Low Temperature Hydrogen Production from Ethanol over Cerium and Cickel Based Oxyhydrides

C. Pirez, L. Jalowiecki-Duhamel, M. Capron, F. Dumeignil
Low Temperature Hydrogen Production from Ethanol over Cerium and Cickel Based Oxyhydrides

Cyril Pirez, L. Jalowiecki-Duhamel, M. Capron, F. Dumeignil, UCCS Unité de Catalyse et de Chimie du Solide, Université des Sciences et Technologies de Lille, France

1 Introduction

In theory, hydrogen production from biomass or biomass derived liquids can be a carbon-emission free process since all carbon dioxide produced can be recycled back to plants using solar energy. Besides, ethanol is also safe, simple to handle, transport and store, so ethanol lends itself very well to a distributed-production strategy. A very interesting use of hydrogen is based on its conversion into power in fuel cell systems. The wide-spread application of fuel cells becomes closer to reality, so increased attention is focused on hydrogen production technology. Solid oxide fuel cells (SOFCs) are under development as energy production devices, they allow the use of carbon-monoxide resistant nickel anodes and the use of fuels different from hydrogen at the anode, in the so-called direct internal reforming SOFC. However the high operating temperatures undergo catalytic deactivation due to sintering of nickel crystallites and carbon deposition. Hence, worldwide efforts are in progress to discover novel, more active and more stable catalysts. Performing the reaction at lower temperature than 600 °C is a challenging goal.

\[
\text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \rightarrow 2 \text{CO}_2 + 6 \text{H}_2
\]  

Hydrogen production from ethanol steam reforming \((\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH} = 3)\) was investigated over cerium nickel \(\text{CeNi}_x\text{O}_y\) and \((0 < x \leq 5)\) mixed oxide catalysts. The influence of different parameters was analysed, such as reaction temperature, Ni content and in-situ pre-treatment in \(\text{H}_2\). While an ethanol conversion of 100 % is reached at 400 °C, a stable activity i.e. ethanol conversion, and \(\text{H}_2\) selectivity can be obtained at very low temperature (200 °C) when the solid is previously in-situ treated in \(\text{H}_2\) in a temperature range between 200 °C and 300 °C. In the present study, we report on \(\text{H}_2\) formation activity over \(\text{CeNi}_x\text{O}_y\) catalysts for reforming of ethanol. The aim of this work was to develop a highly active, selective, stable and cost effective catalyst at relatively low temperature which should avoid carbon formation and also allow an application to fuel cells.

2 Experimental Methods

Catalytic performances were conducted at atmospheric pressure with a quartz fixed-bed reactor (inner diameter 10 mm) fitted in a programmable oven, in the temperature range of 50-480 °C. When noted, the catalyst was previously in situ treated in \(\text{H}_2\) at 200 °C for 10 h. The water:ethanol mixture (molar ratio 3:1) is pumped into a heated chamber and vaporized. The water-ethanol gas (\(\text{N}_2\)) stream (total flow: 60 mL/min) is then fed to the reactor
containing 0.2 g of catalyst. The gases at the outlet of the reactor were taken out intermittently with the aid of a sampler directly connected to the system and analyzed on-line by FID and TCD gas chromatography. Reaction data were collected as a function of time and reported after about 5 h when the steady state was obtained for each temperature. Carbon is also formed but the quantity was not analyzed.

X-ray powder diffraction (XRD) analysis was carried out with a D 5000 Siemens diffractometer using a copper target and a secondary beam monochromator. The XRD patterns were registered in the 2θ domain (15-80 °) with a measured step of 0.02 ° and the time of integration was fixed to 12 seconds. The crystallites size was calculated using the Scherrer equation, from the most intense reflections observed for the NiO and CeO₂ crystallographic structures: (111), (200), (220).

Temperature-programmed reduction (TPR) was performed on a Micromeritics Autochem 2920 analyser, and hydrogen consumption was measured by a TCD detector: 25 mg of the sample was treated in the 5% H₂ – 95% Ar gas mixture (2 l/h). The temperature was increased to 800 °C at a heating rate of 10 °C/min.

