Hydrogen Production By Steam Reforming Of Ethanol Over Ni/Sio$_2$ Catalysts

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Ethanol steam reforming has been studied over Ni/SiO$_2$ catalysts under a wide range of operating conditions, and the effect of Ni loading on catalyst properties and H$_2$ yield and selectivity has been analyzed. Surface area and pore volume significantly decrease with nickel content, but there is only a slight decrease in mean pore diameter. XRD patterns show peaks corresponding to NiO but no evidence of nickel silicate species has been found. Ni/SiO$_2$ catalysts are active for H$_2$ production by ethanol steam reforming over 400 °C. Ethanol conversion and H$_2$ yield considerably increase with temperature and Ni loading. Up to 3.9 mol$_{H2}$/mol$_{EtOH}$ is obtained at 600 °C and 8.3 g$_{catalyst}$min/g$_{EtOH}$, although lower temperatures (500 °C) are more suitable for minimizing CO selectivity. An improvement in catalyst performance is observed for high values of time-on-stream, which is explained by coke deposition in the form of carbon fibers.

1. Introduction

Nowadays there is a growing interest in the development of alternative energy systems to fossil fuels. In this context, hydrogen is considered to be the most viable energy carrier for the future (Marbán et al., 2007). It can be used in a fuel cell to generate electricity with high efficiency, and it is extremely clean as the only by-product is water. The steam reforming of ethanol is a promising way to produce hydrogen, as ethanol represents a renewable and CO$_2$-neutral fuel that can be readily obtained from biomass fermentation and is easy to store, handle and transport in a safe way, and high ethanol conversion can be achieved at lower temperatures than those required for steam reforming of other fuels (Haryanto et al., 2005; Ni et al., 2007).

The reaction pathways for ethanol steam reforming depend on catalyst and operating conditions, which affect significantly the hydrogen production. Together with the main products, H$_2$ and CO$_2$, undesirable products such as CO and CH$_4$ are usually formed in the reaction. Acetaldehyde and ethylene are important intermediates formed at low temperatures. In addition, the formation of coke is also common, mainly formed from ethylene intermediate produced via dehydration reactions of ethanol on acid sites. Moreover, certain transition metals like Ni may promote dehydrogenation and graphitization reactions and are used to produce nanostructured carbon materials (Sevilla and Fuertes, 2009). Thus, the high formation of superficial carbon deposits should be taken into account. Therefore, the selection of a suitable catalyst plays a vital role in ethanol steam reforming for hydrogen production.

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The most suitable catalysts used in bibliography are those based on Ni, Co, Rh, Pd and Pt, preferably supported on neutral or basic supports such as MgO, ZnO and CeO_2, which can significantly inhibit ethanol dehydration, reducing coke formation (Haryanto et al., 2005; Ni et al., 2007). Ethanol steam reforming has been extensively studied over Ni/Al_2O_3 catalysts in fixed bed reactors (Akande et al., 2005; Comas et al., 2004) and promising results have been obtained. The SiO_2 support shows good behavior in similar processes, such as carbon dioxide reforming of methane (Pan et al., 2008), but there is scarce information in the literature concerning its performance in ethanol steam reforming.

Therefore, the aim of this paper is the study of the physical and chemical properties of Ni/SiO_2 catalysts and its performance in the steam reforming of ethanol for H_2 production carried out in a fluidized-bed reactor. The effects of Ni loading and operating variables (temperature, space time, time-on-stream) were investigated in order to optimize ethanol conversion and hydrogen selectivity.

2. EXPERIMENTAL

The catalysts were prepared by impregnating the supports with aqueous solutions of $Ni(NO_3)_2\cdot6H_2O$ (CARLO ERBA Reagents, 99% purity). The impregnated samples were dried at 110 °C overnight and calcined at 550 °C for 4 h in air. Catalysts with different nominal nickel loadings were prepared: 5, 10 and 20 wt% referred as 5NiSi, 10NiSi and 20NiSi, respectively.

