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BOOK OF ABSTRACTS

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Hydrogen Production by Steam Reforming of Ethanol over a Ru/Al_2O_3 Catalyst

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ABSTRACT

The present work aims the evaluation of a ruthenium catalyst supported on alumina (Ru/Al_2O_3) in the reforming of ethanol for the production of hydrogen. The selection of a suitable synthesis method, support and appropriate reagents proportions, play a major role in the catalyst performance within this reaction. Catalyst was synthesized by the incipient impregnation method from a solution of Ruthenium (III) chloride mono-hydrated to get a loading of 10% W, and deposited on α-alumina as support. The catalyst was characterized by: X-ray diffraction (XRD), surface area (BET), scanning electron microscopy (SEM) and a thermogravimetric analysis (TGA). The evaluation of the catalyst was carried out using a bench-scale fixed bed reactor system for the reforming of ethanol and reaction product compositions followed by gas chromatography. Preliminary results indicate that catalyst selectivity was highly dependent on reaction temperature, steam to ethanol ratio and space velocity for the production of a high content hydrogen gas product accompanied with low carbon deposition on the catalyst surface

Keywords: Etanol-Reforming, Ru/Al_2O_3-Catalyst, Hydrogen Production

1. INTRODUCTION

Hydrogen is an important raw material for today chemical and petroleum industry and can be considered a convenient and clean energy carrier, because energy produced from this gas generates water vapor as the only byproduct [1, 2], also hydrogen can be used to produce electricity with high efficiency through fuel cells. Among the main H_2 production processes are: steam reforming and partial oxidation of hydrocarbons, coal gasification and water electrolysis [3]. Due to the difficulties of hydrogen storage, distribution and transportation "on board" hydrogen generation from liquid fuels has become a priority need. Furthermore, the steam reforming of liquid hydrocarbons is considered the most appropriate route because of its mild operating conditions. Among the liquid hydrocarbon fuels that have been studied methanol and ethanol are the most promising candidates. Even though, research efforts in hydrogen production from methanol reforming have been extensive, there exist some disadvantages related to this raw material such as: high toxicity and the fact that its production is based mainly on fossil fuels. In contrast, ethanol can be produced at large scale from biomass and offers several advantages such as natural availability along with safe handling and storage [3]. Additionally, ethanol has the potential to achieve a high H_2 yield because according to the ethanol steam reforming (ESR) reaction (1)

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

six mols of hydrogen can be produced per mol of ethanol fed. Therefore, due to all the above mentioned features, ethanol has become the best raw material candidate for hydrogen production through the steam reforming of liquid hydrocarbons.

Besides, an optimal fuel cell performance requires a compact, clean and powerful source of hydrogen. Recently, RuO_2 nanoparticles were used as an efficient catalyst for oxidation reactions with good activity and selectivity [4, 5], In that study it was found that Ru nanoparticles supported on carbon nanotubes ($Ru \cdot xH_2O/CNT$) showed excellent performance for aerobic oxidation of alcohols

Therefore, it would be very attractive to find a suitable catalyst (non-susceptible to carbon formation) for the ethanol steam reforming reaction 1 to produce high purity hydrogen. Some expected advantages of this Ru based catalyst are in principle, that a smaller amount of CO would be formed as a byproduct, since reaction (1) is based in a complete oxidation of ethanol with steam. In contrast, the steam reforming of methane (SMS), produce a larger amount of CO because is based on the partial oxidation of methane.

$$CH_4 + H_2O \rightarrow CO + 3\ H_2 \quad (2)$$

followed by oxidation of CO through the water gas shift (WGS) reaction

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

Other potential advantages include: the production of a higher amount of hydrogen since six mols of H_2 are produced per mol of ethanol in the ESR, while only 3 mols H_2 are produced per mol of methane fed (SMR) and a lower reaction temperature of the ESR compared to the SMR, where potential energy savings are expected.

Therefore, the main objective of the present research is to synthesize, characterize and evaluate an alternate ethanol reforming catalyst to Ni/Al_2O_3 non susceptible for carbon formation based on Ru supported on α-Al_2O_3 for the production of hydrogen through the ethanol steam reforming reaction.

