

Hydrogen Production by Steam Reforming of Bioethanol over Pt Based Catalysts

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Hydrogen production from renewable raw material as bioethanol by steam reforming has been studied over several Pt based catalysts with different characteristics with respect to the nature of the support and the reaction pathways. Our research revealed that Pt/CeO₂ catalyst is significantly more active and selective for hydrogen production, and his catalytic performance was interpreted by means of intervention of CeO₂ support in the reforming reaction mechanism and its high activity to direct dehydrogenation of ethanol to acetaldehyde.

Keywords: hydrogen, Pt catalyst, ethanol, steam reforming, ceria

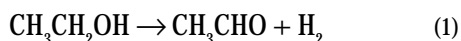
Hydrogen is a valuable source of energy and considering the decreasing of fossil fuels resources the biomass could substitute the increasing energy demand.

By the way there is a growing necessity to find alternative ways to produce energy with lower emissions of pollutants. One such option is the hydrogen and obtaining it by steam reforming of ethanol was reported by many scientific papers [1-6].

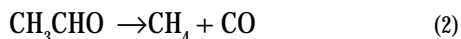
An issue of great importance is the formulation of reforming catalyst with high activity, selectivity and stability in the process. On the other hand, to obtain products of reaction requires certain experimental conditions in order to be further reformed. As a result, an overall process which leads to an effluent containing mainly H₂ and CO₂ without other undesirable products seems to be very difficult.

The mechanism of steam reforming is very complex because many reactions are in equilibrium under the experimental conditions in which the process is conducted.

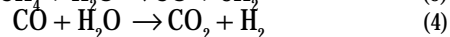
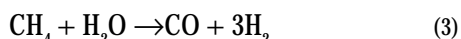
The first reaction promoted by metallic centers of Ni, Pd, Co and Rh catalysts was found to be the dehydrogenation of ethanol:



The dehydrogenation reaction is produced by two intermediate species of ethoxide (CH₃CH₂O⁻) and acetaldehyde which is further decomposed into CH₄ and CO.



Then, depending on temperature, methane reforming and/or shift reaction may occur, deciding final product distribution:



So the reforming of ethanol is represented by a series of elementary steps involving a number of organic intermediates that can produce many side effects depending on the reaction conditions and the catalyst used.

In general, transition metals have shown good activity and selectivity for the reforming of ethanol. The main

problem that arises in the use of these catalysts is given by sintering or deposition of coke [2].

In the literature, several articles have been published in order to present the biomass reforming using a series of metallic catalysts. One of the first studies on ethanol reforming was reported by Rampe et al. [3]. The catalysts are based on Pt, Ru, Pd and Ni or bimetallic Ni-Pt and Ni-Pd on Al₂O₃. Their performances were evaluated at pressures of 2, 5 or 9 bar and a temperature in the range of 600-800°C. Jacobs et al. [4] investigated the Pt/CeO₂ system on ethanol steam reforming at temperature between 200-550°C in diluted medium (H₂O/EtOH/N₂+H₂ = 33/1/29). They observed that the cerium oxide plays an important role in the mechanism of the reaction. Ethanol is adsorbed on the centers of ceria species to form ethoxide which in turn is converted to acetate species. The catalyst is essentially deactivated by coke which creates a barrier at the interface of the metal-support which inhibits decomposition of acetate. Oxygen from water strongly reduces coke formation and increases catalyst stability [5, 6]. Platinum has also been used to improve the stability of Ni by decreasing the formation of coke in the case of bimetallic Ni-Pt catalyst [7-11].

Finally, the latest discoveries in the field of mesoporous molecular sieves, particularly MCM-41 and SBA-15, have shown a great attention. So far, the ethanol reforming on mesoporous support as SBA-15 was studied by Vizcaino et al. [12-15]. The paper [12] presents the results obtained for ethanol steam reforming over catalysts such as Cu-Ni/SBA-15 prepared by direct synthesis or by impregnation. The same researchers [14] changed the catalyst formula used in the previous study, by introducing cerium and lanthanum or magnesium and calcium. It was found that several properties as acidity, metal dispersion and metal-support interaction were modified with changes of ethanol conversion and hydrogen selectivity [15].

