Production of hydrogen for fuel cells by catalytic partial oxidation of ethanol over structured Ni catalysts

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Abstract

Cordierite monoliths, ceramic foams made from mullite and zirconia–alumina as well as γ-Al_2O_3 pellets were employed as supports for Ni/La_2O_3 structured catalysts for the production of hydrogen by catalytic partial oxidation of ethanol. Although all catalysts were very active for ethanol conversion and very selective towards the desired products, the one supported on the zirconia–alumina ceramic foam produced slightly better results. Tested under a wide variety of process conditions, the catalyst supported on the monolith exhibited excellent catalytic performance and long-term stability. In addition to this catalyst, which was prepared by washcoating the active phase on the support, catalysts were prepared on monoliths by adsorption and sol–gel techniques. Adsorption from solutions produced the catalyst with the weakest performance while the sol–gel method resulted in a catalyst with intriguing behavior. Overall, catalysts produced by washcoating on cordierite monoliths are the most promising candidates for the production of hydrogen by partial oxidation of ethanol. Other supports and preparation methods have the potential to produce better catalytic materials but require further optimization.
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1. Introduction

Environmental and public health problems stemming from automotive and power generation sources, in addition to energy supply diversification and security issues, have pushed forward new ideas for energy production in the last few years. One of the most promising solutions appears to be fuel cells. Although the development of fuel cells meeting the criteria of high efficiency, portability and affordability faces significant technical challenges, a major hurdle remains the sourcing of hydrogen and the development of efficient, safe and affordable production processes.

In theory, hydrogen can be extracted from any hydrocarbon. In practice, natural gas, gasoline, diesel and methanol are the most commonly mentioned sources. These sources, however, are fossil fuel based and suffer from some of the same disadvantages attributed to the established power generation process: they do not reduce reliance on fossil fuels or emissions of pollutants and greenhouse gases. A viable alternative, gaining acceptance in recent years, is bio-fuels. They offer high energy density, safety and ease of handling so that they can be used for on-demand production of hydrogen for automotive and distributed power generation applications. The most promising among the liquid bio-fuels is bio-ethanol.

Bio-ethanol is a renewable energy source that can be easily produced from many biomass sources, including energy plants, grains, waste materials of the agricultural and forestry industries and even from the organic fraction of municipal solid wastes. It is widely available, easy to store and transport and safe to handle. It has been used for many years either as a primary fuel or a fuel blending component for automobile engines in Brazil and the USA. Furthermore, a bioethanol-to-hydrogen system has the significant advantage of being nearly CO_2 neutral since the carbon dioxide produced in the process is consumed for biomass growth, offering a nearly closed carbon loop.

The increasing attention paid to ethanol has resulted in a number of studies on hydrogen production from ethanol via steam reforming or catalytic partial oxidation [1–6]. Thermodynamic analysis has established the feasibility of the process [7–9] and several catalysts have been proposed that show sufficient activity and stability to be considered for practical applications [10–16]. Although a series of metals have been tried as the active catalytic component, a common denominator for most of the studies has been the use of Ni supported catalysts, owing to the significant body

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of knowledge gained from industrial steam reforming processes. A limitation of these studies has been the use of catalysts in powder form. Handling and pressure drop problems make such a form unsuitable for practical applications. Especially for applications where very high reliability and low pressure drops are required, such as automobiles, the catalysts must be deposited on structural supports that have excellent structural stability and can operate in harsh environments that include vibrations, thermal cycling and thousands of start-ups and shut-downs.

A major consideration in the development of ethanol-to-hydrogen processes is the endothermicity of the reforming reaction, which necessitates provisions for the supply of great amounts of heat in order to maintain the system at a steady reaction temperature:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2$$
$$(\Delta H_r = 173.1 \, kJ \, mol^{-1}) \tag{1}$$
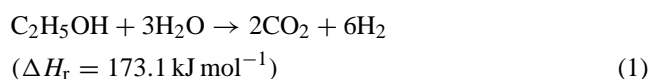
Heat can either be supplied externally by burning some type of fuel, or internally by co-feeding oxygen or air and burning a portion of the ethanol at the expense of hydrogen production. At least 0.61 mol of oxygen per mole of ethanol are required to achieve thermal neutrality

$$C_2H_5OH + 0.61O_2 + 1.78H_2O \rightarrow 2CO_2 + 4.78H_2$$
$$(\Delta H_r = 0 \, kJ \, mol^{-1}) \tag{2}$$
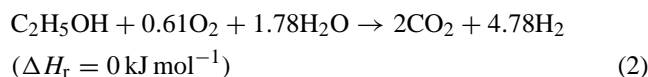
In one embodiment of this process, combustion occurs in the gas phase before the catalyst bed. This process is termed as auto-thermal. When combustion takes place on the same catalyst as the reforming reaction, the process is usually termed catalytic partial oxidation. Due to the nature of the process, combinations of the above can easily be created. In this study, we examine the catalytic partial oxidation of ethanol over a number of Ni catalysts deposited on different supports.

