

Steam reforming of ethanol over a NiZnAl catalyst. Influence of pre-reduction treatment with H₂

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Abstract The ethanol reforming reaction has been studied as an alternative for H₂ production by using a NiZnAl catalyst. This reaction was examined under different operation conditions in order to study the influence of the catalyst pre-reduction with H₂. At low temperatures, the pre-reduced catalyst was more active than the catalyst without pre-reduction treatment. However, the catalyst without pre-reduction treatment becomes active from 450 °C, achieving ethanol conversions of 100% with high yields to H₂.

Keywords Ethanol reforming · Hydrogen production · NiZnAl catalyst

Introduction

Ethanol steam reforming is being investigated as a potential generator of hydrogen for fuel cells. Different catalytic systems have been studied being promissory those Rh-based catalysts [1–3]. Very good results have also been reported over catalytic systems containing Ni [4–7]. This metal is very advantageous for its low cost and high availability compared to precious metals. However, the great drawback is the tendency to suffer deactivation by coke formation, sintering and/or the formation of inactive phases. In almost all the cases reported in literature, the catalysts are reduced in hydrogen before the reforming reaction which can be an inconvenience in a reformer-purificator-fuel cell assembly. Besides, the previous treatment in H₂ is carried out at high temperatures with a consequent sintering of Ni particles Matsumura and Nakamori [8] reported that Ni/Al₂O₃ was not reduced appreciably with H₂ at 500 °C and was inactive in methane reforming at the same temperature,

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and that $\text{Ni}/\text{Al}_2\text{O}_3$ became active only after the reduction at 700 °C. Recently, Blume et al. [9] have shown by in situ XPS how the actual surface state of a catalyst could dynamically change with the temperature and the reactant partial pressures. They have shown that a RuO_2 catalyst undergoes reduction under CH_3OH -rich mixtures and the reduction can terminate in RuO_{1-x} or metallic Ru depending on the reactants partial pressures. In a previous work, we have reported the results of the ethanol steam reforming over NiZnAl catalysts with Ni loading varying between 1 and 25 wt% [10]. They were tested in the reforming reaction without a previous reduction and they showed to be very active and selective. The characterization of used catalysts showed a high extent of Ni reduction. In this study, we compared the results with and without pre-reduction treatment by using a NiZnAl catalyst with 25 wt% Ni. The possibility of excluding this step is analyzed.

Experimental

The NiZnAl catalyst containing 25 wt% of Ni and a molar ratio $\text{Zn}:\text{Al} \cong 0.6$ was prepared by the citrate method. Details of the preparation were described elsewhere [10]. The sample was characterized using different physico-chemical methods. The BET surface area was measured using a Micromeritics Accusorb 2100E instrument by adsorption of nitrogen at -196 °C. The TG analyses were recorded by using TGA 51 Shimadzu equipment from room temperature to 1000 °C at a heating rate of 10 °C min^{-1} with an air flow of 50 mL min^{-1} . Scanning electron micrographs were obtained in a LEO 1450 VP.

The ethanol steam reforming reaction was carried out in a fixed-bed quartz tubular reactor operated at atmospheric pressure. The feed was a gas mixture of ethanol, water and helium. Ethanol and water were fed through independent saturators before mixing. The flow rate was 70 mL min^{-1} at room temperature with an ethanol molar composition of 3%. The $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ molar ratio was 3.9 in all experiments. The catalyst weight was 300 mg without dilution. The catalyst was heated to the reaction temperature under He flow, then the mixture with $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ was allowed to enter the reactor to carry out the catalytic test. The reactants and reaction products were analyzed on-line by gas chromatography. H_2 , CH_4 , CO_2 and H_2O were separated by a 1.8 m Carbosphere column and analyzed by TCD. Besides, CO was analyzed by a FID after passing through a methanizer. Higher hydrocarbons and oxygenated products ($\text{C}_2\text{H}_4\text{O}$, C_2H_4 , $\text{C}_3\text{H}_6\text{O}$, $\text{C}_2\text{H}_5\text{OH}$, etc.) were separated in RT-U PLOT capillary column and analyzed with FID. Two kinds of experiments with and without a previous reduction in H_2 were carried out:

- (i) Experiments varying the reaction temperature, from 300 °C to 700 °C every 50 °C step without removing the catalytic bed. The catalyst was held at each temperature for 2 h. The samples were labeled as NZA-T and NZA-TR without and with previous reduction, respectively.
- (ii) Isothermal experiments at 600 °C during 4 h. The samples were named NZA-600 and NZA-600R, without and with a previous reduction, respectively.