All the researches on steam reforming of ethanol categorically reveal the role played by the metal deposited on support. For this reason our study is focused on the influence of the support on ethanol reforming and hydrogen selectivity. Our tested catalysts contain platinum as metallic component and different supports as: Al₂O₃, CeO₂ and mesoporous silica SBA-15 respectively. The effect of other parameters (temperature, WHSV) on the ethanol

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conversion and hydrogen production are also reported herein.

Experimental part

Material and Methods

Chemicals

The reagents type poly-(ethyleneglycol)-block-poly-(propyleneglycol)-block-poly-(ethyleneglycol) (EO₂₀PO₇₀EO₂₀, Pluronic P₁₂₃), 1,3,5-trimethylbenzene (TMB) and tetraethyl ortho-silicate (TEOS) were purchased from Sigma Aldrich. The hydrochloric acid (conc. 37.0 wt %), potassium chloride and ethanol were provided by Carl Roth. Hydrogen and helium for GC were purchased from Linde. The platinum chloride salt used for the impregnation process was purchased from Fluka and cerium oxide was purchased from Sigma Aldrich. Alumina support was provided by ICECHIM Bucharest.

Catalysts preparation

The mesoporous silica support used in this study was synthesized according to a well-established procedure [16] under acidic conditions using Pluronic P123 triblock copolymer (EO₂₀PO₇₀EO₂₀) as template and tetra-ethyl-ortho-silicate (TEOS) as silica source. Typically 2 g of P123 (EO₂₀PO₇₀EO₂₀ pluronic triblock copolymer), and 1.54 g of KCl were dissolved in 60 g of deionized water and 11.8 g of HCl at room temperature until the solution become transparent. Then, in obtained solution was added 1.5 g TMB (1,3,5 trimethylbenzene) with stirring. After 10 h of stirring, was added drop wise 4.3 g of TEOS (tetra-ethyl-ortho-silicate), and then stirred vigorously for 10 min. The resulting mixture was kept in the oven for 24 h and then transferred to an autoclave under static conditions at 373 K for 24 h. The resulting product was filtered (the residue in the container was washed with deionized water), washed in 50 mL deionized water, filtered again and dried at 333 K in an oven overnight. The removal of the organic residue was accomplished by heating in air using a heating rate of 4 degrees/min from room temperature to 813 K and calcined at 813 K for 10 h under the same conditions, followed by cooling the mesoporous silica with the same rate (4 degrees/min) from the temperature of 813 K to room temperature.

Finally all the catalysts were prepared by impregnation method using an aqueous solution of platinum chloride (PtCl₂). After impregnation with Pt (2%), the samples were dried for 48 h in an oven at 373 K.

Catalyst characterization

The catalysts were characterized by X-ray diffraction performed on a Bruker D8 Advance, X-ray diffractometer with Cu K α radiation ($\lambda_{Cu} = 1.5406 \text{ \AA}$) operating at a voltage of 40 kV and a current of 40 mA. Data were collected in 2θ range from 20 to 70 $^\circ$.

Textural proprieties of the catalysts were obtained by using a Quantachrome Autosorb Automated Gas Sorption system. Nitrogen physisorption experiments were carried out at 77K to obtain BET surface area, pore volume and pore size distribution.

Steam reforming tests

The experimental program of catalytic reforming of ethanol was carried out in the continuous system, using a micro pilot unit with a fixed bed catalyst and downward flowing of the reactants. Control of the temperature in the catalyst zone of the reactor is done automatically.

The catalyst is arranged in the middle of the reactor, at a sufficient distance from the upper flange to allow the pre-

heating of the reactants to the reaction temperature. The catalytic volume was in the range of 10 to 20 cm³.

The gas phase separated in the separator was analyzed chromatographically by direct sampling of flow by means of a Varian gas chromatograph GC 450 equipped with TCD-type detector in order to measure the hydrogen and all organic compounds present in the flow.

The liquid phase obtained was analyzed on a CARLO ELBA gas chromatograph. In the liquid phase we identified the following compounds: water, ethanol, and acetaldehyde.

To establish the material balance we considered the feedstock (alcohol + water) that was obtained by extracting from the initial feedstock (ethanol solution) the water obtained at the end of the experience, considering the remaining water an inert product. Then the liquid or gas yield was obtained comparing them to the feedstock using the following formulas:

$$g_{\text{feedstock}} = g_{\text{ethanol solution}} - g_{\text{collected water}} \quad (5)$$

$$\eta_{\text{gas}} = \frac{g_{\text{gas}}}{g_{\text{feedstock}}} \times 100 \quad (6)$$

$$\eta_{\text{liquid}} = \frac{g_{\text{liquid}}}{g_{\text{feedstock}}} \times 100 \quad (7)$$

The process performance was assessed by the conversion of ethanol and the yield of the desired product (hydrogen).