2. Experimental

2.1. Catalyst preparation

Supports used in this work included: (i) 1/16 in. pellets of γ-Al$_2$O$_3$ with a specific area of 180 m^2/g from Engelhard, (ii) monoliths of the type used in automobile exhausts with 400 channels per square inch, (iii) ceramic foams made from a proprietary formulation of alumina and zirconia (ZA), having medium porosity (50 pores per square inch) and (iv) ceramic foams made from mullite, having larger porosity (30 pores per square inch). All catalysts contained Ni/La$_2$O$_3$ as the active phase at an average loading of 13 wt.%.

The catalyst supported on γ-Al$_2$O$_3$ pellets was prepared by wet impregnation. The pellets were first impregnated with aqueous solutions of La(NO$_3$)$_3$·6H$_2$O, then dried at 120 °C and calcined at 900 °C for 30 h. Ni was added by

impregnation with aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O. The material was dried at 120 °C and calcined at 500 °C for 5 h.

A series of Ni/La$_2$O$_3$ catalysts supported on cordierite monoliths were prepared by washcoating. A Ni/La$_2$O$_3$ powder catalyst was prepared by impregnating La$_2$O$_3$ with an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O followed by drying at 120 °C and calcination at 550 °C. A dense suspension of this powder in de-ionized water was created and the catalysts were coated by successive immersions in the suspension followed by drying at 120 °C and calcination at 550 °C. A final calcination at 1000 °C took place before testing.

Another Ni/La$_2$O$_3$ catalyst was deposited on a cordierite monolith by adsorption. In this case, the monolith was immersed in aqueous solutions of La(NO$_3$)$_3$·6H$_2$O, dried at 120 °C and calcined at 550 °C. The lanthana coated monolith was then immersed in an aqueous solution of Ni(NO$_3$)$_2$·6H$_2$O and La(NO$_3$)$_3$·6H$_2$O. The catalyst was dried and calcined under the same conditions before being loaded in the reactor. This method resulted in the lowest catalyst uptake, ∼9 wt.%, even after repeating the procedure seven times.

A sol–gel method was used for the preparation of Ni/La$_2$O$_3$ supported on cordierite monoliths and mullite and ZA foams. A sol–gel was prepared using Al[OCH(CH$_3$)$_2$]$_3$, Ni(NO$_3$)$_2$·6H$_2$O and La(NO$_3$)$_3$·6H$_2$O as precursors. Monoliths or foams were immersed in the sol–gel without any other pretreatment, removed and dried at 120 °C. A final calcination at 550 °C completed the preparation.

As a base case, a plain monolith, with no catalyst, was also tested. All catalysts were reduced in situ before reaction at 750 °C under flow of pure hydrogen.

2.2. Apparatus and procedures

The apparatus employed consisted of a feed system, a reactor and an analysis system. The feed system included a set of mass-flow controllers (MKS) regulating gas flows and an HPLC pump (Marathon) feeding liquid reagents. Liquids were evaporated and heated to 150 °C in an evaporator and fed to the reactor via heated lines.

The reactor was made from two connected quartz tubes of different diameters (Fig. 1). The small diameter tube acted as the inlet section. The evaporated reagents (ethanol and water) and air were kept separate from each other to minimize
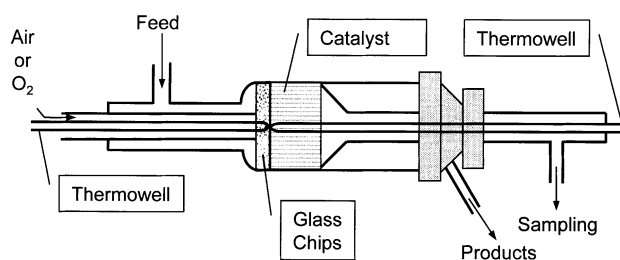

Fig. 1. Schematic diagram of the reactor employed for the ethanol partial oxidation studies.

gas phase reactions. They were mixed in the first part of the main reactor, which was packed with quartz chips, designed to provide complete mixing and uniform distribution of the reactants before entering the catalyst. Glass wool provided support and a seal between the catalyst and the reactor walls. Thermowells running the length of the reactor, and passing through the catalyst, allowed monitoring of the temperature profile. The whole reactor was placed inside an electric furnace.