In the experimental runs with previous reduction, the catalyst was in situ reduced in a mixture of 5% H_2/N_2 (flow: 100 mL min^{-1}) at $600 \text{ }^\circ\text{C}$ for 1 h. After reduction, the catalyst was cooled down in helium flow to the reaction temperature.

Results and discussion

Experiments varying the reaction temperature from $300 \text{ }^\circ\text{C}$ to $700 \text{ }^\circ\text{C}$

In Fig. 1, the ethanol conversion as a function of reaction temperature is shown. As can be expected, the dramatic change in the catalyst chemical state from oxide to metal affects the overall catalytic activity. At $300 \text{ }^\circ\text{C}$, the conversion is 2% for the sample without reduction, whereas the activity for reduced sample is significantly higher, with an ethanol conversion of 83%. At $400 \text{ }^\circ\text{C}$, the conversion is 89% for NZA-T and 100% for NZA-TR. From $450 \text{ }^\circ\text{C}$, the behavior of both samples is similar with a complete ethanol conversion. These differences clearly show the role of Ni^0 in the reforming reaction of ethanol. By TPR, the reduction of Ni^{+2} begins around $400 \text{ }^\circ\text{C}$ [10], temperature in which the conversion reaches high values. The product distributions for NZA-T and NZA-TR are presented in Fig. 2. For NZA-T, acetaldehyde (not shown) is the only product at $300 \text{ }^\circ\text{C}$. From $400 \text{ }^\circ\text{C}$ to $450 \text{ }^\circ\text{C}$, the activity significantly increases and different products are detected: H_2 , CO_2 , C_2H_4 , C_3H_6 , CH_3COCH_3 , traces of CH_4 and CO , besides CH_3CHO . From $500 \text{ }^\circ\text{C}$, the only products are H_2 , CO , CO_2 and CH_4 . CO_2 selectivity presents a maximum at this temperature and then decreases. The same behavior is observed for CH_4 formation which goes to zero at $700 \text{ }^\circ\text{C}$. CO selectivity increases from $450 \text{ }^\circ\text{C}$, Fig. 2a.

Similar trends are observed for the reduced catalysts, Fig. 2b. At $300 \text{ }^\circ\text{C}$ the activity for NZA-TR is important, being the reaction products H_2 , CH_4 , CO , CO_2 , C_2H_4 , C_3H_6 , CH_3COCH_3 and CH_3CHO . From $400 \text{ }^\circ\text{C}$, the main products are H_2 , CO , CO_2 and CH_4 . Traces of C_2H_4 are also observed in the temperature range

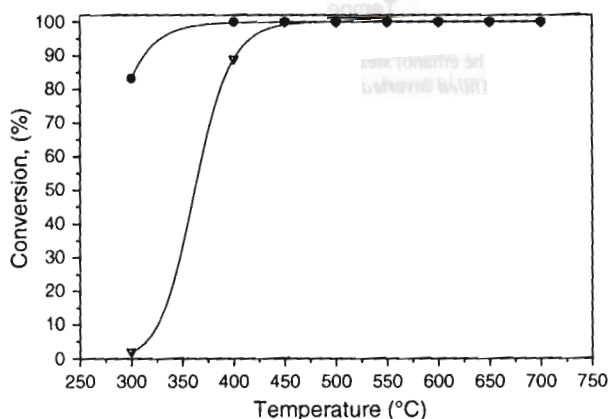


Fig. 1 Ethanol conversion as a function of reaction temperature, (filled circle) NZA-TR and (inverted triangle) NZA-T