The formulas used to calculate the conversion of ethanol and the hydrogen yield were:

$$X_{\text{EtOH}} = \frac{\text{moles EtOH in} - \text{moles EtOH out}}{\text{moles EtOH in}} \times 100 \quad (8)$$

$$\eta_{\text{product}} = \eta_{\text{H}_2} = \frac{g_{\text{H}_2}}{g_{\text{feedstock}}} \quad (9)$$

where:

X_{EtOH} - ethanol conversion

n_{EtOHin} - moles of ethanol fed

n_{EtOHout} - moles of ethanol produced

η_{H_2} - hydrogen yield

g_{gas} - mass of gas produced in the experiments, g

$g_{\text{feedstock}}$ - real raw mass, g

$\% \text{H}_2$ - weight % of H₂ obtained by gas chromatographic analysis

Results and discussions

Catalyst characterization

For mesoporous silica SBA-15 (fig. 1) the regular hexagonal structure with cylindrical walls is confirmed by a single peak sharp enough corresponding to angle $2\theta = 0.5^\circ$. Therefore this support has a well-developed mesoporous structure; not affected by the small amount of platinum impregnated.

Also, the catalyst Pt/SBA-15 XRD spectrum (fig. 1) shows at high angles a larger portion of the peak over $2\theta = 20^\circ$ that is characteristic for amorphous silicon oxide substrate composition. On the other hand, in this spectrum it can be observed characteristic peaks of platinum at the angle $2\theta = 36.5, 46.2$ and 67.6° , which are generally attributed of interplan spaces of the structure of platinum, which suggests the existence of chemical interactions between the support SBA-15 and the metal used as mentioned in literature [17].

In the case of Pt/CeO₂ catalyst (fig. 2), no peaks were observed corresponding to platinum oxide (PtO or PtO₂) because the main peaks for PtO₂ (27.90 $^\circ$) and PtO (33.90 $^\circ$)

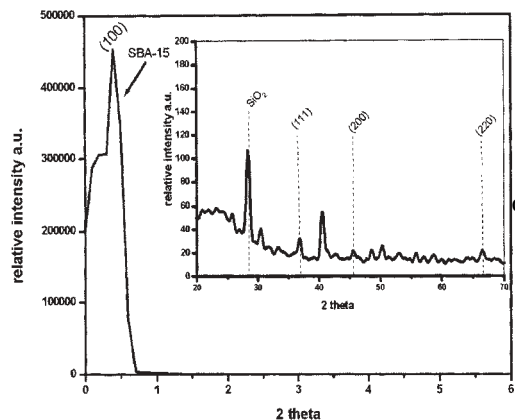


Fig. 1. X-ray diffraction pattern of Pt/SBA-15 catalyst

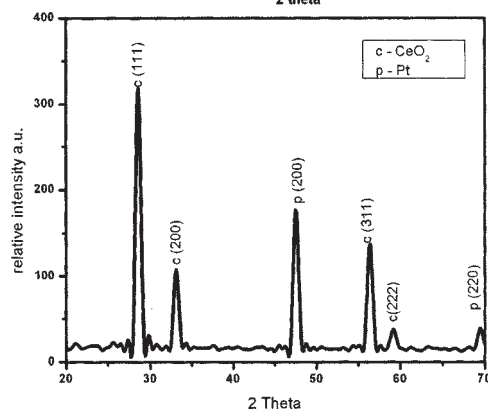


Fig. 2. X-ray diffraction pattern of Pt/CeO₂ catalyst

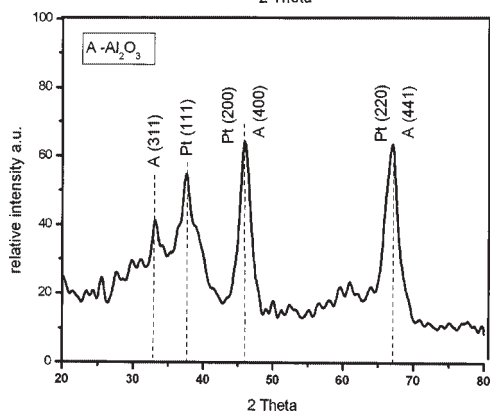


Fig.3. X-ray diffraction pattern of Pt/Al₂O₃ catalyst

are relatively close to the two peaks of the CeO₂ (28.80° and 33.70°) and are probably covered.