1. Experimental

1.1 Synthesis

A 10%W Ru-based reforming catalyst supported in α-Al_2O_3 was synthesized using the incipient impregnation technique. Precursors used were α-Al_2O_3, previously stabilized at 800°C for 4h, and a impregnating solution of Ruthenium (III) chloride mono-hydrated (J.T. Baker). After impregnation the catalyst was dried and calcined at 700°C for 4h.

1.2 Characterization

The crystalline structure was determined by X-ray diffraction (XRD) in a Phillips X'PertMPD with a Cu-Kα radiation source (1.5406Å); from 10 to 80º 2ɵ interval and using a 0.6º min^{-1} scanning step. BET surface area of the samples was determined by N_2 physisorption in an Autosorb 1 (Quantachrome Inc), while morphology and elemental analysis was examined in a JEOL JSM-5800LV scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS), respectively. Carbon content after reaction was determined through thermogravimetric analysis (TGA) using a TA Instruments Q500.

1.3 Ethanol Reforming Evaluation

The catalytic activity was evaluated in a stainless steel fixed-bed reactor (9.2 mm diameter) packed with a reforming catalyst (150g).

Before the reforming reaction evaluation tests a catalyst activation procedure was performed that consisted of a reduction with a stream of 20% H_2/N_2 for 2 h at 600°C. The catalytic evaluation was performed in a fixed-bed reaction system and this is presented in Figure 1.

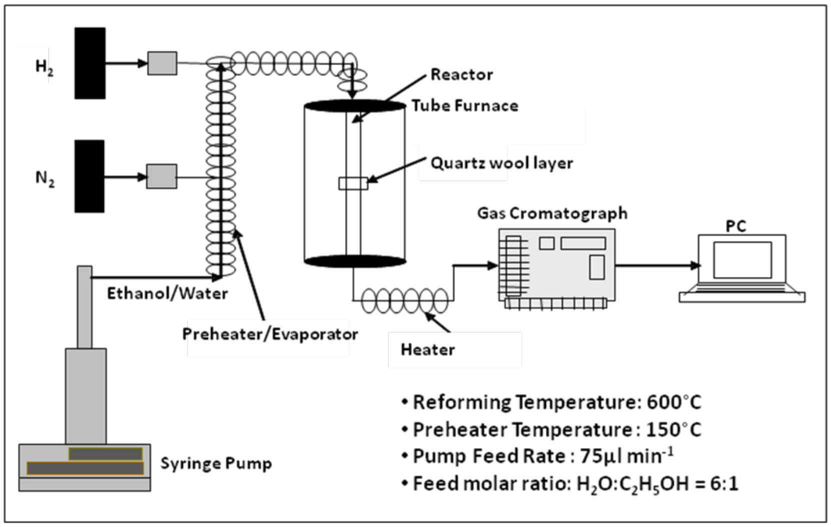

Figure 1. The fixed-bed reaction system for the AEER evaluation tests

The feed to this system composed of a mixture of water/ethanol in a H_2O/EtOH = 6/1 molar ratio, which was fed for a 100DX-Teledyne Isco syringe pump at a rate of 0.0075 ml/min and evaporated by several heating tapes (preheating section) kept at 150° C. This mixture was then carried with a stream of N_2 (7.5ml/min) to be introduced to the reactor. The reactor temperature was 600° at atmospheric pressure. Reactor product gas concentration was monitored using a gas chromatograph (GC, Perkin Elmer Instruments Clarus 500) equipped with TCD and FID and a Porapack Q column. An empty reactor test was performed in order to determine the homogeneous contribution to the reforming reaction caused by the thermal decomposition of ethanol at 600°C. Results indicated the presence of methane, carbon monoxide, carbon dioxide and acetaldehyde as the main product species, which agree with those reported in the literature [1].

The ethanol reforming reaction performance was evaluated in terms of the conversion (X_i) and selectivity (S_i) of the reactant gases (i), which was calculated through a transient system using the following equations:

$$S_{H_2} = \frac{F_{H_2 out}}{3\left(F_{EtOH\ in} - F_{EtOH\ out}\right) + \left(F_{H_2O\ in} - F_{H_2O\ out}\right)} \times 100 \quad (4)$$

$$S_i = \frac{c_i F_{i\ out}}{2\left(F_{EtOH\ in} - F_{EtOH\ out}\right)} \times 100 \quad (5)$$

$$X_{EtOH} = \frac{\left(F_{EtOH\ in} - F_{EtOH\ out}\right)}{F_{EtOH\ in}} \times 100 \quad (6)$$

where c_i is the number of carbon atoms of i and F_i is the molar flowrate of the gas i at the entrance (in) and at the exit of the reactor (out) [2, 5].