Product analysis was accomplished using two gas chromatographs (Shimadzu). The first GC was used for the analysis of all organic species and water and was equipped with two packed columns (Porapak-Q and Carbosieve) and two detectors (TCD, FID) with He as the carrier gas. A condenser was placed before the inlet to the Carbosieve column to remove most of the water. This stream was also fed to the second GC which was equipped with a Carbosieve column and a TCD detector with N_2 as the carrier gas and was used solely to determine the H_2 concentration in the reformate. The chromatographs were calibrated with gas streams of known composition. Ultrahigh purity gases were supplied from high-pressure gas cylinders (Air Liquide) and analytic grade ethanol was obtained from Merck.

In a typical experiment, the fresh catalyst is reduced in situ at $750\,^\circ$C for 2 h under hydrogen flow. The system is then allowed to equilibrate at the desired temperature under He flow and the reactant streams are introduced to the reactor. Catalytic activity is evaluated in terms of ethanol conversion. Selectivities are defined as the ratios of the product moles to the consumed moles of ethanol, accounting for stoichiometry. Hydrogen selectivity is calculated by the hydrogen balance and is defined as the molar fraction of hydrogen produced to the total hydrogen in the product stream. All experiments were performed at atmospheric pressure.

3. Results and discussion

The catalytic performance of all materials was examined as a function of temperature and space velocity, while some catalysts underwent stability tests. We will first present typical results obtained with one of the catalysts, the Ni/La_2O_3 washcoated on the cordierite monolith, and then will compare the different supports and preparation methods.

3.1. Effect of reaction temperature on ethanol conversion and product distribution

The effect of temperature on the catalytic performance of the Ni/La_2O_3 catalyst washcoated on the cordierite monolith is shown in Fig. 2A, where ethanol conversion (X_{EtOH}) and selectivities towards reaction products (S_i) are plotted as functions of furnace temperature. The catalyst exhibits very high activity, with very high ethanol conversion at $500\,^\circ$C and complete conversion for temperatures above $550\,^\circ$C. The catalyst is also very selective towards the desired products.
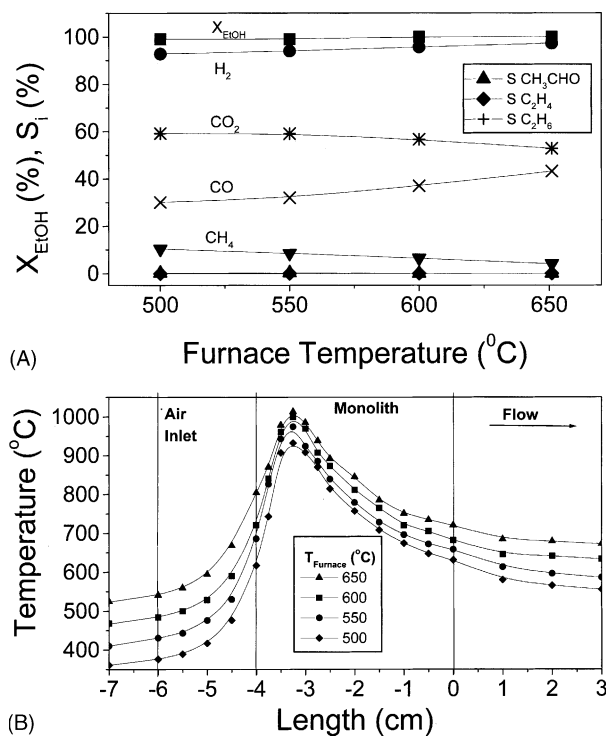

Fig. 2. Effect of reaction temperature on the conversion of ethanol (X_{EtOH}) and on the selectivities (S_i) towards products (A) and the associated temperature profiles (B) over the Ni/La_2O_3 catalyst supported on a cordierite monolith. Experimental conditions: HSV = $7245\,h^{-1}$; H_2O:EtOH = 3:1; O_2:EtOH = 0.61:1.

Selectivity towards hydrogen is 94% at $500\,^\circ$C and reaches >97% at $650\,^\circ$C. The main byproduct is methane, but its selectivity decreases substantially with increasing temperature. Other byproducts, such as CH_3CHO, C_2H_4 and C_2H_6 are observed at trace amounts, if at all. The very high selectivity towards CO_2 compared to the selectivity towards CO, indicates reasonably good ability of the catalyst to promote the water gas shift reaction.