Figure 3 shows the characteristic peaks of alumina γ -Al₂O₃, highlighting the crystallinity of the pore walls. The peaks at $2\theta = 36.5$, 45.52 and 67.01° are assigned to γ -Al₂O₃. Also from figure 3 it can observe that the characteristic Pt peaks overlap with those of alumina, the one that stands out is that of $2\theta = 36.5^\circ$.

Table 1 summarizes the BET surface area, pore volume, and average pore size of catalysts with different support. It is shown that the BET surface area and pore volume decreased with the impregnation of Pt on the support.

Steam reforming tests

The efficiency of prepared catalyst was assessed by the ethanol conversion and hydrogen yield in the ethanol steam reforming reaction at a temperature range of 300-500°C, weight hourly space velocity (WHSV) 9 h⁻¹ and a concentration of 10% alcohol in the raw material.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (nm)
Pt/Al ₂ O ₃	469.51	0.41	18.74
Pt/CeO ₂	33.54	0.05	1093.61
Pt/SBA-15	824.91	0.47	24.95

Table 1
CHARACTERISTICS OF CATALYSTS
IMPREGNATED WITH PLATINUM

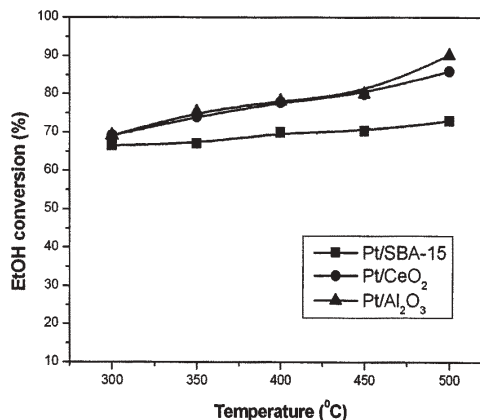


Fig.4. Ethanol conversion on Pt catalysts (10% ethanol, WHSV = 9h⁻¹)

Figure 4 shows the results of ethanol steam reforming reaction, in the presence of Pt catalysts using three different supports: SBA-15, CeO₂ and Al₂O₃.

Higher values for ethanol conversion are obtained with Pt/Al₂O₃ and Pt/CeO₂.

The important role of the support surface in the ethanol reforming reaction was highlighted in the literature [18]; the catalyst of platinum supported on CeO₂ presents comparable values of ethanol conversion with Pt/Al₂O₃. If for Al₂O₃ and SBA-15, the surface area is crucial for the ethanol conversion, thus high ethanol conversion of Pt/CeO₂ catalyst is explained by a different reaction mechanism.

The first step is ethanol adsorption on the centers of the ceria species to form ethoxide which in turn is converted to acetate species that are hydrogenated by the metal to the carbon dioxide and methane (table 2). Similar results were reported by Jacobs in his paper [4].

Figure 5 shows the hydrogen yield obtained by ethanol reforming reaction in the temperature range of 300-500°C and the concentration of ethanol in the feed of 10% and a weight hourly space velocity of 9 h⁻¹, in the presence of catalysts of Pt supported on SBA-15, CeO₂ and Al₂O₃.

It can see that CeO₂ support ensures best hydrogen yield compared to other supports. Ethane low yields obtained on the Pt/CeO₂ catalyst show that the reforming reactions take place in particular by dehydrogenation to acetaldehyde and less by dehydration with the formation of ethylene which is saturated to ethane by hydrogen consumption. In addition, the literature mentions that CeO₂ has a moderate activity against dehydration reaction [19].

On the alumina support, the conversion of ethanol is good, but the hydrogen yield is lower because this support promotes the dehydration reaction which consumes hydrogen to form ethane through ethylene saturation.

On the other hand, it is known that under certain reaction conditions Al₂O₃ is able to promote desorption of the secondary reaction products [20]. As a result, the surface is poisoned and the decomposition of ethanol is obstructed, leading to the occurrence of other by-products such as ethylene obtained by ethanol dehydration which consumes hydrogen, leading to the formation of ethane.

