



BIOENERGY II

Temperature effect on hydrogen production from reactions between ethanol and steam in the presence of Pd-Ru/Nb₂O₅-TiO₂ catalyst

Christian G. Alonso¹, Andréia C. Furtado¹, Mauricio P. Cantão², Onélia A. A. Santos¹ and Nádia R.C. Fernandes-Machado^{1*}

¹ *Dep. de Engenharia Química, Fundação Universidade Estadual de Maringá, Av. Colombo, 5790, Bl. D-90, CEP 87020-900, Maringá – PR – Brasil.*

² *LACTEC – Instituto de Tecnologia para o Desenvolvimento, BR 116, Km 98, s/n, CEP 81531-980, C.P. 19067, Curitiba – PR – Brasil*

email address: nadia@deq.uem.br

1. Introduction

Hydrogen has been pointed out as the alternative fuel, and the scientific community has oriented a lot of research works to the generation, storage and transportation of hydrogen leading to the emergence of what is now known as the “hydrogen economy” .

Alcohols are attractive for hydrogen production from steam reforming in large scale.

Ethanol presents several advantages when compared with other fuels, since it is easier to store, handle and transport in a safe way due to its lower toxicity and volatility.

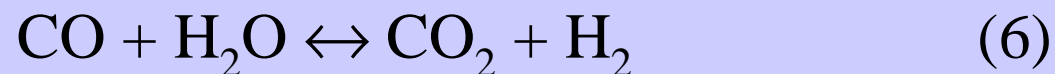
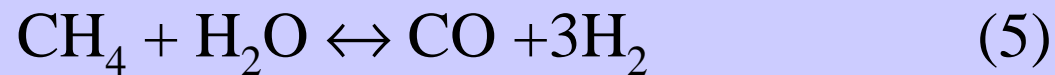
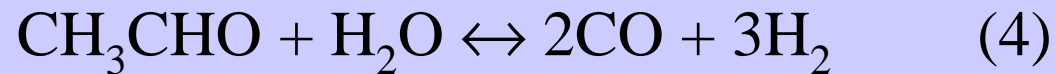
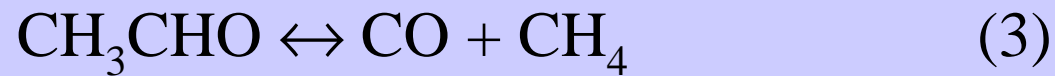
The ethanol steam reforming is a cleaner process than methane steam reforming, because of the CO₂ “free” cycle, which is generated in the reforming of ethanol and consumed by sugarcane photosynthesis.

In Brasil we have many small communities that don't have electricity, so a fuel cell is one solution. If the hydrogen is produced by ethanol, which is present in almost all cities of the country, the process become attractive.

The steam reforming of ethanol involves a complex reaction pathway and the selectivity for hydrogen is affected by many undesirable side reactions. The process takes place according to the stoichiometric reaction:



That may occur through a sequence of reactions, that explain results of many author:

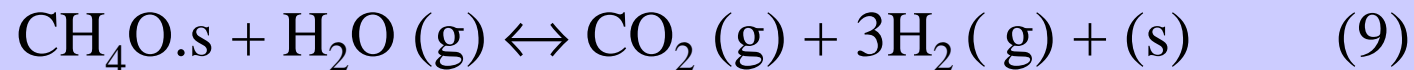


Which involves many stable intermediaries, so it is difficult to establish conditions where CO_2 and H_2 are only the products found.

To increase H₂ production we need to select a catalyst that change the mechanism which produce H₂ and CO₂ only.

This mechanism was proposed by Akande et al.*, but until now it is only a goal to be reached.

Using a Eley Rideal mechanism, they proposed:



*International Journal of Hydrogen Energy, 31 (2006), 1707-1715

Catalysts based on Cu, Ni, Co, Rh, Pt, Pd and Ru supported in different materials have been evaluated with relative success.

It was demonstrated the importance of the catalytic support. So, the success of the process depends on the perfect combination of the active phase and its content with the support composition and nature.

Thermodynamic studies have demonstrated that temperatures higher than 230°C are needed in order to carry out the reaction of ethanol steam reforming and suggest that molar ratios $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$ higher than the stoichiometric one, prevent formation of coke and so, the catalyst deactivation.

