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MESOPOROUS SILICA CATALYST FOR STEAM REFORMING PROCESS

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The aim of this paper was to evaluate the behavior of Pd/SBA-15 catalyst for steam reforming of bio-ethanol. Bioethanol was obtained by alcoholic fermentation of different sweet fruits and the alcohol content is in the range of 5–15 %v/v. The Pd/SBA-15 catalyst was prepared using pore volume impregnation method and characterized by several techniques as X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and N_2 adsorption/desorption isotherms. The catalytic test showed that Pd/SBA-15 catalyst is able to perform higher ethanol conversion and hydrogen yield in a quit low temperature range (573-773 K).

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1. Introduction

In recent years, the hydrogen production was in the center of a great interest especially for its many applications mostly in the fuel cell technologies. The efforts to control pollution and greenhouse gas emissions have generated a great interest for alternative sources of energy, where hydrogen is a recognized solution [1]. The processes that the aim are “generation of hydrogen” from biomass have been recognized as a more practical and viable option for the future due to their renewable and carbon-neutral nature. In this way the catalytic steam reforming of ethanol provides an attractive pathway in obtaining hydrogen. Moreover, many researchers start studying the steam reforming reaction, concluding that the nature of the metal phase and the support exert a great influence on catalytic performances [2].

As an energy supplier, hydrogen seems to be one of the most promising fuels, especially when it is used to feed the proton exchange membrane fuel cells. When it is obtained from a renewable source, it has the potential to reduce the dependence for non-renewable fossil fuels and to lower the quantity of harmful emissions. The steam reforming reaction of ethanol is an interesting option in order to obtain a rich feed in hydrogen and methane with a low content of carbon monoxide. The thermodynamic analysis indicated that the most interesting mode of operation, for increasing the production of hydrogen and for minimizing the production of carbon monoxide and coke, needs lower pressures, high temperature and high water-ethanol ratio. On the other hand, despite its endothermic nature, the reforming reaction might take place at low temperatures, in order to increase the thermal efficiency.

Therefore, the most important requirement for the reforming catalysts is the potential to obtain high hydrogen yields and high selectivity for converting carbon to carbon oxides with minimum yields of residual hydrocarbons [3].

Our choice for the metallic phase was Palladium because is well known the behavior of the supported Pd catalysts that show promising catalytic performance for hydrogenation-dehydrogenation reactions and ethanol could be transformed into a series of valuable products [4-6].

Goula et al. [7] studied ethanol steam reforming for hydrogen production over a commercial alumina supported palladium catalyst. The authors concluded that the hydrogen

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selectivity was proportional to the water-ethanol ratio and ethanol was completely converted, even at relatively low temperature values.

In other paper, Yamaguchi et al. [8] claim that the high reactivity of Pd surfaces in C-H bond activation reflects their strong binding for C and H and this behavior was tested by steam reforming of methane.

Our study try to extend the actual level of knowledge by using a catalyst of Palladium supported on mesoporous silica (SBA-15), which is a class of materials discovered in Mobil labs in the early 1990's. So far, the mesoporous support SBA-15 has been studied only by Vizcaino et al. [9-11], but these researchers used Cu-Ni (modified with Cerium and Lanthanum) as metal phase. They reported good catalytic performance at temperature of 873 K. Also, Vizcaino [9] tried to improve the catalyst performances of Cu-Ni/SBA-15 catalyst adding magnesium and calcium. Unlike the previous studies, in this case, both the promoting effects of Mg and Ca lead to a better catalytic behavior of Cu-Ni/SBA-15 in the ethanol reforming improving hydrogen selectivity.

Ghita et al. [12] compared the performance of Pt/Al_2O_3 and Pt/SBA-15 in the ethanol steam reforming reaction. Pt/Al_2O_3 and Pt/SBA-15 are successfully prepared by impregnation method, and characterized by BET methods, SAXRD (small-angle X-ray diffraction), WAXRD (wide angle X-ray diffraction), XP Spectroscopy and TGA techniques. The authors concluded that platinum catalysts show high activity for the production of hydrogen by steam reforming of ethanol on Pt/Al_2O_3 catalyst. The catalyst development for steam reforming will focus on studying the performance of SBA-15 support for this type of reaction.