Real nickel content was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Surface areas (S_{BET}) and pore volumes (V_p) of the catalysts were measured by N_2 adsorption at 77 K, using a Micromeritics ASAP 2010 instrument. X-ray diffraction patterns were produced with a Philips PW 1710 diffractometer, using Cu Kα radiation, in steps of 0.04° with integration times of 12 s/step between 2θ= 15 and 80°. TPR profiles were recorded using an AUTOCHEM II 2920 provided with a thermal conductivity detector (TCD). The experiments were conducted in a quartz reactor from 40 °C to 900 °C with a heating rate of 10 °C/min in a flow of 10% H_2/Ar (30 ml/min) while the TCD signal was recorded. H_2 chemisorption measurements were performed using a Micromeritics ASAP 2010C. The samples were degassed for 1 h at 100 °C before measurement and reduced at 500 °C in pure hydrogen. The chemisorptions measurements were conducted at 35 °C. Specific nickel surface area was calculated assuming a stoichiometric factor of 1 (Ibrahim et al., 2007) for the adsorption of H_2 on a nickel atom.

Steam reforming of ethanol was carried out in an isothermal fluidized bed reactor at atmospheric pressure, connected on-line to a MicroGC Agilent 3000A for analysis of reaction products. Prior to catalytic tests the catalysts were reduced in situ under flowing hydrogen (10 vol%) at 550 °C. Dynamic experiments with increasing steps of temperature have been used to analyze the effect of temperature on activity and selectivity, whereas long duration runs at constant temperature have been performed to analyze the effect of time-on-stream. The operating conditions are: 300-600 °C; atmospheric pressure, water/ethanol molar ratio of 6, space time in the 1.8-30 $g_{catalyst}min/g_{EtOH}$ range, and time-on-stream up to 20 h.

3. RESULTS

3.1 Catalyst characterization

Table 1. Chemical composition and textural properties of the catalysts

Samples	Ni content (wt%)	S_{BET} (m^2/g)	V_p (cm^3/g)	D_{pore} (nm)
SiO$_2$	--	410.4	1.43	12.5
5NiSi	4.95	333.2	1.08	11.9
10NiSi	9.25	285.1	0.94	11.3
20NiSi	18.28	259.9	0.85	11.2

The chemical compositions obtained by ICP-AES of the supported Ni catalysts after calcination at 550 °C are shown in Table 1. There is a good agreement of these values with the nominal formulation of the precursor solutions, which indicates that Ni impregnation has been carried out satisfactorily.

The textural properties (S_{BET}, pore volume and mean pore diameter) of the catalysts and support are summarized in Table 1. The incorporation of nickel to the support changes the textural properties of the bare support. The S_{BET} and pore volume notably diminish with nickel content, indicating blockage of pores. However, the mean pore diameter decreases slightly, indicating that the pore blockage is not selective.

The XRD patterns of the fresh support only exhibited a wide peak at 23.5° corresponding to an amorphous structure. However, the XRD patterns of the catalysts presented peaks at 2θ= 37.4°, 44.5°, 62.6° and 75.2° that correspond to peaks of NiO according to Ref. 00-022-1189 (ICDD, 1995). No evidence of nickel silicate species was found.

The TPR profiles of Ni supported catalysts showed a peak in the 370-390 °C range and a second peak in the 460-490 °C range, similar to those obtained in the literature (Pan et al., 2008). Although samples with higher Ni content need a higher reduction temperature, 500 °C is enough to carry out the reduction of the catalyst before the kinetic experiments. The first peak could be assigned to the formation of nickel oxide on the silica surface, which is a weakly interacting support. The second peak could be assigned to an interaction with the support at high temperatures (Mile et al., 1988).

The dispersion level of nickel on the catalyst is relatively low (between 1.23-2.56 %), as typically observed for high Ni content catalysts.