3 Results and Discussion

3.1 Characterization

Fig. 1 reports the diffraction patterns obtained with different CeNiₓOᵧ solids. A ceria like phase is apparent in every solid analyzed (34-0394 JCPDS file) while crystallized NiO (4-0835 JCPDS file) appears when x ≥ 0.4. As already reported in previous studies for CeNiₓOᵧ compounds, a careful examination of the patterns shows that the addition of nickel affects not only the broadness of the ceria peaks, but also their position, attributed to the substitution of Ce⁴⁺ cations by Ni²⁺ cations inside the CeO₂ lattice and interpreted by the formation of a cerium-nickel solid solution. As a matter of fact, the nickel ionic radius (Ni²⁺: 0.07 nm), is smaller than the cerium ionic radius (Ce⁴⁺: 0.09 nm). It was reported that the highest proportion of solid solution is obtained for the CeNi₀.₅Oᵧ compound, as also observed here, when the molar ratio Ni/M_T = 0.33 (M_T = Ni + Ce, Ni/M_T = x/(1+x)). The studied CeNiₓOᵧ mixed oxides with x < 0.4 correspond to a solid solution with the substitution of Ni²⁺ ions in the CeO₂ lattice, to compounds in which crystallized NiO and solid solution coexist when 0.4 ≤ x < 1, and to a mixture of CeO₂ and NiO when x > 1.

The Temperature-Programmed Reduction (TPR) profiles in H₂ of the catalysts are shown in Fig. 2. A first temperature reduction peak at about 270 °C is more intense for a low Ni content, when x = 0.1. When x increases from 0.1 up to 0.4 a second peak at about 370 °C increases. For higher Ni contents, the first peak decreases while the second peak shifts to higher temperatures (390 °C). It was already observed that a shoulder at 440 °C is emerging in the shape of the curve obtained for higher Ni contents. The reduction peak obtained at about 400 °C increases with the Ni content. For temperatures lower than 600 °C, a linear relationship is obtained between the total hydrogen consumed during TPR with the Ni content of the CeNiₓOᵧ compounds (Fig. 5), showing that H₂ is consumed in majority to reduce nickel species in this range of temperatures. The low temperature peak can be attributed to nickel species: i) belonging to the solid solution and/or to ii) small NiO particles, easily reducible, but with the simultaneous reoxidation of a part of these species by reduction.
of the Ce$^{4+}$ ions in their vicinity into Ce$^{3+}$ species as the existence of a redox system was established (equations 2 and 3), then larger NiO crystallites are reduced when increasing temperature.

![Figure 1: XRD patterns of CeNiXOY compounds. x = a) 0 b) 0.01 c) 0.2 d) 0.4 e) 0.5 f) 0.9 and g) 2.3. CeO2 (+), NiO (O).](image)

**Figure 2: TPR of CeNiXOY compounds. x = a) 0.2, b) 0.4, c) 0.7 and d) 0.9.**

### 3.2 Ethanol steam reforming

Ethanol transformation in presence of water was studied as a function of reaction temperature, activation treatment in H$_2$ and metal loading of CeNi$_x$O$_y$ catalysts. Fig. 3 and 4 show, as examples, the results obtained over the fresh and treated in H$_2$ CeNi$_{0.5}$O$_y$ catalyst versus reaction temperature. Over the fresh catalyst, an ethanol conversion is observed at temperatures higher than 300 °C, as expected it increases with temperature, and reaches 100 % at 480 °C (Fig. 3). When the CeNi$_{0.5}$O$_y$ catalyst is previously in-situ treated in H$_2$ at 200 °C during 10 h, there is globally an increase versus temperature but with the existence of an optimum at about 30 % of conversion for a reaction temperature of 250 °C. Finally, total ethanol conversion is obtained at 480 °C and 400 °C over, respectively, the fresh and H$_2$ treated catalyst with about 50 % of H$_2$. So total ethanol conversion with about the same H$_2$ yield are obtained at 80 °C lower with an adequate pre-treatment of the catalyst in H$_2$.

Over the treated in H$_2$ CeNi$_{0.5}$O$_y$ catalyst, the other products obtained are acetaldehyde, CO, CH$_4$ and CO$_2$ (Fig. 4). Whatever the temperature, ethylacetate and acetone formations are lower than 0.5 %. Acetaldehyde decreases with temperature and disappears at 400 °C. CO and CH$_4$ present optima at 250 °C following conversion (eq. 5), for temperatures higher than 300 °C CH$_4$ increases while CO remains at about 10 %. Concentration of CO$_2$ is lower than 1 % at 200 °C so as expected, the steam reforming of ethanol is negligible at these low temperatures, and it increases for higher temperatures.

Over the fresh CeNi$_{0.5}$O$_y$ catalyst, between 200 °C and 300 °C the products observed are acetaldehyde and ethylacetate, typical of dehydrogenation reaction (with a very low ethanol conversion ~ 1%), and at 300 °C, H$_2$ is observed at about 70 %. Ethylacetate, acetaldehyde,
and acetone are found in concentration range between 5 and 10%, depending on the reaction temperature. For temperatures higher than 300 °C ethylacetate disappears, while acetone appears at 300 °C and presents an optimum of 10% at about 400 °C. CO₂ appears at temperatures higher than 250 °C and increases with temperature, while CO and CH₄ are formed at temperatures higher than 400 °C.