On the other hand, Lindo et al. [13] keeps only Nickel as metallic phase, inserting all Aluminum in the mesoporous support. The researchers have found that the incorporation of Al in mesoporous sieve structure is responsible for the formation of catalytic acid centers and this strong interaction between metallic Ni and Al-SBA-15 produces large quantities of ethylene and coke, with a much lower selectivity of hydrogen as compared with un-promoted catalyst. Thus, the best catalytic performance in terms of hydrogen selectivity and coke deposition for SRE (ethanol steam reforming) process were obtained on Ni/SBA-15 catalyst.

Our study evaluates a catalytic formula of Pd/SBA-15 for steam reforming of a raw material (bioethanol) with low content of ethanol (5-15%v/v) i.e. exactly that is obtained in alcoholic fermentation processes. Using bioethanol with low alcohol content is an economical way to transform a cheaper product in more valuable products as hydrogen and methane.

2. Experimental

2.1. Catalyst synthesis

The following chemicals were used in synthesis of Pd/SBA-15 catalyst: Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$), (Sigma Aldrich) with average molecular weight (M_n) of 5,800, -Brookfield viscosity of 350.000 cps (60^0C) and Tetra-Ethyl Ortho-Silicate (TEOS) (Aldrich purity > 99%) as the organic template and silica sources respectively. Palladium chloride (Fluka) was used as a metal precursor.

SBA-15 was prepared as described elsewhere [14]. Briefly, 2 g of triblock poly (ethylene oxide) – poly (propylene oxide) – poly (ethylene oxide) and 1.5 g of potassium chloride (KCl) was added to a mixture of 60 g of deionized water and 12 g HCl (~37%), and stirred for 6 hours. The 1.5 g of 1,3,5-trimethylbenzene (TMB) was added under stirring continuously for 10 h. To the end another 4.3 g of tetraethyl orthosilicate (TEOS) was slowly added. The gel mixture was transferred to Teflon bottles and aged at 100^0C for 24 h under static conditions. The resulting solid was filtered, washed with deionised water several times, dried at 60^0C, and finally calcined in air at 813 K for 10 h to remove the organic template. The Pd/SBA-15 catalyst was prepared by impregnation method using a solution of $PdCl_2$. The Pd content was 2 wt %. Finally, the catalyst sample was dried at 393 K for 8 h and calcined at 773 K for 6 h.

2.2.Characterization

The characterization of the catalyst was made by different techniques: X-ray diffraction (Small Angle XRD and Wide Angle XRD), Nitrogen adsorption/desorption and X-ray photoelectron spectroscopy.

In this case the X-ray diffraction analysis was performed on a Bruker Advance D8 diffractometer with CuKα radiation (40 mA, 40 kV) with λ=1.54 A with a scanning speed of 2 sec/step.

The X-ray photoelectron spectroscopy data were obtained on a thermo scientific K-alpha X-ray spectrometer with the following general characteristics: double-focusing hemispherical analyzer, multi-element, high transmission spectrometer input lens 250 mm Rowland circle monochromator, computer controlled monochromator alignment, maximum analysis area 60x60 mm, maximum sample height 20 mm, energy ranges 100 eV to 3eV.

Adsorption/desorption isotherms provides data for the characterization of porous structure and pore size, pore volume and isotherm type which characterizes a specific structure. Nitrogen physisorption data were obtained on a Quantachrome Autosorb Automated Gas Sorption system at 77 K, after out-gassing at 473 K under vacuum.

The morphology of the sample was examined using a scanning electron microscope Quanta.

