Steam Reforming of Bioethanol over Pt/CeO_2 Catalyst

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The performances of steam reforming ethanol process was investigated on CeO_2 supported catalyst with a content of metal of 2 wt%. Catalyst was obtained by the pore volume impregnation method using aqueous solutions of metal salt. The catalytic activity of the steam reforming reaction was investigated at atmosferic pressure in the temperature range of 300-500 ^{0}C established by using an automatic panel control, in a fixed bed reactor monitored by an on-line gas chromatography VARIAN CP 3800. The influence of operating parameters, such as reaction temperature, water/ethanol feed, weight hourly space velocity (WHSV) were investigated.

Keywords: steam reforming, catalyst, hydrogen.

In response to the need for cleaner and more efficient energy technology, a number of alternative processes to the current energy supplys have rised. In this context, steam reforming of ethanol for producing hydrogen, has been recognized as a practical and viable option due to its carbon neutral nature. Ethanol comparing with others alcohols is less toxic, easily transportable, safe to handle and the most important, it is renewable and biodegradable. Supported platinum catalysts are widely used in many chemical processes, such as hydrogenation, oxidation, and reforming. Much effort has been devoted to the development of platinum-based catalytic materials [1].

The nature of support strongly influences the catalytic performance of supported Pt catalyst for hydrogen production since it affects dispersion and stability of the metal as well as it may participate to the chemical reaction.

CeO_2 is a basic support and has redox properties. It has oxygen storage capacity and hence its presence improves the resistance to coke deposition. It also promotes the action of precious metals. For instance, the addition of CeO_2 to Pt prevents sintering of Pt metal particles and ensures high dispersion of Pt over CeO_2. CeO_2 is also active in the water gas shift reaction (WGS) [2].

Steam reforming of ethanol is globally, an endothermic reaction that produces only hydrogen and carbon dioxide if ethanol reacts in the most desirable way. However, the process of ethanol steam reforming comprises several catalytic steps. Such reaction mixture may include dehydration, decomposition and dehydrogenation of ethanol into ethylene, methane and acetaldehyde, respectively, besides the water-gas shift reaction (WGSR) and methanation reaction [3].

In the present work the Pt/CeO_2 catalyst was investigated in the steam reforming of bioethanol. The study was carried out by varying the reaction temperature, the ethanol content of the raw material and weight hourly space velocity (WHSV).

Experimental part

Chemicals and reagents

The following chemicals were used for catalyst synthesizing: for support we used cerium (IV) oxide (powder, <5μm) purchased from Sigma Aldrich. The hydrochloric acid (conc. 37.0 wt %) was provided by Carl Roth and the metallic precursor for the impregnation process, respectively, platinum chloride ($PtCl_2$, purity > 71% Pt) was purchased from Fluka.

For steam reforming experiments, a mixture of distillated water and ethanol (Chemical, purity > 96%) was used as a feedstock.

Preparation of supported CeO_2 catalyst

Cerium (IV) oxide powder was used as support for the preparation of the catalyst by impregnation method. The synthesis started by dissolving about 2 grams of platinum chloride ($PtCl_2$) in almost 34 mL of hydrochloric acid (HCl) followed up by a vigorous stirring up to complete dissolution. This sollution was mixed with about 68 g of cerium oxide and then the content was dried for 48 h at a temperature of 393 K. Finally, the synthesized catalyst has got a metal content (Pt) of 2wt%.

Experimental procedure and apparatus

The steam reforming of ethanol was carried out under atmospheric pressure in a fixed bed reactor. The catalyst was loaded between two layers of glass beads inside the reactor and the reaction temperatures were measured by a thermocouple and controlled by a digital temperature controller. Prior to reaction, the catalyst was reduced in situ by hydrogen at 550^{0}C for 6h. The products were analysed on-line using a Varian gas cromatography equipped with a capillar columns Pora Plot and a TCD. Helium was used as the carrier gas. After each reduction of the catalyst, the reactor temperature was fixed for the reaction temperature (300, 350, 400, 450, 500^{0}C). The feed composition was adjusted in order to obtain the correct percentage of ethanol in the feed (5, 10, 15%).

Results and discussions

Steam reforming reactions

Bio-ethanol steam reforming reaction is an endothermic reaction.

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2; \quad \Delta H_{298} = 173\ kJmol^{-1} \quad (1)$$

Although the steam reforming reaction seems to be simple, in many cases the scheme of reaction is complicated by the presence of other reactions occcuring in the system, depending mostly on reaction temperature and catalyst composition.

