Nowadays, there is a struggle to search alternative renewable energy sources and environmentally friendly fuels [1-4]. The use of biofuels or hydrogen produced from renewable sources provides sustainable energy development and reduces emissions, protecting on long term the environment. Currently, mostly of the ethanol production from biomass is used as additive in the spark ignition engines. Worldwide, the use of bioethanol is related to the resources of biomass and fossil fuel disposals, and also on the environmental restrictions. The hydrogen used as alternative fuel may be obtained directly from ethanol via a number of processes, one of which is steam reforming of the alcohol. An issue of great importance is the preparation of a catalyst for ethanol reforming showing, activity, selectivity and high stability in the process. In this case, an ideal catalyst is the one that will drive the reaction to obtain hydrogen and carbon dioxide, preventing the formation of other byproducts. Therefore, a total catalytic system which leads to an effluent containing mainly H₂ to obtain hydrogen and carbon dioxide, preventing the case, an ideal catalyst is the one that will drive the reaction. The Co/Al₂O₃ catalyst was tested in a fixed-bed reactor system employing steam reforming of ethanol. During tests, high ethanol conversions were obtained ranging from 70-90% and high yields in hydrogen about 50%. The main secondary products of the ethanol reforming process are carbon dioxide and methane.

**Key words: ethanol, steam reforming, hydrogen, Co/Al₂O₃ catalyst**

The performances of ethanol steam reforming were investigated using cobalt on alumina supported catalyst. This catalyst was obtained by the pore volume impregnation method, using cobalt nitrate. The Co/Al₂O₃ catalyst was tested in a fixed-bed reactor system employing steam reforming of ethanol. During tests, high ethanol conversions were obtained ranging from 70-90% and high yields in hydrogen about 50%. The main secondary products of the ethanol reforming process are carbon dioxide and methane.

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The following chemicals were used for catalyst synthesizing: Al₂O₃ for support was purchased from National Institute of Research and Development for Chemistry and Petrochemistry Bucharest, and the metallic precursor for the impregnation process, respectively Co(NO₃)₂·6H₂O (98%), was purchased from Sigma Aldrich. For the steam reforming tests, a mixture of distilled water and ethanol (Chemical, 98%) was used as a feedstock.
Preparation of supported Al₂O₃ catalyst

The catalyst used in this study was prepared by pore volume impregnation method. The Al₂O₃ support was treated in air flow at 773 K for 3h prior to the impregnation in order to eliminate surface impurities. The support was impregnated with Co(NO₃)₂· 6H₂O, dried at 373 K and then calcined in air flow at 823 K for 6h.

Catalytic tests

The ethanol reforming experimental program was achieved in a continuous system, using a micropilot unit containing a stainless steel fixed bed reactor [12]. The unit is equipped with a control panel which provides: control and registration of the reactor temperatures and indicates the temperature along the catalytic bed. The setting of the temperature in the two zones of the reactor is made automatically, because the reactor was equipped with four thermocouples to read both the temperature in the upper zone and in the lower part of the reactor. The amount of catalyst used in the test was 30 cm³. The experimental steps are the following:

- after the test pressure was done, the inert gas was introduced to activate the catalyst at an appropriate reactor conditions of the activation process, in this case 550°C for 6;
- adjusting the temperature in the reactor to the desired reaction temperatures 350, 400 and 450°C respectively;
- preparing an aqueous solution of ethanol to a desired concentration of 8% and 10 vol% ethanol;
- ethanol solution was pumped in the reactor with a flow of 1 mL/min and 3 mL/min respectively;
- after stabilization of the process the concentration in the gas phase (hydrogen, methane, ethane, ethylene, carbon dioxide, carbon monoxide) and liquid phase (ethanol, acetaldehyde) were measured. The gas phase characterization was made by using a Varian 450-GC gas chromatograph with porous layer open tubular columnn and a Carlo Erba Strumentazione chromatograph for the liquid phase.

The performances of the process were assessed by the conversion of ethanol and hydrogen yield.

The mathematical relations used to calculate the efficiency of the conversion of ethanol and the hydrogen selectivity are the following:

Ethanol conversion

\[ X_{\text{EtOH}} = \frac{n_{\text{EtOH, in}} - n_{\text{EtOH, out}}}{n_{\text{EtOH, in}}} \times 100 \]  

Hydrogen yield

\[ \eta_{\text{H}_2} = \frac{\eta_{\text{H}_2}}{g_{\text{H}_2}} \times 100 = \frac{\% \text{H}_2 \cdot g_{\text{gas}}}{g_{\text{H}_2}} \]  

where:

- \( X_{\text{EtOH}} \) - ethanol conversion
- \( n_{\text{EtOH, in}} \) - moles of ethanol fed
- \( n_{\text{EtOH, out}} \) - moles of ethanol produced
- \( \eta_{\text{H}_2} \) - yield of hydrogen
- \( g_{\text{gas}} \) - mass of gas produced in the experiments
- \( g_{\text{H}_2} \) - real raw mass
- \% \( \text{H}_2 \) - weight percent of \( \text{H}_2 \) gas obtained by chromatographic analysis.