In this work, reaction temperature effect on the performance of 0.5% Pd-0.5% Ru/Nb₂O₅-TiO₂ catalyst was evaluated. Tests were carried out at 300, 375 and 450 °C at atmospheric pressure. Instead of micro-reactors, a reactor with 7 g was used, close to industrial application.

2. Experimental

2.1. Catalysts Preparation and Characterization

The niobium pentoxide (referred to as N) were obtained from niobic acid HY-340, supplied by the Companhia Brasileira de Metalurgia e Mineração, CBMM, after washing with deionized water followed by drying at 90 °C/72 h and calcination in furnace at 500 °C/5 h.

2.1. Catalysts Preparation and Characterization

TiO₂ was used without previous treatment.

Nb₂O₅-TiO₂ (NT) mixed support was prepared through mechanic mixture of the respective pure oxides maintaining the atomic ratio metal/metal equals to 1. The resultant mixture was calcined at 500°C/5 h prior to the catalyst preparation.

The 0.5%Pd-0.5%Ru/Nb₂O₅-TiO₂ (PRNT) catalyst was prepared using the wet impregnation method from alcoholic solutions of PdCl₂ and RuCl₃ .

2.1. Catalysts Preparation and Characterization

The following characterization techniques were used:

- **X-Ray Fluorescence**, in a RIX 3100 Rigaku equipment.
- **X-Ray Diffraction (XRD)**, in a XRD 6000 Shimadzu equipment, radiation source of $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$), scanning speed of $2^\circ/\text{min}$.
- **Thermogravimetry and Differential Thermal Analysis (TG/DTA)**
- **Textural Analysis**, from adsorption/desorption isotherm of N_2 .
- **Temperature Programmed Reduction (TPR)** -in samples with 0.2 g calcined at $500^\circ\text{C}/5 \text{ h}$ and submitted to temperature range of $10^\circ\text{C}/\text{min}$ in the presence of the mixture H_2/Ar (1.75% H_2) at flow rate of $30 \text{ cm}^3/\text{min}$ from room temperature to 1000°C .
- **Temperature Programmed Desorption of NH_3 (TPD- NH_3)**- adsorption of NH_3 carried out at 100°C in samples of catalysts reduced *in situ* at 500°C , desorption process under N_2 flow ($20 \text{ cm}^3/\text{min}$) and heating rate of $10^\circ\text{C}/\text{min}$, at temperatures ranging from 100°C to 500°C .

2.2 Catalytic Tests

Catalysts performance was evaluated in an experimental unit with a stainless steel reactor (18 cm long and 2.1 cm i.d.).

The tests were carried out at atmospheric pressure at 300 °C, 375 °C and 450 °C. The reagent mixture flow (1.52 g/min, in liquid phase), H₂O/C₂H₅OH molar ratio in feeding (10/1) and catalyst mass (7 g) were kept constant.

Reagent mixture feeding to the system was carried out in the liquid phase by means of a peristaltic pump. Prior to the tests, catalysts were activated *in situ* with heating steps at 100 °C (0.5 h), 200 °C (1 h) and 500 °C (4 h), under flow of N₂-H₂