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And so the exit stream contains not only hydrogen, but also a lot of other compounds [4]. A list of possible reactions that occur in the reactor is presented below, as follows:

- ethanol steam reforming to syngas:

$$CH_3CH_2OH + H_2O \rightarrow 2CO + 4H_2 \quad (2)$$

- ethanol cracking:

$$CH_3CH_2OH \rightarrow 3/2\, CH_4 + \square CO_2 \quad (3)$$

$$CH_3CH_2OH \rightarrow CH_4 + CO + H_2 \quad (4)$$

- ethanol dehydrogenation :

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \quad (5)$$

- acetaldehyde decarbonylation:

$$CH_3CHO \rightarrow CH_4 + CO \quad (6)$$

- acetaldehyde steam reforming

$$CH_3CHO + H_2O \rightarrow 3H_2 + 2CO \quad (7)$$

- ethanol dehydration

$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \quad (8)$$

- ethylene steam reforming

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \quad (9)$$

- methane steam reforming

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad (10)$$

- water gas shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (11)$$

Effect of reaction temperature

To investigate the effect of the reaction temperature on ethanol conversion and product distribution, the weight hourly space velocity was fixed at $3h^{-1}$.

Figure 1 shows the notable effect of reaction temperature on ethanol conversion. The lowest conversion (54%) was obtained at 300^0C whereas the highest one (88%) was achived at 500^0C .

Also from figure 1 results that a higher conversion is obtained when bioethanol content of raw material, increases from 5% vol to 15% vol.

The production rates for hydrogen and methane, are plotted in figure 2. Hydrogen production descreases with increasing temperature from 89.75 wt.% at 300^0C to about 24.18 wt% at 500^0C, while the highest methane production of almost 31.59 wt % is observed at 300^0C as compared to 6.18 wt% at 500^0C. The results, when combined with the data on CO_2 production and CO production rates (fig. 3), suggest that bioethanol steam reforming with methane formation becomes significant, since methane and carbon dioxide production is favoured.

At higher temperature, the CH_4 decreases, showing that the effluent composition may be affected by the thermodynamic equilibrium of methane steam reforming reaction. Furthermore, when CO_2 production increases, this product will react with the excess of water, so the water gas shift reaction takes place. It is worth mention that in literature [5] was establish that the production of H_2, CO and CO_2 is interconected with water gas shift reaction and

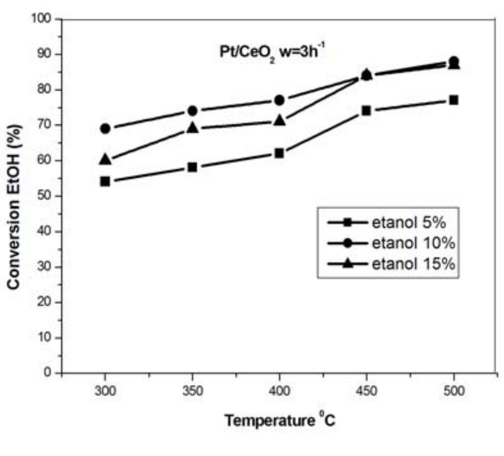

Fig. 1 Effect of temperature on ethanol conversion

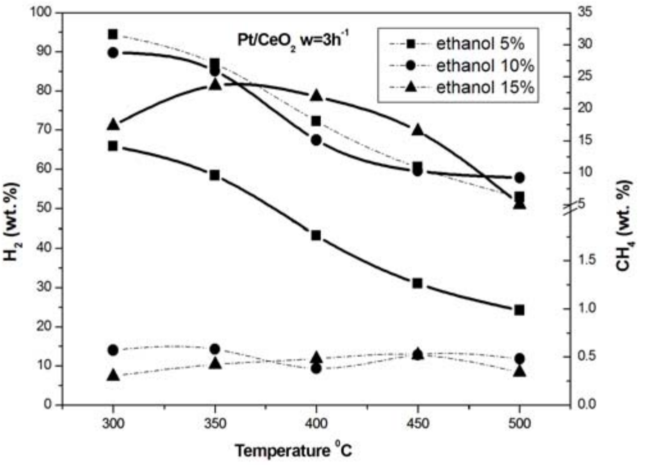

Fig. 2. Variation of hydrogen and methane production rates with temperature (solid lines and left y axis represent H_2 production, dotted lines and right y axis represent CH_4 production)

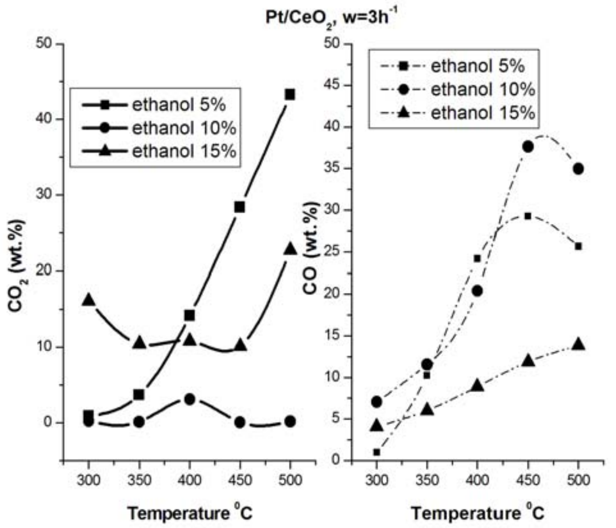

Fig. 3. Variation of carbon dioxide and carbon monoxide production rates with temperature