2.3. Steam reforming experiments

The steam reforming reaction was carried out at atmospheric pressure in a fixed bed reactor made of a stainless steel tube. In each run of experiments 20 cm^3 catalysts were used and previous to the experiments, the catalyst was reduced in situ with hydrogen at 823 K for 6 h.

Water and ethanol were mixed resulting three types of raw material – with 5%, 10% and 15% ethanol respectively and fed into the reactor at different flows of 0.5 to 1.5 ml/min. The reaction temperature was established in the range of 300-500^{0}C.

The process performance was assessed by the conversion of ethanol and product distribution. The formula used to calculate the conversion of ethanol was:

$$x_{EtOH} = \frac{molesEtOH_{in} - molesEtOH_{out}}{moles\ EtOH_{in}} \times 100 \tag{1}$$

The liquid components in the outlet stream were collected and analyzed individually. On the other hand the gaseous components were fed to on-line gas chromatography Varian CP-3800 equipped with capillary columns and thermal conductivity detector (TCD) which allows us to detect and measure the concentration of H_2, CO, CO_2, CH_4, C_2H_4 and C_2H_6.

3. Results and discussion

3.1. Catalyst characterization

The small and wide angle of XRD patterns of Pd/SBA-15 synthesized by the impregnation method are shown in Figure 1. It is observed, that at small angle the sample exhibit one intense peak at almost 0.84^0 which correspond to 100 reflection plan. These XRD patterns underline the presence of a typical hexagonal structure of mesopores SBA-15. At wide diffraction angles, we notice the presence of a broad diffraction peak at 2θ ~ 23^0 ascribed to the amorphous framework of SBA-15 and three other peak assign to PdO species and Pd metallic.

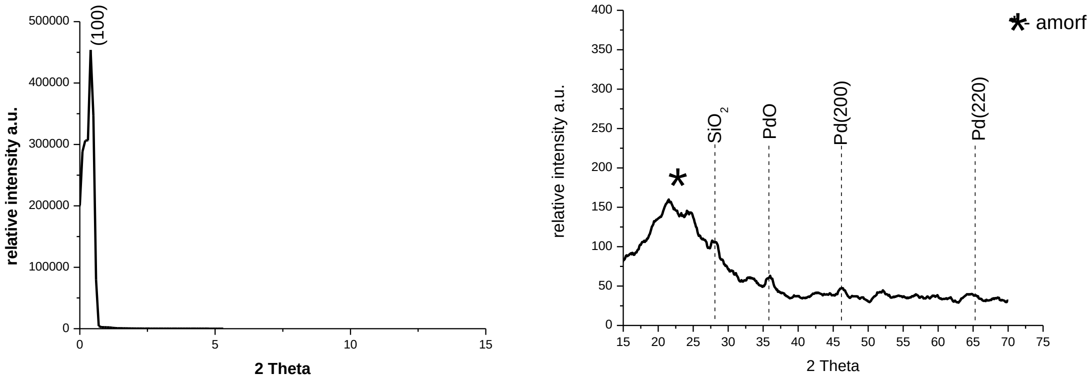


Fig. 1. SAXRD and WAXRD pattern of Pd/SBA-15 catalyst.

The adsorption-desorption isotherms for SBA-15 and Pd/SBA-15 catalyst are shown in Fig. 2. SBA-15 exhibited the type IV of isotherms with a regular type H1 hysteresis loop. The type IV of isotherm is maintained after Pd impregnation only the inflection of the adsorption branch of the isotherm occurred at a lower relative pressure, suggesting a decrease in the pore diameter.

Data obtained from N_2 adsorption isotherms (BET method) of SBA-15 gave us the possibility to calculate the pore diameter of 7.6 nm and a pore volume of 0.553 cm^3/g. Adsorption of palladium did not change the pore diameter but instead it was observed a reduction of BET surface from 750 m^2/g (SBA-15) to 608.92 m^2/g (Pd/SBA-15). This behavior is explained by the blockage of some small pores by Pd deposits.