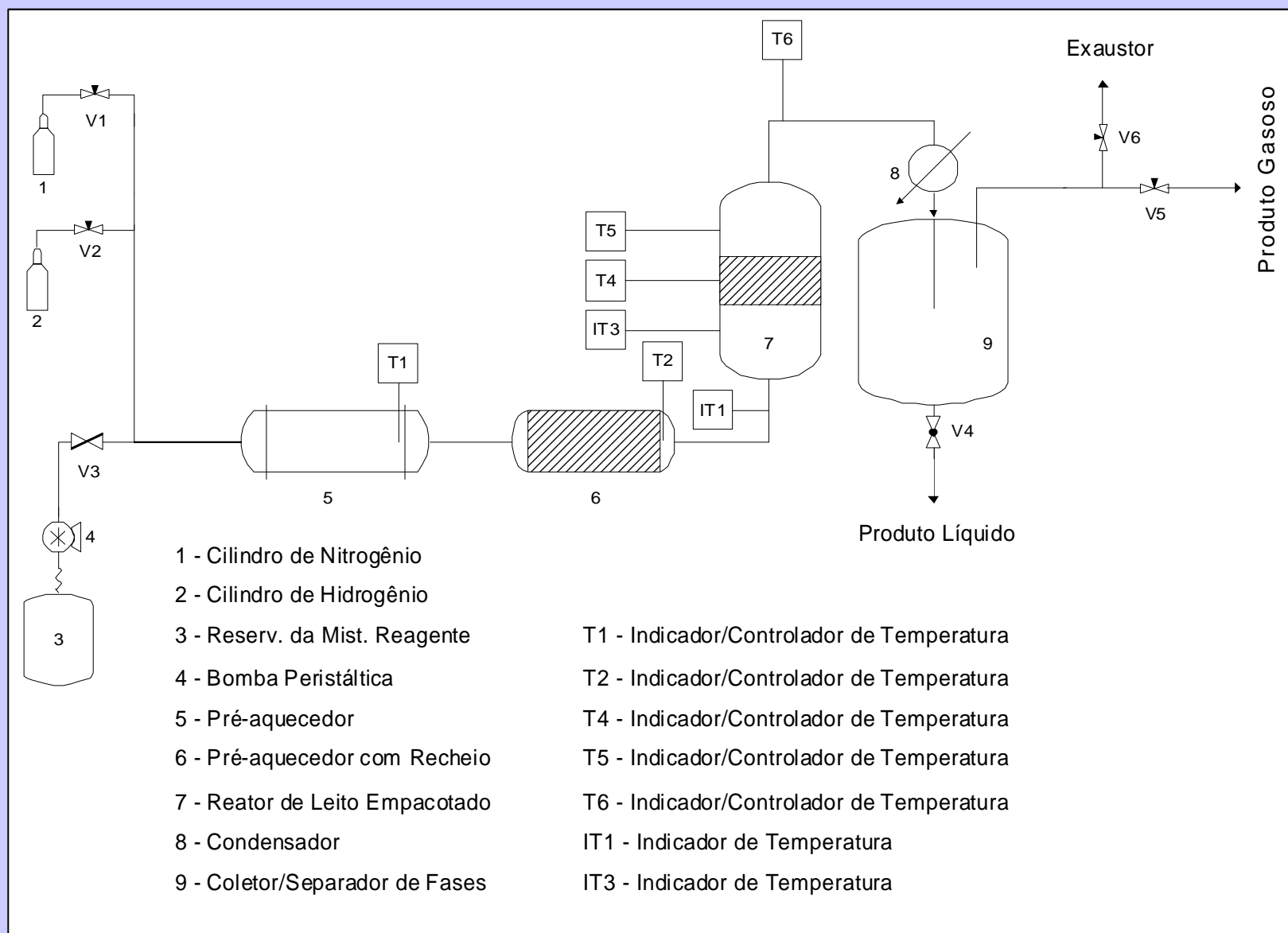


Figure 1 – Layout of the reaction unit

3. Results and Discussion

3.1 Catalyst characteristics

Its real composition is:

0.47 Pd/0.39 Ru/59.15 Nb₂O₅/39.92 TiO₂

It is crystalline and don't have microporous.

It has a low acidity, 0.059 mmol/g_{cat} NH₃

Pd and Ru are totaly reduced and Nb₂O₅ is parcialy reduced.

3.2 Catalytic Tests

$$X_{ethanol} = \frac{(F_{ethanol}^{in} - F_{ethanol}^{out})}{F_{ethanol}^{in}} \times 100\%$$

$$S_p = \frac{F_p^{out}}{\sum_{\substack{i \neq C_2H_5OH \\ i \neq H_2O}} F_i^{out}} \times 100\%$$

$$D_{cat} = \frac{X_{ethanol}^{t=1h} - X_{ethanol}^{t=8h}}{X_{ethanol}^{t=1h}} \times 100\%$$