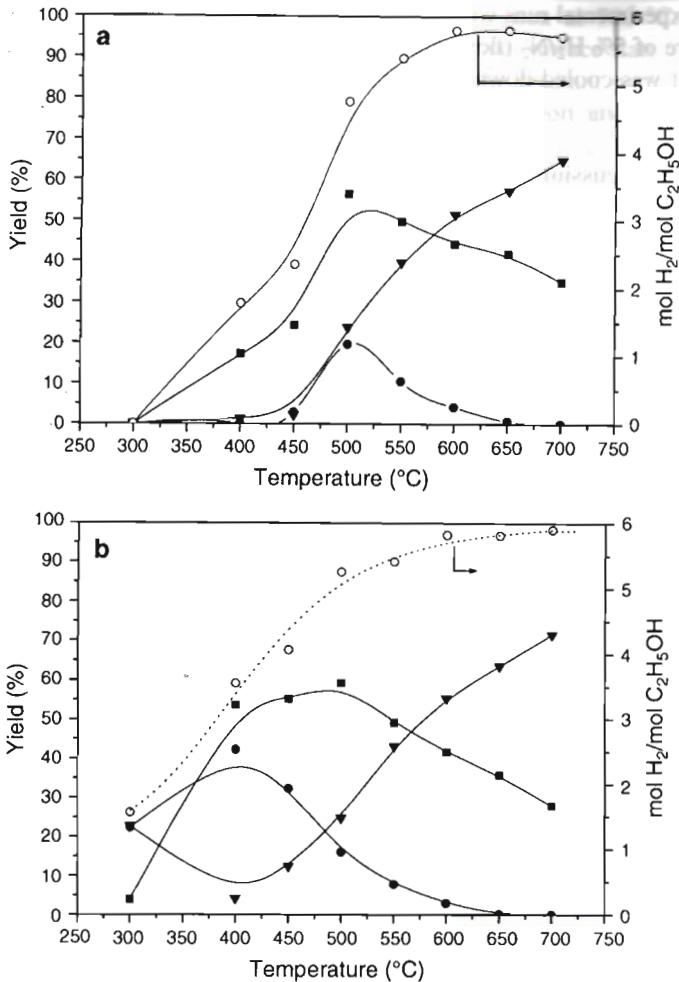


Fig. 2 Product distribution in the ethanol steam reforming over **a** NZA-T catalyst and **b** NZA-TR. (*open circle*) H₂, (*filled circle*) CH₄, (*filled inverted triangle*) CO, (*filled square*) CO₂

between 400 °C and 500 °C. At 600 °C, the H₂ yield is similar for both samples and represents a selectivity of 95%.

Isothermal experiments

At 600 °C, both samples are equally active with ethanol conversions of 100%. The results are illustrated in Fig. 3. The carbon products are CO, CO₂ and a minor amount of CH₄ being the average molar ratio CO/CO₂ \cong 0.83 for the reduced sample and \cong 1.38 for the unreduced one. The yield of CH₄ is around 3% for both samples. The hydrogen yield is 5 and 5.8 mol of H₂ per mol of fed ethanol for NZA-600 and NZA-600R, respectively. From the experimental results an increase in H₂

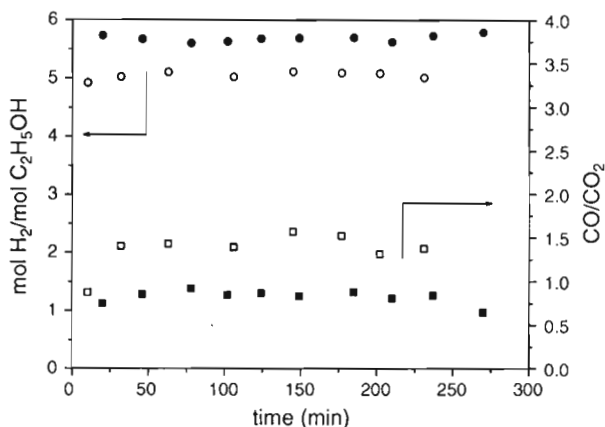


Fig. 3 Product distribution in the ethanol steam reforming over NZA-600R (full symbols) and NZA-600 (empty symbols). (filled circle, open circle) H_2 yield; (filled square, open square) CO/CO_2 molar ratio

selectivity is observed when the sample is pre-reduced in H_2 before the reforming reaction. Thus, H_2 selectivity increases from 83% for NZA-600 to 95% for NZA-600R. This difference could be attributed to a major contribution of water gas shift reaction over reduced sample.

Although the behavior of both samples is similar above $450\text{ }^\circ\text{C}$, the post-reaction characterization led to the identification of the same differences which are important in the catalyst stability.