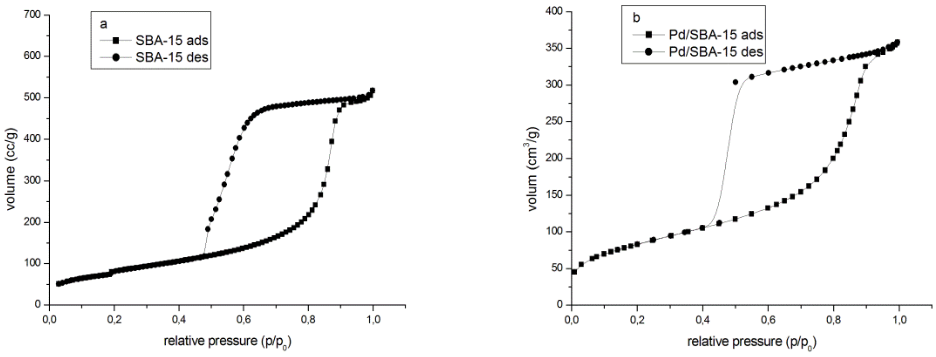


Fig. 2. N_2 adsorption-desorption isotherms for SBA-15 (a) and for Pd/SBA-15 (b) catalyst

According to the NIST XPS Database (http://srdata.nist.gov/xps/), the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ peaks binding energy at 343.70 eV and 338 eV respectively, are both associated with the Pd (II) species. All the species observed from XPS data are presented in table 1.

Table 1. Data from XPS results

Sample Survey Pd/SBA-15	O 1s		Si 2p		Cl 2p	
	BE (eV)	At%	BE (eV)	At%	BE (eV)	At%
	533.03	73.74	103.48	26.26	199.3	1.09

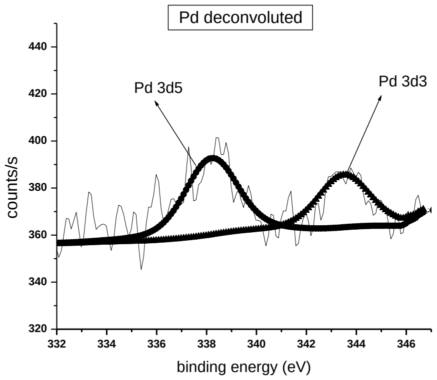


Fig. 3. Pd 3d deconvoluted XP spectra of Pd/SBA-15 catalyst.

Scanning electron microscopy (SEM) is used to determine the particle shape, particle morphology and particle size distribution of samples. The SEM micrographs of the mesoporous Pd/SBA-15 catalyst are shown in figure 4.

It is observed that SBA-15 possesses typical long-chain architecture, the pore structure is regular and highly ordered with a pore size of 5.9 nm.