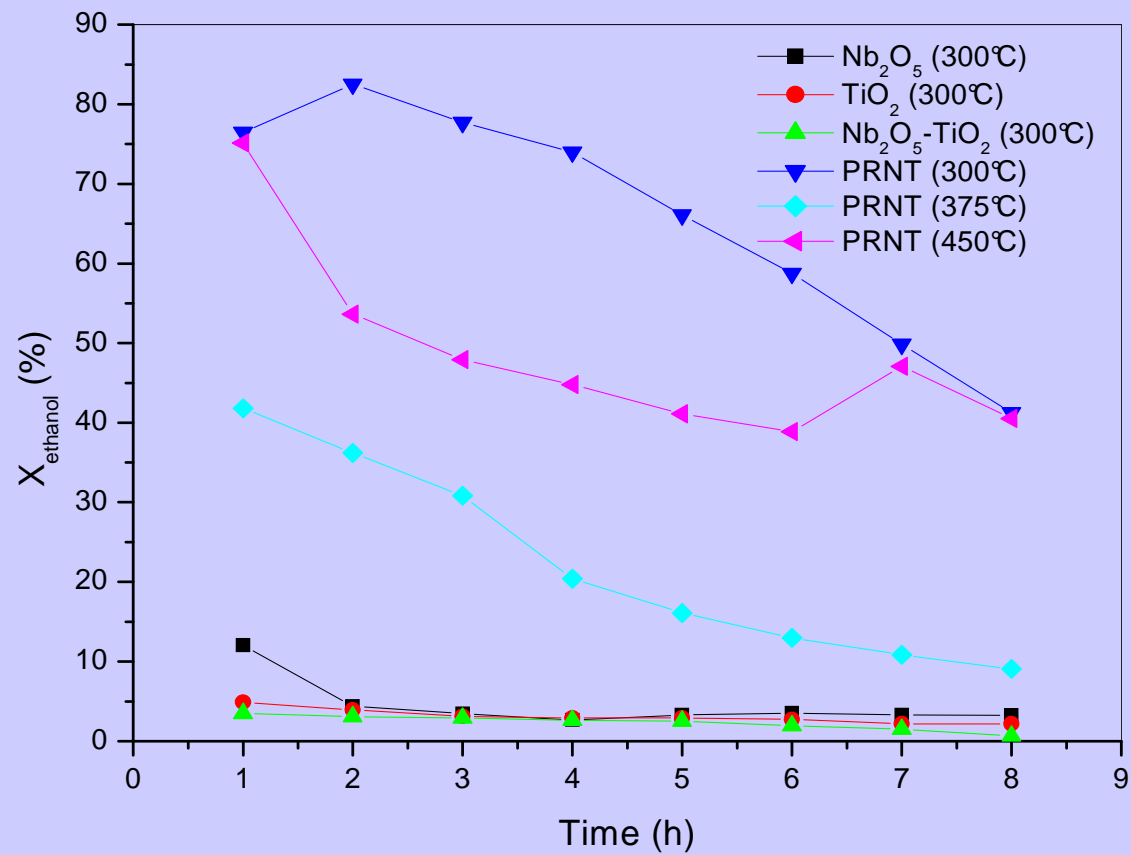


Figure 2: Ethanol conversion for support and catalyst

At 300°C the catalyst is more activit

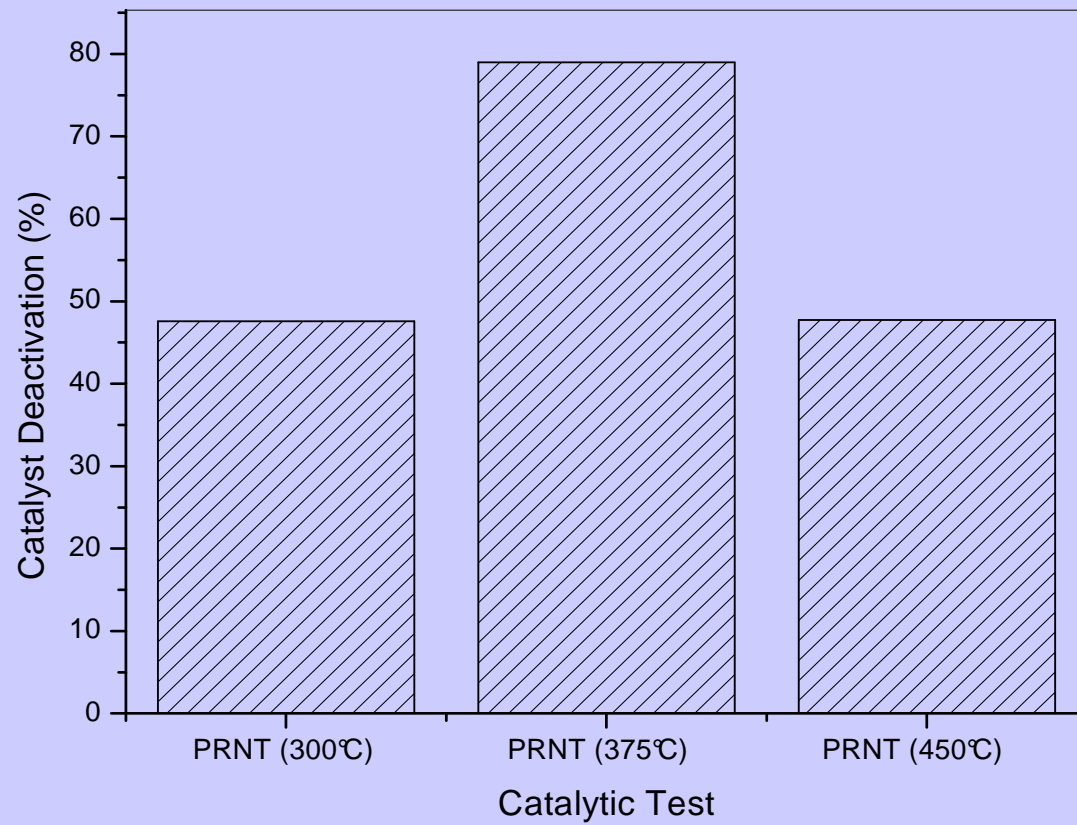