The exothermicity of the oxidation reactions renders any attempt to attain constant temperatures at the catalyst inlet impractical, if not infeasible, so the furnace set points are used as references in Fig. 2A. This exothermicity is clearly demonstrated in Fig. 2B, which presents the temperature profiles along the centerline of the reactor. The monolith is approximately 4 cm long and the air enters the quartz chip bed 2 cm before the catalyst. Temperatures at the mixing point are significantly lower than the furnace set points due to the low temperatures of the incoming streams and the heat losses of the system. Temperatures rise inside the quartz chip bed, especially as we approach the catalyst inlet, due to heat contacted and radiated from the hot catalyst. Although we cannot rule out initiation of the combustion reactions in this bed, the fact that the temperature maxima develop well inside the monolith indicates that the majority of the combustion reactions take place inside the catalyst. The sharpness of these maxima points to a well established and thin combustion zone. This is desirable since any oxygen diffusing

downstream will consume the produced hydrogen. The goal is to provide enough heat to drive the reforming reactions to completion. These reforming reactions consume heat and the temperatures downstream the reactor drop and reach the furnace set point 3–5 cm after the catalyst. The average and the maximum temperatures inside the catalyst rise with increasing furnace set point since the furnace provides greater amounts of heat to the reactor. The greater amounts of heat, in turn, result in greater extend of reaction and almost complete reforming.

3.2. Effect of space velocity on catalytic activity and product distribution

The high activity of this catalyst was also demonstrated by varying the space velocity as shown in Fig. 3A. The feed composition and the furnace set point were maintained constant while the feed flow varied for this experiment. Equipment limitations determined the range of space velocities examined (3620–$9055 \, h^{-1}$). Ethanol conversion is complete in the entire range of space velocities examined. Interestingly, there is a very slight increase in selectivity towards hydrogen accompanied by a small decrease towards the main byproduct, methane. Selectivity towards CO_2 also decreases slightly, accompanied by a small increase in selectivity towards CO. All other byproducts appear only in

trace amounts. The temperature profiles, shown in Fig. 3B, may provide an explanation for these observations. For practically every point inside the catalyst, the temperatures increase with increasing flow. As the flow increases, more ethanol is combusted within the same catalyst volume, releasing more heat. As the thermal mass of the catalyst is the same, the temperatures keep on rising driving the system closer to adiabatic operation. Higher temperatures mean that the reforming reactions are driven closer to completion. They also mean higher CO concentration as the thermodynamic equilibrium between CO and CO_2 is shifted in its favor with increasing temperatures.

Noteworthy is the temperature profile at the lowest space velocity examined. The relatively small exotherm may indicate combustion reactions taking place homogeneously, to a significant extent, inside the quartz chip bed before the catalyst. This, in addition to the much lower temperatures inside the catalyst may explain the small variations in product selectivities. An interesting reaction engineering phenomenon is evident in this experiment. Increasing space velocity means decreasing residence time and one would expect a drop in ethanol conversion and selectivity towards hydrogen. On the other hand, increasing feed flow produces higher temperatures that result in higher ethanol conversion and H_2 selectivity. Because the reaction is, in all cases, at a rather insensitive state (i.e. almost complete conversion and very high H_2 selectivity) the two factors seem to balance out and the net effect is very small variations in catalytic performance with increasing feed flow rate. The effects are apparent only at the extremes of the flow range.

3.3. Catalyst stability

The Ni/La_2O_3/monolith catalyst remained on stream for 70 h allowing us to return at regular intervals to a standard set of conditions and test its stability. Although harsher conditions (e.g. higher space velocity) may have leaded to accelerated aging, the aim here was to test catalyst stability at varying operating conditions, approaching commercial operation. In between the data points obtained at standard conditions, there were multiple start-ups and shut-downs while the feed flow varied by a factor of 2.5 and the furnace temperatures ranged from 500 to 650 °C. The catalyst shows remarkable stability during this run (Fig. 4). There may be a lineout period initially, but ethanol conversion and selectivities towards products remain essentially constant after 20 h on stream.

Nickel based catalysts are known to accumulate significant amounts of carbon in reforming or partial oxidation service. Therefore, even though there was no apparent deactivation of the catalyst, a regeneration was performed after 47 h on stream to estimate coke formation and to test catalyst regenerability. Regeneration was accomplished under controlled air supply and temperature conditions approximating commercial procedures. CO and CO_2 evolution was monitored and provided an estimate of the carbon
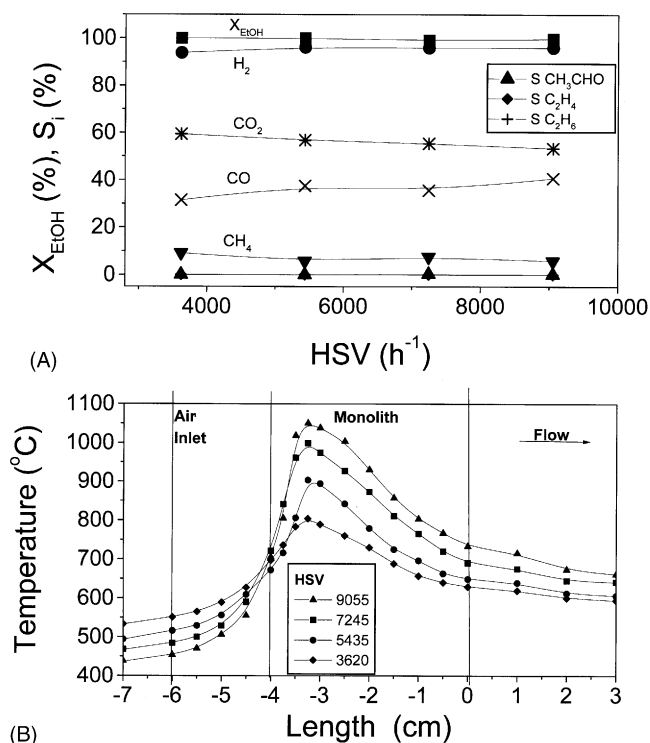