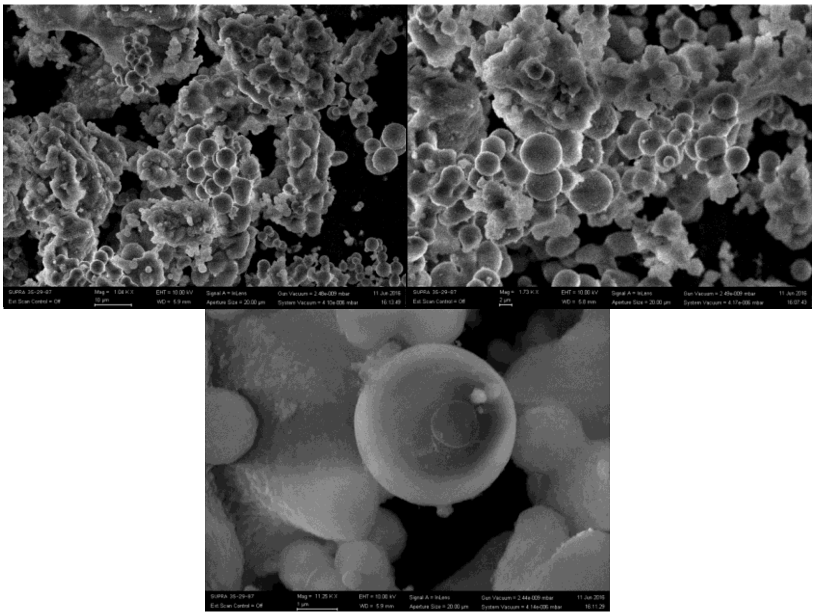


Fig.4. Scanning electron micrographs of the Pd/SBA-15

3.2. Steam reforming of bio-ethanol

The steam reforming of ethanol is a complex process where the main reaction (1) is competitive to other reactions, as following:

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (1)$$

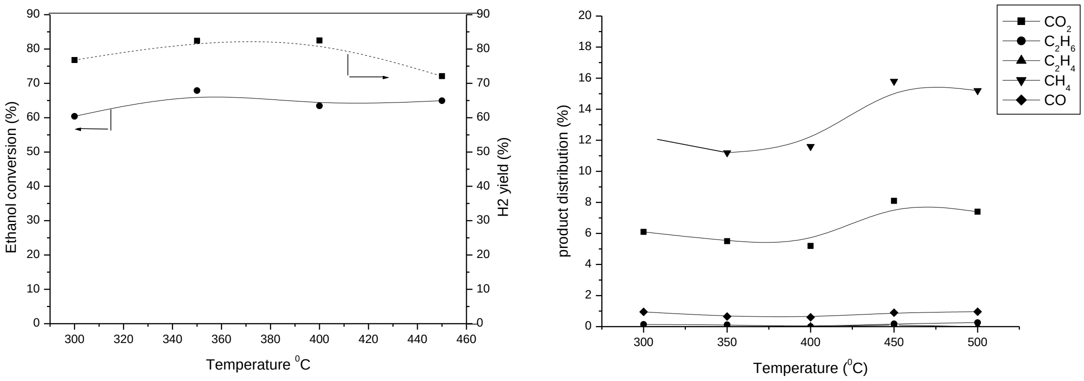
$$C_2H_5OH \rightarrow CH_4 + H_2 + CO \quad (2)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (3)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \quad (4)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (5)$$

One of the most interesting observations of our test is the range of temperature where this catalyst is active for steam reforming. Figure 5 presents the ethanol conversion, H_2 selectivity and product distribution obtained by the steam reforming of 5%v/v ethanol raw material at WHSV=3h^{-1}. It is easy to observe that in the range of 300-450^{0}C the catalyst is very active with a maximum of H_2 selectivity at 350^{0}C.



(a) *(b)*

Fig. 5. Effect of temperature on conversion and selectivity to hydrogen (a) and distribution of products (b)

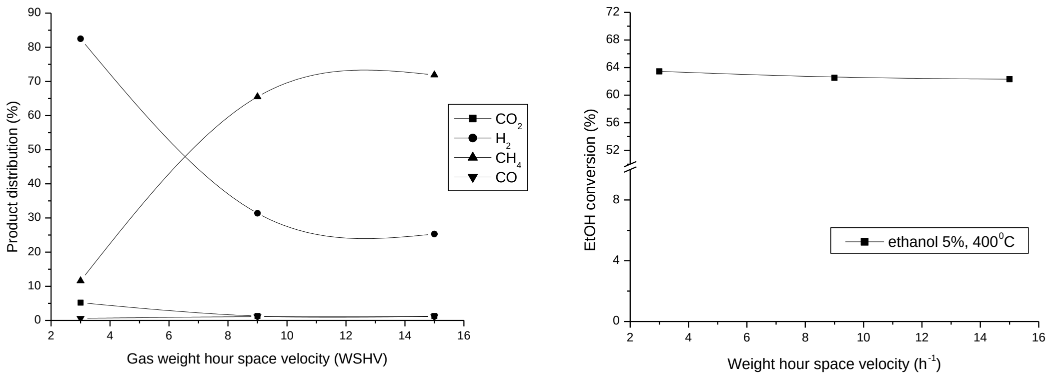
On the other hand, from figure 5b, the concentration of CO_2 and CH_4 has a similar trend, increasing with temperature while CO concentration remains almost constant. These variations show that the reforming reaction (1) and ethanol decomposition to methane (2) take place at lower temperatures while water gas shift reaction (3), ethanol dehydration to ethylene (4) and methanation (5) become important at higher temperature.