Figure 3: Catalyst deactivation after 8 h

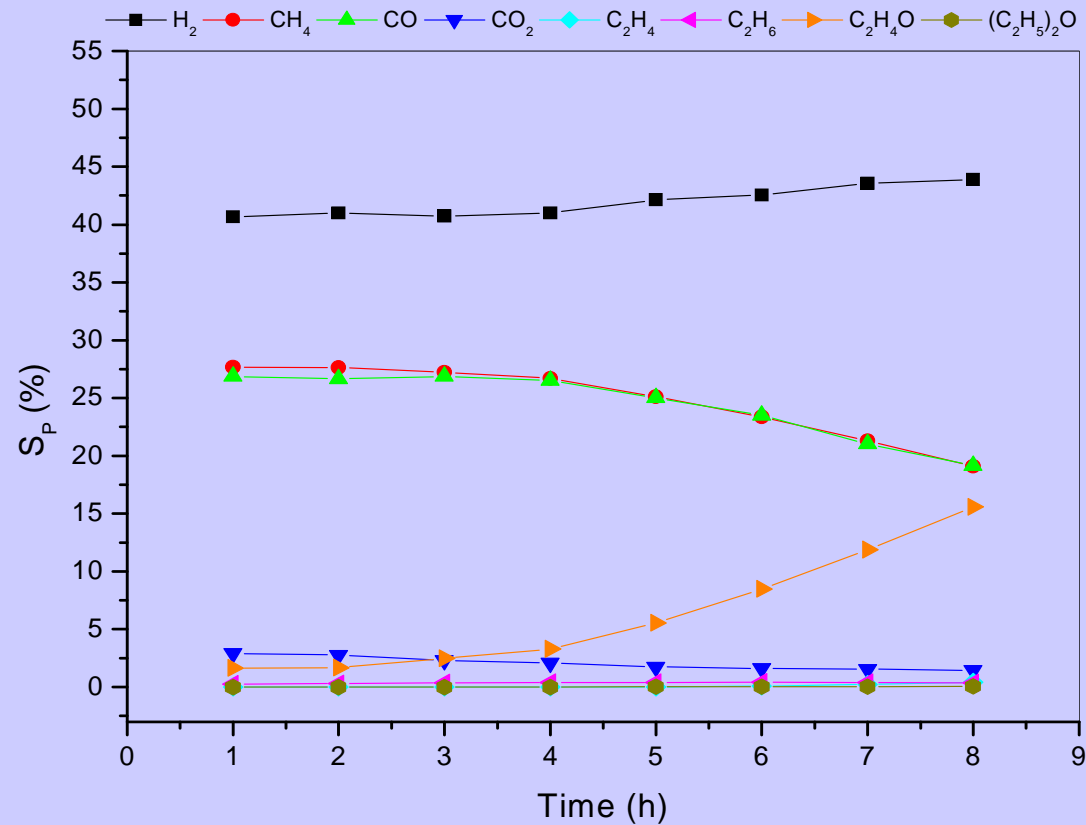


Figure 4: Product selectivity for PRNT catalyst at 300 °C.