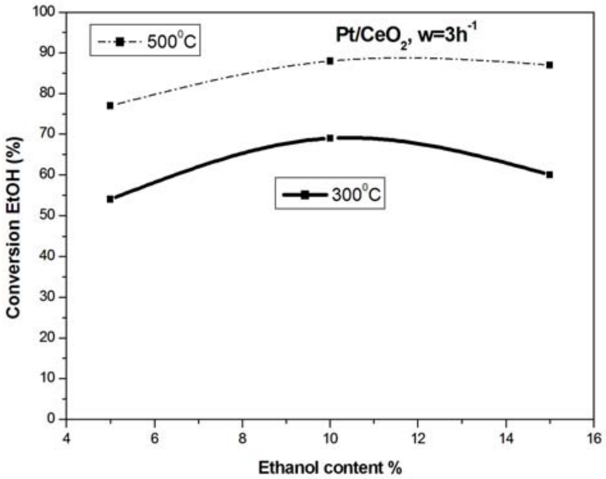

Fig. 4. Effect of ethanol content on ethanol conversion (solid lines for temperature 300^0C , dotted lines for temperature 500^0C)

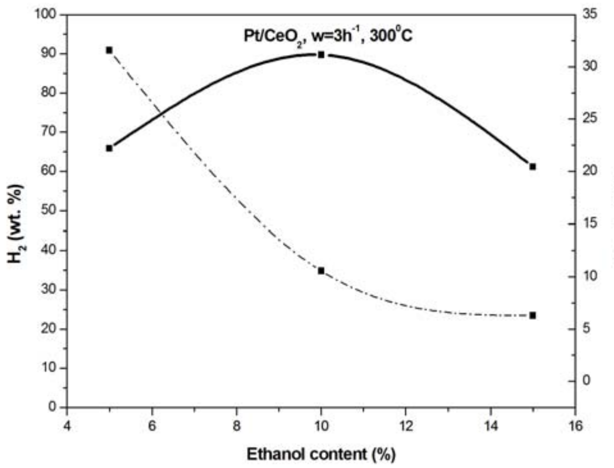

Fig. 5. Variation of hydrogen and methane production rates with ethanol content (solid lines and left y axis represent H_2 production, dotted lines and right y axis represent CH_4 production)

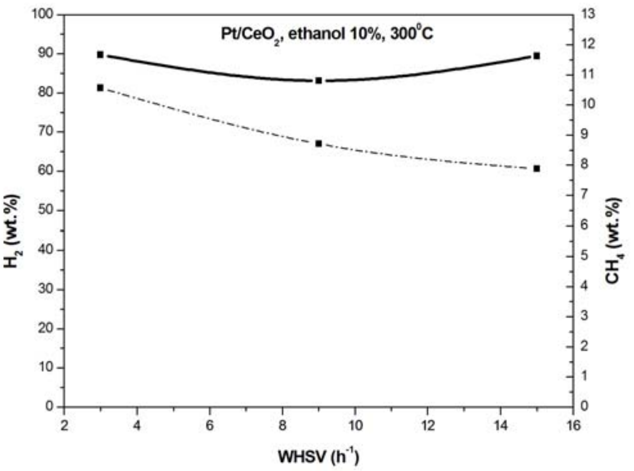

Fig. 6. Variation of hydrogen and methane production rates with WHSV (solid lines and left y axis represent H_2 production, dotted lines and right y axis represent CH_4 production)

methane steam reforming instead CH_4 is a result of ethanol decomposition and steam reforming reactions.

Effect of ethanol content of the raw material

The effect of ethanol content of the raw material on the steam reforming performance was studied at two temperatures, 300 and 500°C and at the same WHSV of $3h^{-1}$ as previoulsy. The variation in total ethanol conversion with the water/ethanol feed at 300°C and 500°C is presented in figure 4, while the coressponding hydrogen and methane production trends at 300°C are shown in figure 5.

Ethanol conversion is more higher for the temperature of 500°C and a maximum of 10% ethanol content in the raw material. Hydrogen production is improved by the increasing of ethanol content with the same trend as the conversion. On the other hand, the methane production decreases with incresing of the ethanol content, meaning that methane reforming can take place at low ethanol content in the feed.

Effect of weight hourly space velocity (WHSV)

Because the ethanol 10% content was the most productive raw material, to study the effect of weight hourly space velocity, we considered this raw material and the temperature of 300°C.

The production of hydrogen is almost constant with incresing of weight hourly space velocity, instead the incresing of WHSV leads to slight decreasing of methane production, in this case the reaction time is shorter and the secondary reactions (specially methane reforming) are not occuring in the reactor.

Conclusions

Pt-doped supports of CeO_2 was synthesized by Pt impregnation using a $PtCl_2$ as source for of platinum atoms. Over Pt/CeO_2 catalyst, a conversion almost 88% of ethanol and good production of hydrogen could be obtained. Hydrogen is the main constituent of the reaction effluent which also contains secondary products as CH_4, CO_2 and CO. Our observation shows that a lower temperature of 300°C offers very good production of hydrogen for which this catalyst is recommended to be used for hydrogen production by steam reforming of bioethanol.

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