3.2 Activity test

The conversion of ethanol, the hydrogen yield and product selectivity have been calculated according to the following expressions (Comas et al, 2004).

$$X_{EtOH} = \frac{F_{EtOH,in} - F_{EtOH,out}}{F_{EtOH,in}} \quad (1)$$

$$S_i = \frac{x_i \cdot F_T}{F_T - F_{EtOH,out} - F_{H_2O,out}} \quad (2)$$

$$Y_i = \frac{F_T \cdot x_i}{F_{EtOH,in}} \quad (3)$$

Table 2. Ethanol conversion, hydrogen yield and selectivities of H_2, CO_2, CO and CH_4 in the 400-600 °C range, atmospheric pressure, water/ethanol molar ratio 6/1 and space time of 8.3 $g_{catalyst}min/g_{EtOH}$ over Ni/SiO_2 catalysts.

Catalyst	T (°C)	X_{EtOH}	Y_{H_2}	S_{H_2}	S_{CO_2}	S_{CO}	S_{CH_4}
5NiSi	400	0.51	0.73	0.46	0.10	0.17	0.20
	500	0.63	1.81	0.62	0.20	0.04	0.12
	600	0.81	3.10	0.68	0.18	0.07	0.04
10NiSi	400	0.58	0.83	0.48	0.13	0.14	0.20
	500	0.75	2.12	0.62	0.20	0.05	0.12
	600	0.89	3.38	0.69	0.18	0.07	0.05
20NiSi	400	0.75	1.27	0.49	0.17	0.08	0.22
	500	0.98	2.70	0.62	0.20	0.05	0.13
	600	0.99	3.91	0.69	0.19	0.07	0.05

Table 2 shows ethanol conversion, hydrogen yield and selectivities of the main products in the ethanol steam reforming at different temperatures over Ni/SiO_2 catalysts with different metal loadings, obtained in the dynamic experiments. Under these conditions, the three catalysts show similar performance. A hydrogen selectivity of 62% is achieved at 500°C. The temperature favours steam reforming and decomposition reactions due to their endothermic nature leading to a hydrogen selectivity of 69 % at 600 °C. These results are in agreement with those obtained in literature (Comas et al., 2004).

Although CO_2 formation slightly increases with temperature up to 500 °C, the H_2/CO_2 ratio also increases, which indicates that there is a competition between steam reforming and decomposition reactions. For 20NiSi, catalyst this ratio increased from 3 at 400 °C to 3.4 and 3.7 at 500 and 600 °C, respectively. Above this temperature, CO_2 selectivity decreases, indicating that r-WGS reaction is favoured due to its endothermic nature.

The increase in CO selectivity from 500 to 600 °C corroborates this hypothesis. However, WGS reaction is favoured up to 500 °C and, consequently, CO selectivity decreases to a minimum at 500 °C. Given that CO is a poison for hydrogen fuel cells, 500 °C would be the suitable temperature to carry out this process. Finally, CH_4 decreases with temperature, which indicates that its reforming is favoured at high temperatures.

Table 2 shows that, for a given temperature, ethanol conversion and hydrogen yield increase with Ni content, due to a higher content of active phase available. It is also observed that ethanol steam reforming is favoured by temperature. Consequently, almost total conversion is attained at 500 °C over 20NiSi catalyst, while total conversion of ethanol is not reached with a lower loading of Ni, even for the highest temperature studied. Although it is not shown in Table 2, a significant conversion of ethanol is obtained at 300 °C. This temperature is sufficient for the dehydrogenation of ethanol to acetaldehyde and for the dehydratation of ethanol to ethylene, but higher temperatures are needed for the steam reforming reaction and for the subsequent transformation of the first products (acetaldehyde and ethylene) and, consequently, hydrogen production is very low at this temperature. At higher temperatures, the intermediate compounds react completely leading to higher hydrogen yields.

Table 3. Effect of the space time in ethanol conversion and hydrogen yield in the steam reforming of ethanol over the 20NiSi catalyst. Operation conditions: 500 and 600 °C, water/ethanol molar ratio 6/1, atmospheric pressure.