When temperature increases to 450^{0}C, the ethanol conversion remains at the same level but the selectivity of H_2 slightly decreases, meaning that hydrogen may be involved in secondary reactions as: $CO_2 + H_2 \rightarrow CO + H_2O$

Otherwise at high temperatures the process is highly selective to hydrogen production.

Other catalyst as Cu-Ni/SBA-15 [10] reported high hydrogen selectivities at temperature of 600^{0}C, but Cu-Ni/SBA-15 modified with Ca and Mg [9] reached 100% ethanol conversion and hydrogen selectivity around 80%. When is promoted with Ce and La the same catalyst, Cu-Ni/SBA-15 [11], made a lower hydrogen selectivity because CeO_2 promotes oxygen mobility which favors the water gas shift reaction against steam reforming. Similar results regarding hydrogen selectivity (65-73%) and ethanol conversion were obtained by [13] using a different catalyst: Ni/Al-SBA-15.

The influence of space velocity (WHSV) on the catalytic performances of the Pd/SBA-15 catalyst at 400^{0}C is presented in figure 6. From (a) it can see an important influence on H_2 and CH_4, while CO_2 and CO are not influenced by WHSV.



(a) *(b)*

Fig. 6. Effect of WHSV on product distribution (a) and ethanol conversion (b)

Also, the ethanol conversion is not influenced by WHSV as is shown in Fig. 6b.This behavior, regarding H_2 and CH_4, is very difficult to be explained, but is clear that they are in competition. A possible explanation could be the methanation reaction (5) where 1 mole of CH_4 is formed by the consumption of 3 moles of H_2. In this way, at very short time of reaction, the selectivity of CH_4 is higher than H_2 selectivity, but this ratio is changed when WHSV increases.

Fig. 7 shows the effect of ethanol content on hydrogen production. Higher ethanol content leads to higher hydrogen production at any temperature, but in this case a maximum of 15%v/v of alcohol can be obtained by alcohol fermentation of sweet fruits.

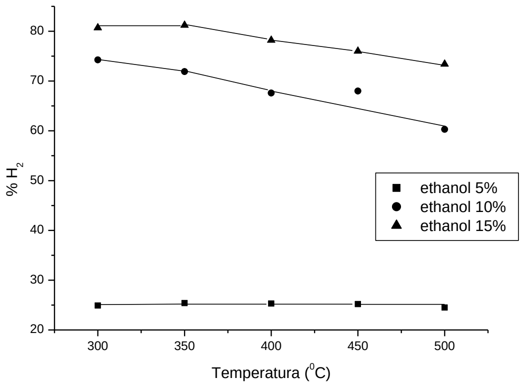


Fig. 7. Effect of ethanol content on production of hydrogen.

4. Conclusions

Our experimental study shows that Pd/SBA-15 catalyst is very active at lower temperatures (573-773 K), even if the steam reforming of alcohols occurs, normally, at temperatures over 850 K.

The results obtained are very useful for future researches because was demonstrated that hydrogen could be obtained by steam reforming of alcohols using Pd/SBA-15 catalyst with lower energy consumption. The best results were obtained at a temperature of 623 K, higher ethanol concentration (15%) and lower WHSV (3 h^{-1}).

Reforming of bioethanol provides a promising future way to produce hydrogen from renewable sources. Due to their porous structure and high surface area, mesoporous silica SBA-15 is in a continuously developing as catalytic support. This combination between palladium and SBA-15 assured synergy that was able to obtain more than 60% of ethanol conversion and 80% of hydrogen yield.

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