H₂ is produced by reactions 2 and 3, ethanol decomposition

CO₂ selectivity is 3%, complete reaction has a small contribution (2 – 6)

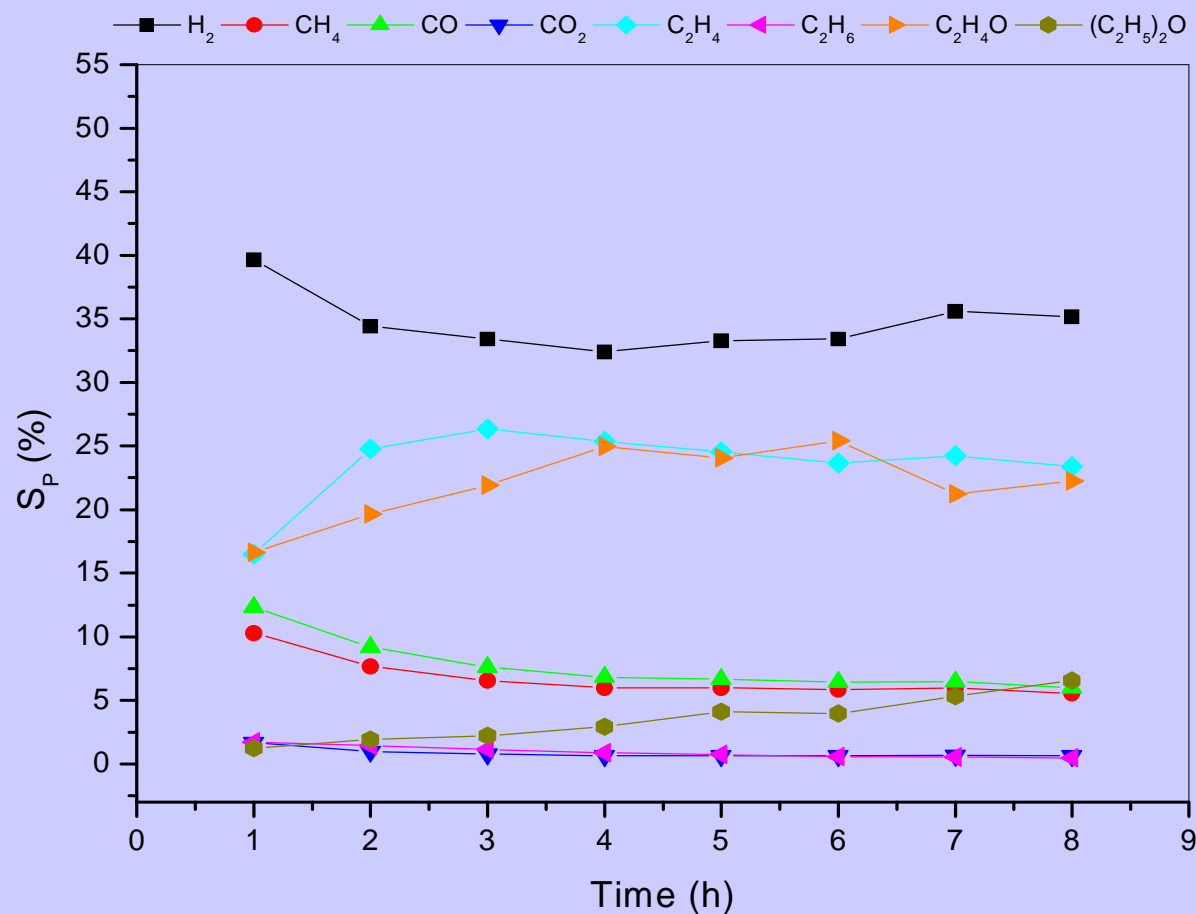


Figure 5: Product selectivity for PRNT catalyst at 375 °C.

