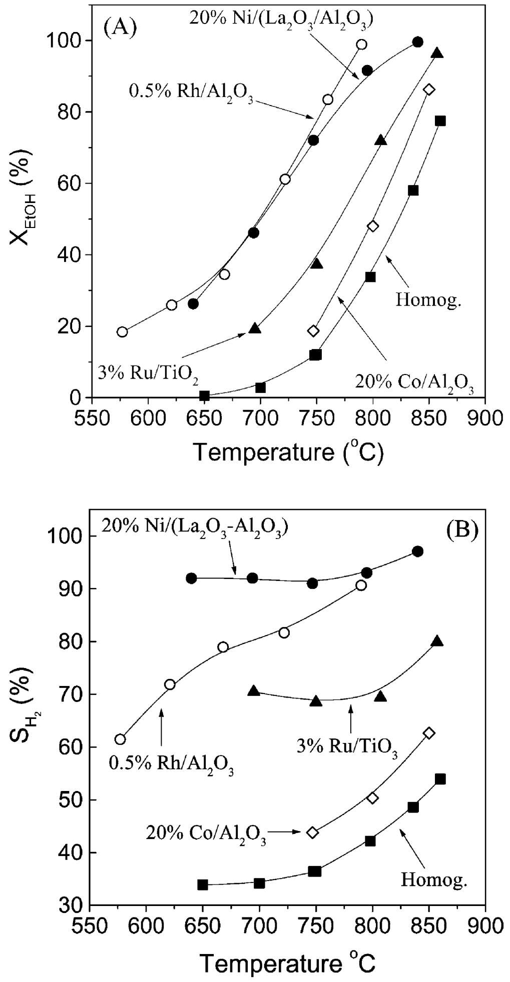

Fig. 6. Conversions of ethanol (A) and selectivities toward hydrogen (B) obtained as functions of reaction temperature over 20% $Ni/(La_2O_3/Al_2O_3)$, 0.5% Rh/Al_2O_3, 3% Ru/TiO_2 and 20% Co/Al_2O_3 catalysts and in the absence of catalyst (homogeneous reactions). Experimental conditions are same as in Fig. 5A.

Results presented above clearly show that Ni catalyst supported on La_2O_3 is very active and stable for the reaction of steam reforming of ethanol, compared to catalysts supported on other oxides, such as Al_2O_3, YSZ and MgO. Of special interest is the uniqueness of the Ni/La_2O_3 in terms of its long term stability, which is more pronounced at relatively low temperatures and lower than stoichiometric water-to-ethanol ratios in the

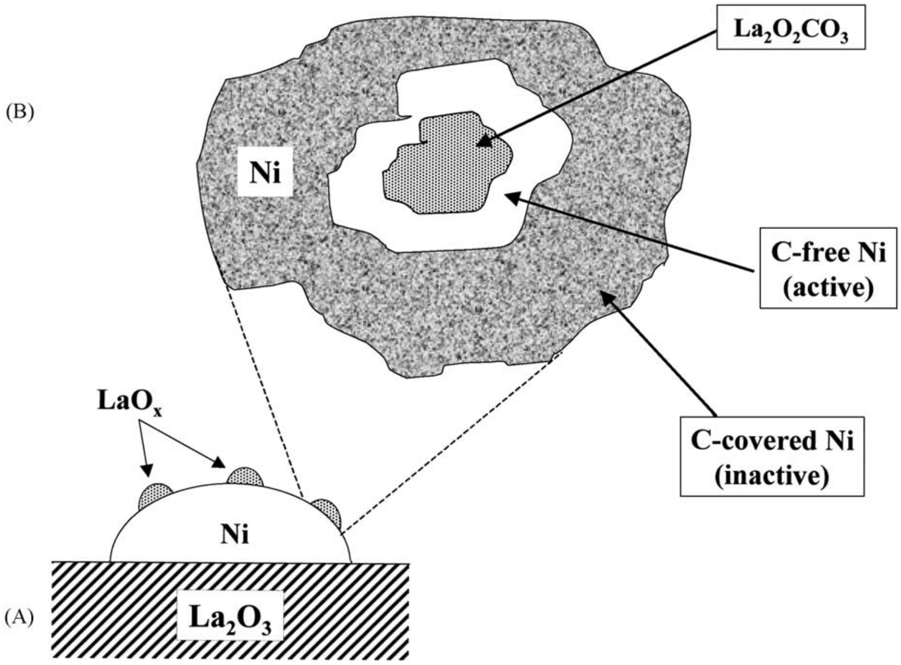

Fig. 7. Schematic representation of the proposed model which describes the exceptional stability of Ni/La_2O_3 catalysts under reforming reaction conditions: (A) Ni particles are decorated with lanthanum oxide species originating from the support; (B) regeneration of the active sites takes place in the vicinity of lanthanum oxide particles with intermediate formation of $La_2O_2CO_3$.

feed. The unusual stability of the Ni/La_2O_3 catalyst, which has also been observed for the reaction of reforming of methane with CO_2 [11] may be explained by taking into account a mechanistic model, which is schematically shown in Fig. 7. According to this model, a thin overlayer of lanthana is formed on top of the nickel particles following the high-temperature pretreatment of the catalyst or exposure to reaction conditions. This has been verified in previous work employing a variety of techniques, such as selective chemisorption of H_2 and CO, XRD and TEM/EDX [14–17].

Under reforming reaction conditions, lanthanum oxide species, which decorate the Ni particles, react with carbon dioxide to form $La_2O_2CO_3$:

$$La_2O_3 + CO_2 \leftrightarrow La_2O_2CO_3 \qquad (10)$$

Lanthanum oxycarbonate species react with surface carbon, at their periphery, thus cleaning the Ni surface of carbon deposits:

$$La_2O_2CO_3 + C \rightarrow La_2O_3 + 2CO \qquad (11)$$

In this way, the surface carbon at the periphery of the oxycarbonate particles is removed, resulting in the observed good stability characteristics of the catalyst.

4. Conclusions

The following conclusions can be drawn from the results of the present study:

(1) An integrated process for the production of electricity from biomass is proposed, which is characterized by high efficiency and nearly zero emissions. The most important catalytic step of the process is the reformation of bioethanol to a hydrogen-rich gas stream, which may be used to produce electricity for mobile and/or stationary applications by means of fuel cells.
(2) The Ni/La_2O_3 catalyst, which is characterized by high activity and selectivity toward hydrogen for the reaction of steam reforming of ethanol could be used in ethanol reforming processors for fuel

cell applications. In contrast to Ni catalysts supported on Al_2O_3, YSZ and MgO, the Ni/La_2O_3 catalyst exhibits good long-term stability, which is improved by increasing the reaction temperature and the water-to-ethanol ratio in the feed.

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