![Figure 3](image-url)  
**Figure 3:** Ethanol conversion (◆,◇) and H₂ (▲,△) formation over fresh (white) and treated in H₂ at 200 °C (black) CeNi₀.5O₇ catalyst.

![Figure 4](image-url)  
**Figure 4:** Products distribution obtained over fresh (white) and treated in H₂ at 200 °C (black) CeNi₀.5O₇ catalyst. a) Acetaldehyde (◆,◇), ethylacetate (+) and acetone (x). b) CO₂ (□,■), CO (〇,●) and CH₄ (▲,△). No ethylacetate, no acetone over treated in H₂ catalyst.

As the treatment in H₂ at 200 °C leads to a dramatic effect on H₂ formation at low temperatures (≤ 250 °C), the influence of the treatment temperature in H₂ was studied over the CeNi₀.7O₇ chosen catalyst. As shown in Fig.5, ethanol conversion at 250 °C presents an optimum for a treatment temperature T in H₂ of 275 °C, following in a quite interesting way the first reduction peak seen by TPR. Moreover, the products distribution in the outlet gas stream depends also on the treatment temperature applied. H₂ is formed with treatment
temperatures in H$_2$ higher than 100 °C. For treatment temperatures $T_T$ in H$_2$ lower than 200 °C, ethylacetate is the main product obtained with acetaldehyde as by-product. Formation of H$_2$ is optimum over a treated in H$_2$ at 200 °C catalyst, but for higher treatment temperatures it remains relatively stable. CH$_4$ and CO concentrations follow same evolutions; they present optima for $T_T \approx 275$ °C like conversion, and when acetaldehyde concentration presents a minimum.

![Ethanol conversion and products](image)

**Figure 5:** Ethanol conversion ($\Diamond$) and products obtained at 250 °C over CeNi$_{0.7}$O$_Y$ catalyst versus treatment temperature in H$_2$. H$_2$ ($\Delta$), CH$_3$CHO ($\cdot$), ethylacetate ($-$), CH$_4$ ($\bullet$), and CO ($\bigcirc$). CO$_2$ (< 1%).

It is well known that physicochemical properties of a catalyst play an important role in the evolution of surface reactions. In ethanol transformation both dehydrogenation to acetaldehyde or dehydration to ethylene can occur upon the nature of the catalyst. Clearly, CeNi$_x$O$_Y$ catalysts possess good dehydrogenation properties, accentuated once treated in H$_2$ at 275 °C corresponding to the first TPR peak.

Besides, after an in-situ treatment in H$_2$ in particular between 200 °C and 300 °C, it was shown that the CeNi$_x$O$_Y$ solids studied become hydrogen reservoirs. During the activation treatment in H$_2$ in temperature, the anionic vacancies created are able to accept hydride species and the solids were called oxyhydrides.

Therefore, H$_2$ production from ethanol transformation certainly involves particular Ni species in strong interaction with Ce species. These Ni species are easily reducible and reoxidable by the presence of Ce in close vicinity (redox system). Clearly, the treatment in H$_2$ between 200 °C and 300 °C leads to a beneficial effect on H$_2$ production. It was shown that this treatment allows the CeNi$_x$O$_Y$ mixed oxides to accept large quantities of hydrogen by the presence of anionic vacancies. Therefore, over the fresh catalyst, up to 300 °C acetaldehyde and ethylacetate are observed and H$_2$ produced from ethanol is certainly consumed by the solid leading to a partially reduced compound. Taking into account that dehydrogenation step requires abstraction of hydrogen species from alcohol, the ability of the solid to accept hydrogen can be a prerequisite condition and “filling” the solid with hydrogen (during the pre-treatment in H$_2$) allows its formation from alcohol at low temperatures.
4 Conclusion

Ethanol transformation in presence of water was studied over CeNi$_x$O$_y$ (0 < x ≤ 5) catalysts. The cerium-nickel solid solution and/or small NiO particles (nanoparticles) involve Ni species presenting the characteristic of being able to be reduced and reoxidized easily and reversibly. The active nickel species belongs to the NiO particles and/or to the cerium nickel solid solution where Ni species are in strong interaction with Ce species. Hydrogen can be produced at low temperature ≤ 250 °C once the CeNi$_x$O$_y$ mixed oxides are previously in-situ treated in H$_2$ at about 250 °C leading to the formation of oxyhydrides. Finally, an active site is proposed based on the presence of anionic vacancies able to abstract hydride species from ethanol.