Fig. 3. Effect of space velocity on the conversion of ethanol (X_{EtOH}) and on the selectivities (S_i) towards reaction products (A) and the associated temperature profiles (B) over the Ni/La_2O_3 catalyst supported on a cordierite monolith. Experimental conditions: $T_{furnace} = 600\,°C$; $H_2O:EtOH = 3:1$; $O_2:EtOH = 0.61:1$.
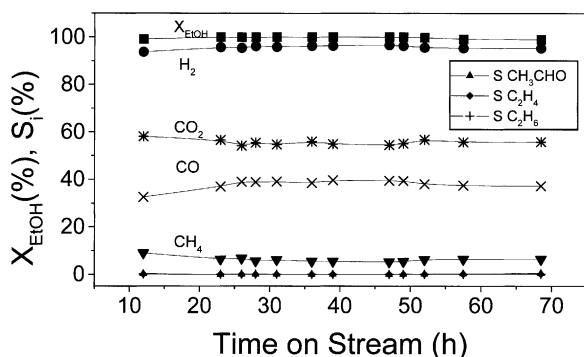
Fig. 4. Long-term stability test of the Ni/La$_2$O$_3$ catalyst supported on a cordierite monolith. Experimental conditions: $T_{furnace} = 600\,^\circ$C; HSV = 7245 h^{-1}; H$_2$O:EtOH = 3:1; O$_2$:EtOH = 0.61:1.

accumulation on the catalyst. Based on these results, we calculated that 1.2 g of carbon are deposited on the catalyst for every liter of ethanol processed. Another regeneration was performed at the end of the run and the results gave essentially the same carbon accumulation rate. Although a more extensive study is required, the preliminary results indicate that the carbon deposition rate remains constant with time. The encouraging result was the complete regenerability of the catalyst with no apparent effect on either ethanol conversion or selectivities towards the reaction products.

3.4. Comparison of catalyst supports

In addition to the cordierite monolith discussed above, the Ni/La$_2$O$_3$ catalyst was also supported on γ-Al$_2$O$_3$ pellets, a ceramic foam made from mullite and a ceramic foam made from zirconia–alumina (ZA). Although these catalysts were tested under a variety of conditions, we will focus on a standard set of conditions to compare the catalytic performance of these materials. The feed was a mixture of water and ethanol at a 3/1 molar ratio and air was supplied at a flow providing 0.61 mol of O$_2$ per mole of ethanol. The furnace set point was maintained at 600 °C. The catalysts will be compared for their ability to process given reactant flows. Although the diameter of the samples was essentially the same, their length and volume varied, resulting in different space velocities at the same flow rate. Apparatus flow limitations did not allow scanning all space velocities for all samples.

All catalysts are able to convert ethanol completely at the lower space velocities tested (Fig. 5A) while ethanol conversion progressively drops as space velocity increases. The catalyst supported on the monolith and the one supported on the mullite foam retain their activity best, while the catalyst supported on pellets is the one most affected by increasing flow. For comparison purposes, we also present results obtained with a monolith without any catalyst. Surprisingly, the plain monolith achieves reasonably high conversions that increase with increasing flow. Our previous studies [6] have established that ethanol decomposition is feasible even in
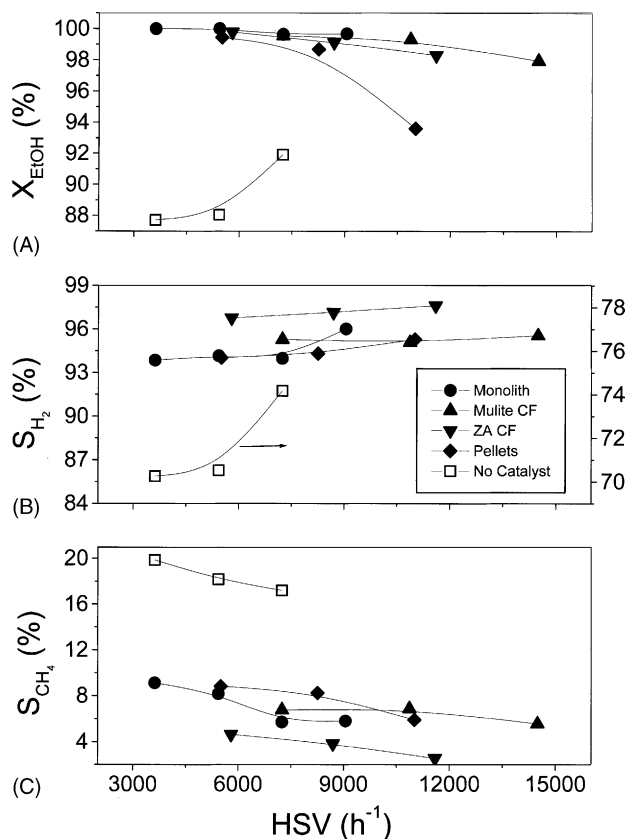