H₂ is produced by reaction 2

there is a side reaction, $C_2H_5OH \leftrightarrow C_2H_4 + H_2O$ (11)

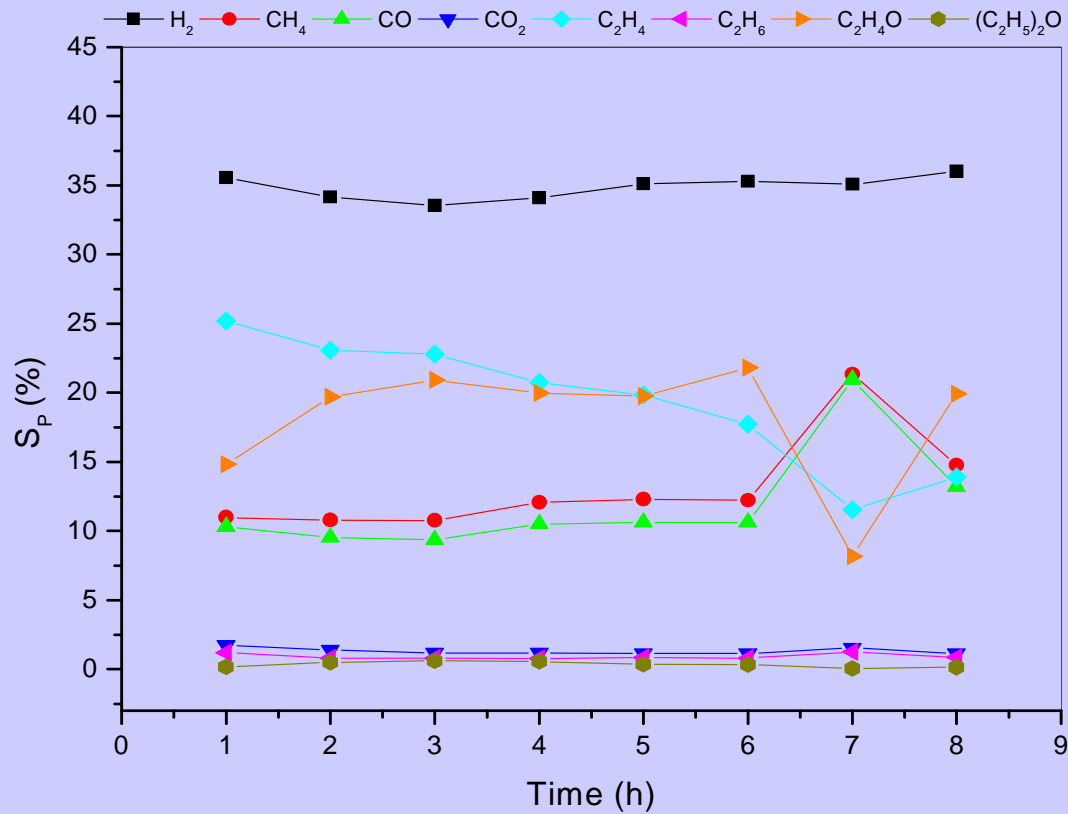


Figure 6: Product selectivity for PRNT catalyst at 450 °C.

**H₂ is produced by reaction 2, but ethanol also produce ethene,
reaction 11**

4. Conclusions

- At 300 °C the process seems to be dominated by ethanol dehydrogenation and decomposition.
- At 375 °C, dehydration seems to compete for active sites with ethanol dehydrogenation and decomposition reactions.
- At 450 °C there is an increase of catalytic selectivity with a slight increase of selectivity to products of ethanol decomposition associated to the decrease of selectivity to diethyl ether but with dehydration reaction to ethene basically competing at the same level with ethanol dehydrogenation and decomposition reactions.

Hydrogen production on PRNT catalyst is maximized at 300 °C by suppression of ethanol dehydration reaction to ethene and high selectivity demonstrated by the catalyst to dehydrogenation reactions and acetaldehyde decomposition.

Thank you for your attention !!