We consider that the formation of ethylene by dehydration reaction is catalyzed by acid centers acids from the support and is even more intense as the support acidity is higher, a fact mentioned by Iwasa and Takezawa [21]. The Al₂O₃ support which has higher acidity compared

Temperature (°C)	Catalyst	CH ₄ (%)	CO (%)	CO ₂ (%)	C ₂ H ₄ (%)	C ₂ H ₆ (%)
300°C	Pt/CeO ₂	0.08	0.17	0.00	0.21	0.38
	Pt/Al ₂ O ₃	0.78	1.47	0.28	0.68	0.56
	Pt/SBA-15	1.63	0.48	0.55	0.00	0.02
350°C	Pt/CeO ₂	0.08	0.17	0.00	0.20	0.49
	Pt/Al ₂ O ₃	1.22	1.78	0.58	0.48	2.08
	Pt/SBA-15	2.06	0.52	0.60	0.00	0.02
400°C	Pt/CeO ₂	0.11	1.10	0.02	0.18	0.56
	Pt/Al ₂ O ₃	1.76	2.77	0.97	0.31	2.94
	Pt/SBA-15	2.61	0.57	0.61	0.00	0.02
450°C	Pt/CeO ₂	0.14	1.53	0.05	0.18	0.57
	Pt/Al ₂ O ₃	1.94	3.43	1.12	0.29	3.63
	Pt/SBA-15	2.62	0.64	0.69	0.00	0.05
500°C	Pt/CeO ₂	0.14	2.04	0.06	0.16	0.99
	Pt/Al ₂ O ₃	2.72	4.63	1.20	0.16	7.75
	Pt/SBA-15	2.80	1.30	1.13	0.00	0.02

Table 2
SECONDARY PRODUCT YIELD (10%
ETHANOL, WHSV = 9h⁻¹)

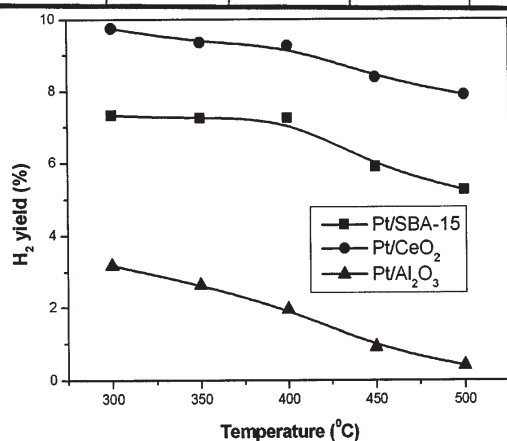


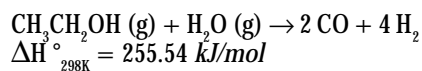
Fig. 5. Hydrogen yield on Pt catalysts (10% ethanol, WHSV = 9h⁻¹)

to other supports will intensify the ethanol dehydration to ethylene, but due to the saturation of ethane by hydrogenation will lead finally to lower H₂ yields.

The efficiency of ethanol reforming reaction is determined by the reaction conditions and the catalytic system used.

The catalytic test data for systems prepared in this study revealed that the best support was CeO₂, and the influence of reaction parameters will be analyzed further.

The global bioethanol reforming reaction is strongly endothermic.



From the thermodynamic point of view, the reaction is favored by higher temperatures, which can be observed in figure 6.

This increasing of the ethanol conversion is justified, by the reaction thermodynamics and, on the other hand by the kinetics because the reaction rate increases with the temperature.

The influence of reaction temperature on the hydrogen yield in the presence of the catalyst of Pt/CeO₂ is shown in figure 6.