Fig. 5. Catalyst support comparison: ethanol conversion (A), selectivity towards hydrogen (B) and selectivity towards methane (C) as functions of space velocity. Experimental conditions: $T_{furnace} = 600\,^\circ$C; H$_2$O:EtOH = 3:1; O$_2$:EtOH = 0.61:1.

the absence of a catalyst and complete conversion is possible at very high temperatures. The role of catalyst, therefore, is to promote the reaction, i.e. achieve complete conversion at lower temperatures, and to increase the selectivities towards the desired products. This effect on selectivities is shown in Fig. 5B. All catalysts exhibit selectivities towards hydrogen greater than 93% while the plain monolith reaches only 70–75%. The catalyst supported on the ZA foam provided the highest selectivities and the ones supported on pellets and the monolith gave slightly lower values. The catalyst supported on the monolith, however, showed the largest increase in H$_2$ selectivity with space velocity. The increases for the other supports were notable, but smaller in magnitude.

The main byproduct was methane and the selectivities of the different catalysts were inversely proportional to those shown for hydrogen (Fig. 5C). The catalyst supported on the ZA foam had again the best performance, and lowest selectivity. All catalysts, however, exhibit far lower selectivities towards methane than the monolith without catalyst.

Other byproducts such as C$_2$H$_4$ and C$_2$H$_6$ were observed only at trace amounts at some flows and are not presented here. Of interest is the selectivity towards acetaldehyde shown in Fig. 6A. All catalysts produced very
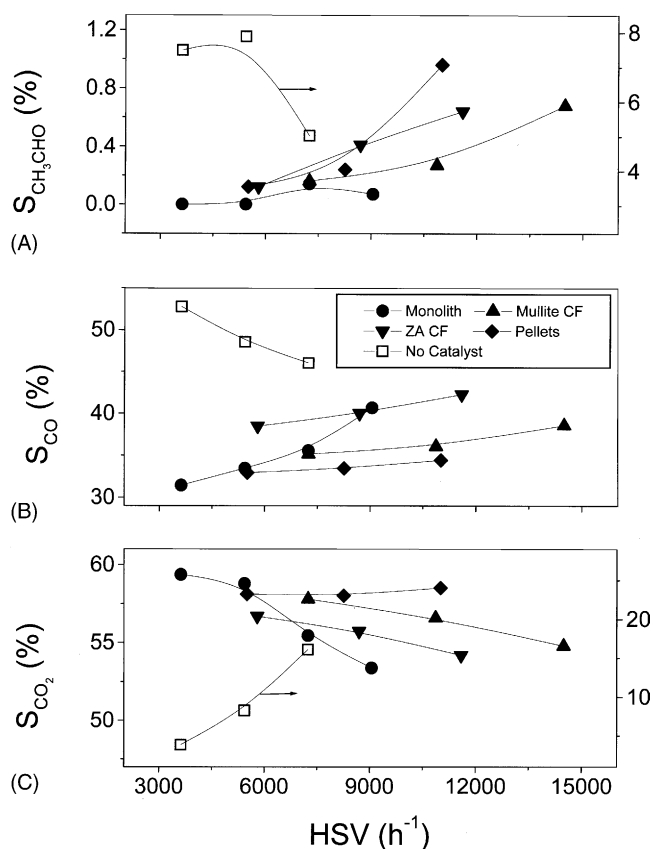
Fig. 6. Catalyst support comparison: selectivity towards acetaldehyde (A), CO (B) and CO_2 (C) as functions of space velocity. Experimental conditions: $T_{furnace} = 600\,^{\circ}C$; H_2O:EtOH = 3:1; O_2:EtOH = 0.61:1.

small amounts at the lower space velocities, but the concentration increased with increasing flow. Comparatively, the plain monolith selectivities are 1–2 orders of magnitude greater, but decreasing with space velocity. Acetaldehyde is produced by ethanol dehydrogenation and is subsequently reformed. Most of the catalysts are able to reform it to a large extend at the lower flows, but as residence time is reduced, the reforming reaction cannot be driven to completion. CH_3CHO can also decompose homogeneously at high temperatures, similar to ethanol. This is shown by the plain monolith where higher flows result in higher temperatures and greater CH_3CHO conversions.