2. Results and discussion

*2.1 **BET Surface Area***

Figure BET surface area results from the support, catalyst and CO_2 absorbents are presented in Table 1.

Table 1. BET Surface Area Results

Material	Description	BET Surface Area (m^2/g)
α-Al_2O_3	Al_2O_3	205
RuAL	10 %wt Ru/Al_2O_3	175

The decrease in surface area observed for the catalyst (RuAL) from 175 m^2/g with respect to the support (α-Al_2O_3, 205 m^2/g) can be explained in terms of the combined effect of the impregnating metal obstructing certain amount of pores and to an increase of the particle size of the material caused to a prolonged exposure to the calcination temperature (700°C).

2.2 X-Ray Diffraction Results (XRD)

XRD analysis was performed before reforming reaction evaluation for the catalyst to determine its crystalline structure present the RuAl sample. Figure 2 shows the diffraction pattern of the catalyst (RuAL) calcined at 700°C.

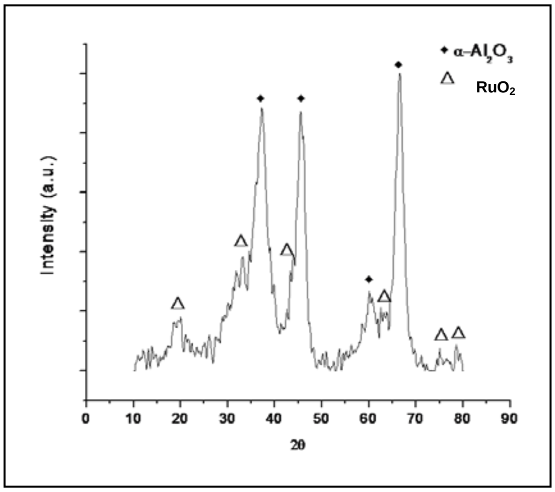

Figure 2. XRD Diffraction Pattern of the Fresh Catalyst Sample (RuAL)

In this Figure it can be observed that the corresponding signals for α-Al_2O_3 (2θ = 36°, 40°, 45°, 60° and 66°, JCPDS 00-016-0394) and RuO_2 (2θ = 37°, 43°, 63°, 75°, and 78°, JCPDS 21-1172) crystalline structures are present in the RuAL sample. It is important to note that the active phase of the catalyst (Ru) appears as RuO_2 because of the air atmosphere used during the calcination of this sample.

2.3 Scanning Electron Microscopy (SEM)

SEM images obtained for sample RuAL (catalyst) before and after reaction are presented in Figure 3 (a and b, respectively).

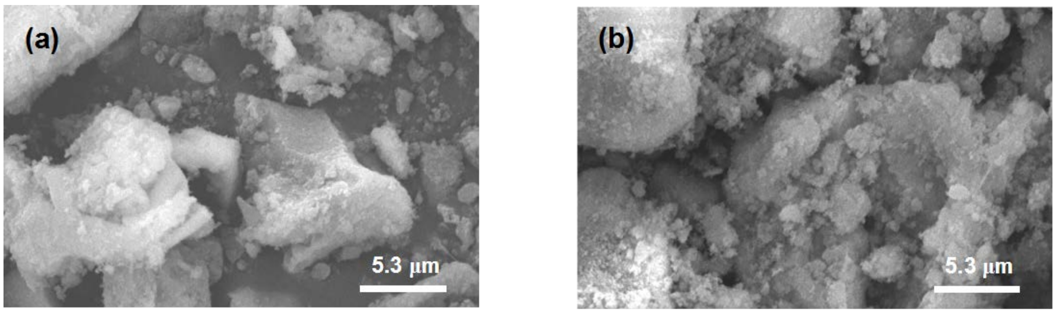

Figure 4. SEM images of RuAL (catalyst) before (a) and after reaction (b).

Morphology of the synthesized RuAL catalyst before reaction (Figure 4a) presented non-porous plain particles with sizes in the range from 5-30 µm, while this catalyst after reaction (Figure 4b) shows an increase in the amount of small particles accompanied with a rough surface, these two features can be attributed to the combined exposure of this material to high temperature and water vapor environment. With the aid of the EDS technique the Ru loading within the catalyst was estimated to be approximately of 10%W Ni, thus confirming that this material contains the desired active metal content.