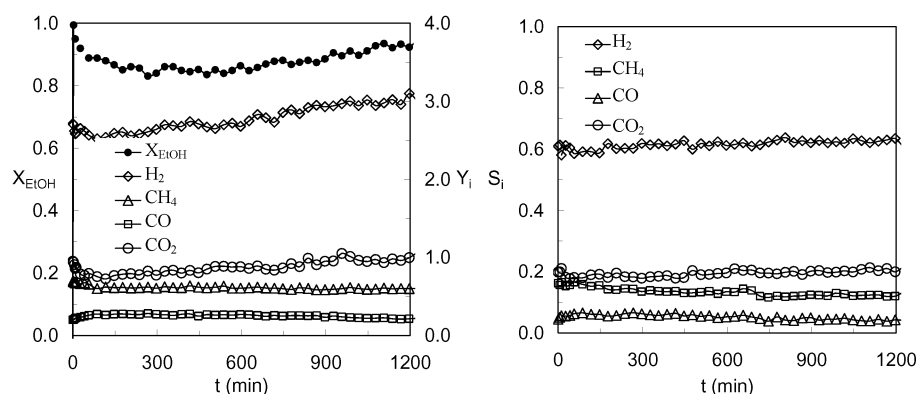| T (°C)	W/F_{EtOH} ($g_{catalyst}min/g_{EtOH}$)			
	1.8	8.3	15	30
X_{EtOH} 500	0.72	0.99	1.00	1.00
600	0.75	0.99	1.00	1.00
Y_{H2} 500	1.96	2.70	2.71	2.70
(mol H_2/mol $EtOH_0$) 600	2.31	3.91	3.89	4

Figure 1: Evolution with time-on-stream of ethanol conversion and product yield throughout ethanol steam reforming on 20NiSi catalyst at 500 °C, 1 atm, water/ethanol molar ratio of 6/1 and 8.3 $g_{catalyst}min/g_{EtOH}$.

The effect of the space time on ethanol conversion and hydrogen yield over 20NiSi catalyst at 500 and 600 °C is shown in Table 3.

It is observed that, for both temperatures, ethanol conversion is complete above 8.3 $g_{catalyst}min/g_{EtOH}$, and rapidly decreases for lower values of space time. Nevertheless, the selectivities of the main products do not change significantly with space time. Consequently, hydrogen yield rapidly increases with space time up to 8.3 $g_{catalyst}min/g_{EtOH}$, and subsequently it remains almost constant.

Figure 1 shows the effect of catalyst deactivation upon ethanol steam reforming over 20NiSi catalyst at 500 °C and $g_{catalyst}min/g_{EtOH}$. As observed ethanol conversion is initially complete, rapidly decreases from 1.0 to 0.85 within the first 2 h, subsequently stabilizes during the following 9 h and finally increases almost linearly to 0.92 at a time-on-stream of 20 h. Consequently, although there is a rapid decrease in H_2 and CO_2 yields during the first 2 h, the production of both products increases monotonously with time-on-stream due to the increase in ethanol conversion and to a slight increase in H_2 and CO_2 selectivities with time-on-stream. The yields of CH_4 and CO decrease very slowly with time on stream.

The evolution of ethanol conversion with time on stream is explained by the different nature of coke deposits as reaction proceeds. Initially, coke deposition occurs mainly by active site coverage (encapsulating carbon), which results in a decrease in ethanol

conversion. Subsequently, carbon deposits over the catalyst without direct deactivation, by a mechanism that results in the formation of filamentous carbon, which results in a better catalyst performance as previously reported (Carreño et al., 2008). Therefore, most of the nickel sites remain available for catalysis and only some are blocked by the growing carbon fibers.

4. Conclusions

Ni/SiO$_2$ catalysts show good performance in steam reforming of ethanol for H$_2$ production above 400 °C. Catalyst activity and selectivity to H$_2$ increase noticeably with temperature and Ni loading. A H$_2$ yield of 3.9 (mol H$_2$/mol EtOH$_0$) is attained at 600 °C and 8.3 g$_{catalyst}$min/g$_{EtOH}$, although a lower temperature (500 °C) is more suitable for minimizing CO selectivity. An improvement in catalyst performance is observed for high values of time-on-stream, which is explained by coke deposition in the form of carbon fibers.

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