CO and CO_2 have both been reported as possible primary products of ethanol reforming [13] and the selectivities towards CO and CO_2 (Fig. 6B and C) may reflect the ability of the catalysts to promote the water gas shift reaction. The catalyst supported on pellets demonstrates the largest promotion of this reaction, exhibiting the lowest selectivities towards CO, while the catalyst supported on the monolith is again most affected by the increases in space velocity. The plain monolith produces the most CO and by far the least CO_2. This tends to support a mechanism where the CO is the primary product of ethanol conversion and CO_2 is produced via the water gas shift reaction.

Overall, all catalysts exhibited very good performance, both in terms of ethanol conversion and in terms of selectivities towards the desired products. The catalyst supported on the ZA ceramic foam produced the best results even though the differences were not dramatic. The catalyst supported on the monolith appeared to be most affected by increases in space velocity, generally improving with increasing flow. This is also the catalyst that had the largest differences in the observed exotherms. As discussed above, the maximum and average temperature in the catalyst increases with increasing flow. The monolith showed a temperature maximum of approximately 800 °C at 3620 h^{-1}, but the maximum exceeded 1050 °C at 9055 h^{-1}. The other catalysts never reached temperatures higher than 970 °C. The very high temperatures achieved at the highest flows may explain the improvement in performance.

3.5. Comparison of catalyst preparation methods

The Ni/La$_2$O$_3$ catalyst was deposited on cordierite monoliths by three different methods: adsorption from solutions, sol–gel and washcoating. The performance of these catalytic systems was tested as function of space velocity at the same conditions mentioned in Section 3.4.
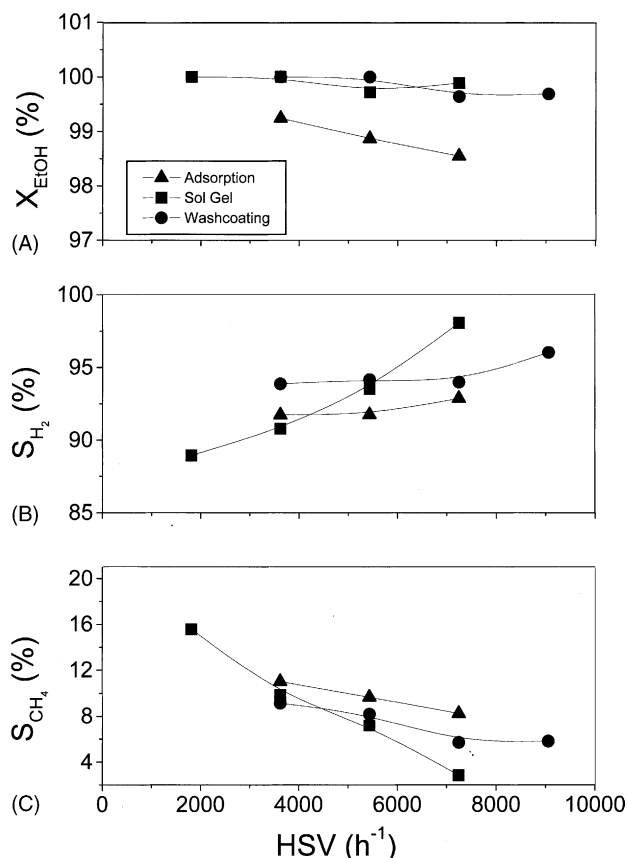

Fig. 7. Catalyst preparation method comparison: ethanol conversion (A), selectivity towards hydrogen (B) and selectivity towards methane (C) as functions of space velocity. Experimental conditions: $T_{furnace} = 600\,^{\circ}C$; H_2O:EtOH = 3:1; O_2:EtOH = 0.61:1.

Catalysts prepared by sol–gel and washcoating show very good activity with very high ethanol conversions over the range of space velocities tested (Fig. 7A). The catalyst prepared by adsorption is slightly less active and is more affected than the other two by increases in flow. It also provides the lowest selectivities towards hydrogen (Fig. 7B). The catalyst prepared by sol–gel exhibits the most dramatic increase in selectivity with increasing flow. This is accompanied by an equally dramatic decrease in selectivity towards the main byproduct: methane (Fig. 7C). The other two catalysts also show improved hydrogen selectivities and decreasing methane selectivities, but the differences are much smaller. Interestingly, these large performance differences are not evident in the selectivity towards CH_3CHO (Fig. 8A). As was the case with H_2 and CH_4, the catalyst prepared by adsorption provides the weakest performance, producing the most acetaldehyde in the reformate. It also produces the largest amounts of CO (Fig. 8B) and the smallest amounts of CO_2 (Fig. 8C), indicating the weakest promotion of the water gas shift reaction among the three catalysts.