The analysis of data presented in figure 6 shows the decrease of hydrogen yield with temperature reaction increasing. The decrease is accentuated at high temperatures close to 500°C. As was mentioned before, in

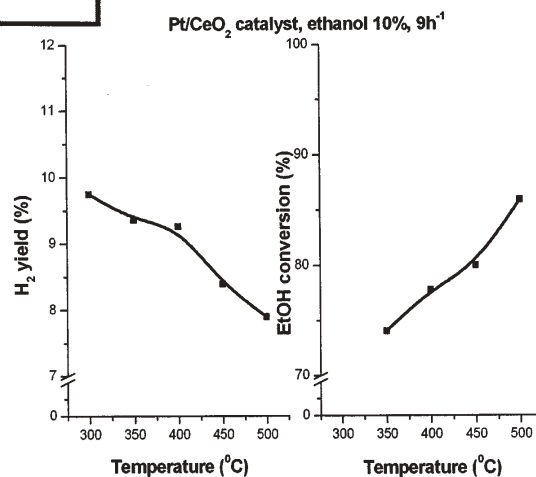


Fig. 6. The ethanol conversion and hydrogen yield on Pt / CeO₂ catalyst

agreement with the data presented in the literature [21], ethanol reforming reaction takes place in multiple stages through dehydrogenation reactions to acetaldehyde and dehydration to ethylene. Further acetaldehyde is reformed with water to CO and H₂, or decarbonated to CH₄ and CO on the other hand ethylene is saturated with H₂ to ethane, if not, it will be transformed in coke deposits by polymerization.

The temperature favors the dehydration reaction of ethanol which has higher activation energy. Because of this, the increasing of the reaction temperature decreases the yield of hydrogen due to the formation of ethylene which is hydrogenated by consuming a part of the hydrogen produced.

The influence of WHSV of ethanol reforming reaction in the presence of the Pt/CeO₂ catalyst was determined at a temperature of 350°C, atmospheric pressure and a feedstock with an ethanol content of 10%.

Figure 7 shows that ethanol conversion decreases when WHSV increases explained by lower reaction times at high WHSV.

From the same figure we notice that hydrogen yield decreased with the increasing of WHSV explained by the fact that higher WHSV implies a lower reaction time. With the increasing of WHSV the hydrogen yield decreases slowly followed by an emphasized decreasing justified by

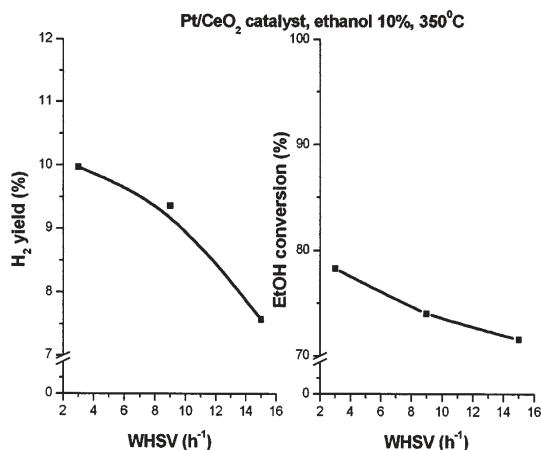


Fig. 7. The influence of weight hourly space velocity on ethanol conversion and hydrogen yield for the ethanol steam reforming reaction on Pt/CeO₂ catalyst

the influence of reaction time on the kinetics of successive reforming reaction which is performed in several steps: dehydrogenation and dehydration followed by reforming reactions of the product from the first stage, and shift reaction. From the kinetic point of view because the primary reactions are slower, the intermediate products are formed in very low amounts which in turn will generate through the secondary reaction less hydrogen.

Conclusions

- The high yield of hydrogen obtained by steam reforming of ethanol presents a great economic advantage, because it allows the safe use of the ethanol from fermentation without the expensive operation of ethanol concentration;

- The steam reforming of ethanol occurs by a complicated reaction mechanism which includes a number of successive and simultaneous reactions in order to produce hydrogen;

- The CeO₂ support ensures the higher hydrogen yield compared to other supports. Ethane low yield obtained shows that on the Pt/CeO₂ catalyst the reforming reactions taking place in particular by ethanol dehydrogenation to acetaldehyde and less by dehydration with the formation of ethylene.

- The Al₂O₃ support is not able to promote desorption of secondary reaction products. As a result, the surface is poisoned and the decomposition of ethanol is obstructed, leading to the appearance of other by-products such as ethylene.

- The Al₂O₃ support which has higher acidity compared to other supports will intensify dehydration of ethanol to ethylene, but due to the hydrogen consumption in the saturation reaction lower hydrogen yields were obtained;

- The high H₂ yields obtained on CeO₂ support can be justified by higher activity of this support to direct dehydrogenation reaction of ethanol to acetaldehyde and by promotion of water gas shift reaction.

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