2.4 Evaluation of the H_2 production through Ethanol Reforming Reaction

The activities for the catalyst and for the catalyst/absorbent mixtures were evaluated towards the hydrogen production according to ethanol reforming reaction in a fixed bed reaction system. According to experimental results, 100% ethanol conversion was reached for all tests. A summary of the reaction evaluation tests is presented in Table 2.

Table 2. Ethanol Reforming Reaction Evaluation Results

Material	X_{C2H5OH} (%)	S_{CH4} (%)	S_{CO} (%)	S_{CO2} (%)	S_{H2} (%)
RuAL	100	21	34	11	85

Results from Table 2 indicate that hydrogen selectivity for RuAL was 85% and this accompanied with a significant decrease in the generation of undesirable byproducts such as CH_4 and CO, which presented selectivities of 21 and 34%, respectively. Some authors [10] have reported that Al_2O_3 have presented catalytic properties when is used as a catalyst support, particularly in reactions such as the CO oxidation (equation 9) and the methane reforming (equation 7).

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \quad (7)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (8)$$

Therefore, the behavior exhibited by sample RuAL that presented a low CH_4 selectivity can be explained through the above reaction scheme: when the reforming reaction takes place this causes an increase of the hydrogen content and lowering the CH_4 concentration in the product gas through reaction (8).

3. Conclusions

Catalyst (10% Ru/Al_2O_3) was successfully synthesized to produce relative high purity hydrogen through the ethanol reforming reaction scheme. The synthesized Ru/Al_2O_3 catalyst presented a high BET surface area (175 m^2/g) and ethanol conversions of 100% and a hydrogen selectivity of 85%.

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REFERENCES

[1] Ni M., Leung D.Y.C. and Leung M.K.H., A review on reforming bio-ethanol for hydrogen production, Int. J. Hydrogen Energy 2007; 32:3238-3247.

[2] Sun J., Qiu X., Wu F., Zhu W., Wang W. and Hao S., Hydrogen from steam reforming of ethanol in low and middle temperature range for fuel cell application, Int. J. Hydrogen Energy 2004; 32**:**1075-1081.

[3] Deng X., Sun J., Yu S., Xi J., Zhu W. and Qiu X., Steam reforming of ethanol for hydrogen production over NiO/ZnO/ZrO_2 catalysts, Int. J Hydrogen Energy 2008; 33:1008-1013.

[4] Lysikov A., Trukhan N., Okunev A., Sorption enhanced hydrocarbons reforming for fuel cell powered generators, Int. J. Hydrogen Energy, 2008; 33: 3061-3066.

[5] Essaki K., Muramatsu T., Kato M., Effect of equilibrium-shift in the case of using lithium silicate pellets in ethanol steam reforming, Int. J. Hydrogen Energy, 2008; 33:6612-6618.

[6] Escobedo Bretado M. A., Delgado Vigil M. D., Salinas Gutierrez J. M., Lopez Ortiz A. and Collins-Martinez V., Hydrogen Production by the High Temperature Combination of the Water Gas Shift and CO_2 Absorption Reactions, J. New Mat. Electrochem. Systems, 2009; 12:23-28.

[7] Galetti A., Gómez M., Arrua L., Marchi A., Abello M., Study of CuCoZnAl oxide as catalyst for the hydrogen procuction from ethanol reforming., Catal. Comm. 2008; 9:1201-1208.

[8] Galetti A., Gomez M., Arrua L., Marchi A., Abello M., Hydrogen production by ethanol reforming over NiZnAl catalysts. Influence of Ce addition on carbon deposition, Applied Catal. 2008; 348:94-102.

[9] Alberton A. L., Souza M, Schmal M., Carbon formation and its influence on ethanol steam reforming over Ni/Al_2O_3 catalysts, Catal. Today 2007; 123:257-264.

[10] Bellido J., Assaf E., Nickel catalysts supported on ZrO_2, Y_2O_3-stabilized ZrO_2 and CaO-stabilized ZrO_2 for the steam reforming of ethanol: Effect of the support and nickel load., J. Power Sources 2008; 177:24-32.