Results and discussions

The values obtained for the ethanol conversion and hydrogen yield, for Co/Al₂O₃ catalyst prepared and tested in the bioethanol reforming reaction, are presented in table 1 and 2, respectively.

The influence of the reaction parameters on the ethanol reforming process

The efficiency of the ethanol reforming reaction is determined by the reaction conditions and catalyst system. The analysis data resulted from experimental test of the catalytic system highlighted the performance of the Co/Al₂O₃ catalyst in ethanol reforming. For this catalyst, we experimentally studied the influence of the reaction parameters on ethanol conversion and hydrogen yield.

The influence of the reaction temperature

The overall steam reforming of ethanol reaction is strongly endothermic.

\[ \text{CH}_3\text{CH}_2\text{OH} (g) + \text{H}_2\text{O} (g) \rightarrow 2\text{CO} + 4\text{H}_2 \]  

\( \Delta H^\circ_{298K} = 255.54 \text{ kJ/mol} \)

From the thermodynamic point of view, the reaction is not favoured by temperatures below 300°C. As seen in figure 1 and 2, the ethanol conversion increases with the raising of the reaction temperature.

This increasing of the ethanol conversion is justified from thermodynamic point of view, by the fact that the reaction is highly endothermic and, on the other hand, it is also

<table>
<thead>
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<th>Temperature</th>
<th>Ethanol 8%, 1mL/min</th>
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<td>59.87%</td>
<td>59.74%</td>
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</table>

Table 1

ETHANOL CONVERSION ON Co/Al₂O₃ CATALYST

Table 2

HYDROGEN YIELD ON Co/Al₂O₃ CATALYST
kinetic because the reaction rate increases with the temperature, according to the Arrhenius relationship. The influence of the reaction temperature on the hydrogen yield in the presence of Co/Al₂O₃ catalyst is shown in figure 3 and 4.

The analysis data presented in figure 3 and 4 show a slight decrease in H₂ yield while the reaction temperature increases. As mentioned before, in agreement with the data presented in literature, the ethanol reforming reaction takes place in more stages, beginning with dehydrogenation of ethanol to acetaldehyde or dehydration of ethanol to ethylene. Raising the temperature favours the dehydration reaction of ethanol that has greater activation energy. Because of that, the rise of temperature causes a decrease in the hydrogen yield due to the formation of ethane by hydrogenation of ethylene obtained in the first step.

The influence of the weight hour space velocity

Figure 5 and 6 show the variations of ethanol conversion and hydrogen yield based on the weight hour space velocity of the raw material. The influence of weight hour space velocity on the bioethanol reforming reaction in the presence of Co/Al₂O₃ catalyst was determined for a temperature of 400°C, atmospheric pressure and two feedstocks with an ethanol content of 8% and 10% respectively.

For gas-phase reactions, the reaction time is correlated to the weight hour space velocity; there exists an inversely proportional dependence between the two. Thus, in figure 5, the ethanol conversion decreases while the weight hour space velocity increases. This aspect can be explained by the lower reaction times at a higher weight hour space velocity.

In figure 6, we can observe a reduction in hydrogen yield with the increase of weight hour space velocity for instance at 8% ethanol the hydrogen yield decreases from 60.73% for w=2h⁻¹ at 60.09% for w=6h⁻¹. This can be explained by the fact that a higher weight hour space velocity requires a lower reaction time. With the increase of the weight hour space velocity the hydrogen yield slowly decreases, which is justified by the influence of the reaction time on the successive kinetics reforming reaction which is performed in several steps: dehydrogenation and dehydration followed by reforming reactions, Shift reaction (the conversion of CO to CO₂ and H₂) or polymerization reaction of ethylene.
The influence of ethanol content

The influence of the ethanol content of the raw material on the performance of the ethanol reforming reaction was studied at 400°C, at a weight hour space velocity of 2 h⁻¹. The influence of ethanol content on the yield of hydrogen is given in figure 7.

The hydrogen yield is greater with the increasing of the ethanol content of the raw material: from 60.73% (raw material with an ethanol content of 8%) to ~ 62% (raw material with an ethanol content of 10%). The higher content of ethanol in the feedstock justifies higher hydrogen yields especially by reaction mechanism where ethanol is decomposed in hydrogen and other gases as CO₂, CO, CH₄ etc. The presence of excess of water will increase reforming reactions of intermediates (acetaldehyde, methane, and ethylene) or CO conversion by Shift reaction.

Conclusions

Throughout this paper, the Co/Al₂O₃ catalyst prepared allows to obtain good ethanol conversion (~80%) and hydrogen yield (~50%) at low temperatures around 350°C which is an advantage from the economic point of view. At any value, a higher hydrogen production is obtained when the ethanol content of the raw material increases.

High hydrogen yield obtained through the bioethanol reforming on the proposed catalytic systems represents a great economic advantage, because it allows the use of the ethanol obtained from fermentation, regardless the costs involving the operations of concentration.

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References

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