The Ni particle sizes, d_{Ni} , are determined using the Scherrer equation (Table 1). They are in the same range for all the used samples and slightly higher for the samples with a previous reduction. In comparison with the Ni crystal size after the pre-reduction step, the Ni particles undergo an important aggregation during reaction. The specific surface areas of used samples are also illustrated in Table 1. The values of previously reduced samples show an important increase whereas no significant changes are observed on samples without reduction. This is in agreement with the carbon amount determined by TG experiments.

To study the influence of carbon deposition, thermal gravimetric experiments are carried out for used samples. The weight loss results from TG analysis are shown in Table 2. In all the cases, an initial weight loss ($-\Delta w\%$) is observed until around $200\text{ }^\circ\text{C}$, which could be attributed to water desorption and adsorbed compounds

Table 1 Specific surface areas and Ni^0 particle size of used NiZnAl catalyst

Samples	NZA fresh	NZA ^a	NZA-TR	NZA-T	NZA-600R	NZA-600
S_{BET} ($m^2\text{ g}^{-1}$)	27	–	56	24	38	24
d_{Ni} (nm) ^b	–	6.0	15.6	14.5	13.4	12.4

^a Reduced sample before being used in reaction

^b Estimated by Scherrer equation

Table 2 TG results of used catalyst in the steam reforming of ethanol

Used sample	$-\Delta w\%$ (up to 200 °C)	$+\Delta w\%$ (200–490 °C)	$-\Delta w\%$ (490–700 °C)
NZA-TR	0.5	3.1	8.8
NZA-T	0.7	1.9	0.50
NZA-600R	0.4	4.5	0.75
NZA-600	0.4	4.4	0.06
NZA ^a	1	4.9	–

^a Reduced sample before being used in reaction

from the atmosphere as a consequence of keeping the samples in air after being used. Then, there is a weight gain ($+\Delta w\%$) between 200 °C and 450–490°C which is mainly caused by the Ni⁰ oxidation. This gain depends on the sample and it is lower than the observed gain in the same temperature range after the TPR experiment (Table 2). This evidence could be an indication that in this temperature range, the combustion of a more reactive carbon deposit also occurs. Between 490 °C and 700 °C, weight losses highly depending on the reaction conditions are observed. NZA-TR is the sample exposed at high ethanol conversions during a long time on stream and it shows the highest weight loss (near to 9 wt%). After 700 °C, all the samples reach a constant weight.

Figure 4 shows the SEM micrograph of used NZA-TR. It is well known that Ni can dissolve carbon and generate carbon filaments [11]. However, after a thorough examination, there is no evidence of the presence of filamentous carbon as expected. This behavior could be associated with the strong interaction of Ni species with the spinel.

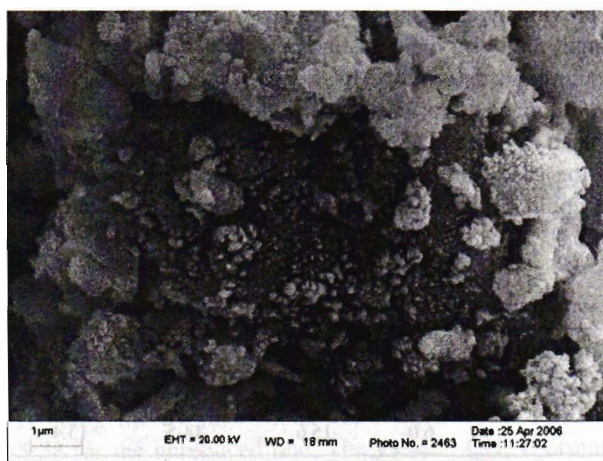


Fig. 4 SEM micrograph of NZA-TR after ethanol steam reforming

Conclusions

A NiZnAl catalyst (25 wt% Ni) was studied in the ethanol steam reforming under different operation conditions. The influence of pre-reduction in hydrogen was examined since this type of treatment would be inconvenient for mobile fuel cell systems. The pre-reduced catalyst was more active at low temperature (300–400 °C) but the activity was similar from 450 °C, independently of the previous treatment, with ethanol conversion of 100%. This is a clear indication of the role of Ni⁰ species and the capacity of the catalyst to be auto-activated under reforming conditions. Regarding the hydrogen yield obtained at 600 °C, the pre-reduced sample exhibits higher values than those obtained on the unreduced sample. However, the differences might not be enough to justify the need of the catalyst pre-reduction treatment.

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