The weak performance of the catalyst prepared by adsorption may reflect both the lower catalyst loading and a smaller availability of active phase on the exposed surface, i.e. a portion of the active phase may have been deposited inside the pores of the monolith. Since reactions at such high temperatures are typically diffusion controlled, material in the pores may not be easily accessible to the reactants, resulting in a smaller number of available active sites and lower activity. We are currently unable to examine the surface of the catalyst for the number and nature of the active sites.

The low selectivity towards H_2, and the corresponding high selectivity towards CH_4, of the catalyst prepared by sol–gel at the lowest space velocity is a result of the very low average temperature ($\approx 650\,^{\circ}C$) inside the catalyst. The maximum temperature is also low (approximately $815\,^{\circ}C$) and appears at the catalyst inlet. Although ethanol is completely converted in the first part of the catalyst, the temperature drops rapidly retarding the reformation of the primary products such as methane and the production of hydrogen. As space velocities increase, both the maximum and average temperature inside the catalyst increase driving the reactions closer to completion and producing significantly better results. At these higher space velocities the catalyst prepared by sol–gel exhibits superior performance and this could be the preferred preparation method. The more stable and predictable performance of the catalyst prepared by washcoating, however, make this method more suitable to commercial applications.

4. Conclusions

Ni/La_2O_3 catalysts supported on four different structured materials provided very good activity and selectivity for the ethanol partial oxidation reaction. The catalyst washcoated on a cordierite monolith exhibited excellent catalytic performance for a wide variety of process conditions and excellent long-term stability, albeit with significant coke formation. The coke deposited on the catalyst, however, did not appear to influence its activity or selectivity characteristics and the catalyst can be regenerated. The catalyst supported on the ZA foam gave marginally better results among all materials tested while very satisfactory results were obtained with the catalysts supported on the mullite foam and the γ-Al_2O_3 pellets. Pellets, however, may not be a suitable support for automotive applications due to possible attrition.

Among the preparation methods tested, adsorption produced the catalyst with the weakest performance, possibly due to active site inaccessibility. Sol–gel produced the more intriguing results and will be developed further. Washcoating resulted in a catalyst with excellent and predictable behavior and, given that it is the most well established technique, may be the preparation method of choice.
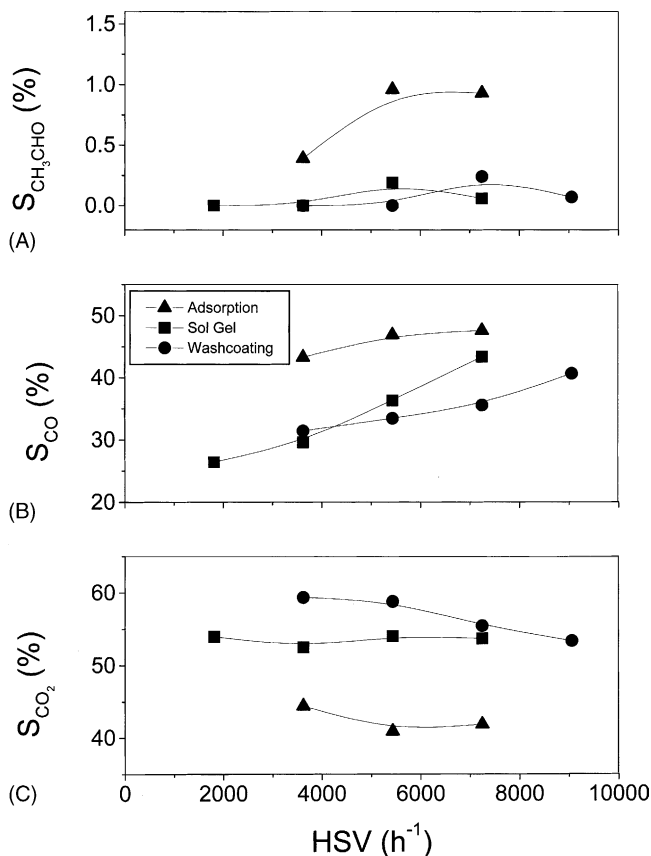

Fig. 8. Catalyst preparation method comparison: selectivity towards acetaldehyde (A), CO (B) and CO_2 (C) as functions of space velocity. Experimental conditions: $T_{\text{furnace}} = 600\,^{\circ}C$; $H_2O:EtOH = 3:1$; $O_2:EtOH = 0.61:1$.

Acknowledgements

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