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SYNTHESIS AND EVALUATION OF A TUBULAR CATALYTIC REACTOR FOR MICROPROPULSION APPLICATIONS

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Abstract. *The development of miniaturized satellites has been studied over the years but there are still many challenges along with it. In spacecraft propulsion system, small-scale combustion may lead to insufficient propellant decomposition resulting in flame quenching. However, reducing the propulsion system size is not the unique main concern. The use of a non toxic and stable propellant, like ethanol, is important. The objective of this present work is to develop a catalytic tubular reactor to be used as a combustion chamber of a microthruster fed with ethanol and air. Alumina tubes were washcoated and impregnated with nickel onto tubes walls. Morphology was made by Scanning Electron Microscopy (SEM). Outlet gases were analyzed in gas chromatography (GC) connected to the reactor outlet to quantify and qualify the combustion products. Images from SEM showed a washcoat thickness of 2.43 µm (± 0.64 µm). Number of immersions did not influence on washcoat thickness. However, each immersion had filled empty spaces between tube irregularities and washcoat layer as long as the tubes were immersed. Cracks on metal surface were formed due to over limit metal saturation. Accentuated increase in methane (CH_4) and hydrogen (H_2) molar fractions was related to catalytic ignition which had occurred between 450 and 475 °C.*

Keywords: *microreactor, washcoat, ethanol, nickel.*

1. INTRODUCTION

Miniaturization of satellites is a straightforward strategy to avoid high cost of launch and operation (Zakirov and Luming, 2005). Micro- and nano- satellites require low impulse bit and low thrust (order of mN to µN) (Shirsat and Gupta, 2013). However, technological barriers have to be faced to allow thrusters to be reliable, effective and low-cost. Small scale combustion may lead to flame quenching due to intensification of heat loss and radical losses onto the reactive walls (Huh and Kwon, 2014). This heat transfer occurs due to the increase of surface-to-volume ratio, making it difficult to sustain the combustion (Chao, *et al*., 2006).

Nevertheless, size and weight are not only the main concerns in a satellite design. In the last decade, most satellites have utilized hydrazine as a monopropellant in propulsion systems. Due to its high cost and toxicity, the interest in storable and nontoxic liquid propellants has been growing recently (Maia, *et al*., 2014). Ethanol (C_2H_5OH) has been selected to many studies as propellant because is appropriated to be stored as liquid into a small tank and has fewer adverse effects to human body if compared to other propellants (Matsushima, *et al.*, 2016).

To overcome those barriers, the use of catalyst has been studied, especially nickel (Ni) and noble metals like platinum (Pt) and palladium (Pd) supported on ceramic supports like alumina (Al_2O_3). Catalysts may form intermediate active complexes so that reactions can occur at a lower temperature, which might keep the reaction even without flame (Liu, *et al*., 2017; Jejurkar and Mishra, 2009).

This work aims at developing a catalytic tubular reactor as a combustion chamber of a microthruster fed with ethanol and air. Synthesis of the tubular reactor with Ni/Al_2O_3 coating was described. Then, products composition were measured as a function of ignition temperature.

2. EXPERIMENTAL PROCEDURE

Experimental procedure was divided into two steps. First, synthesis of the catalytic tubular reactor was carried out, followed by the analysis of products composition and ignition temperature.

2.1 Catalyst suported synthesis

Alumina tubes were used as support for the adhesion of the washcoat layer onto the tubular microreactor wall. The washcoat slurry was prepared with alumina particle size of 0.5 μm and the procedure was based on Agrafiotis and Tsetsekou (2000). Alumina tubes were dried at 110 ºC for 1h before washcoat layer application. Then, samples were immersed into washcoat slurry for 1 min, dried at 110 ºC for 1h30min and then calcined at 600 ºC for 2h. Table 1 shows washcoating conditions with the aid to evaluate the influence of alumina content and the number of immersions. Alumina content is directly related to the viscosity of the slurry (de Jong, 2009; Agrafiotis and Tsetsekou, 2000) whereas successive immersions might reach higher loading content (% wt) (Agrafiotis and Tsetsekou, 2000). Both parameters are important to find out an ideal condition to the thickness and dispersion of alumina coating.

Table 1. Washcoating conditions tested.

Tube	Alumina content (% wt)	Number of immersions
A	30	1
B	40	1
C	30	2
D	30	3

$Ni(NO_3)_2.6H_2O$ provided by Sigma-Aldrich was used as precursor of nickel. Coated tubes were impregnated by wet impregnation technique, filling the tubes with precursor solution for 18h. Then, samples were dried at 150 ºC for 12h and followed by calcination at 600 ºC for 2h. Morphology was made by Scanning Electron Microscopy (SEM).

2.2 Catalytic tubular reactor analysis

Figure 1 shows a schematic of the experimental apparatus used to evaluate the catalytic microreactor. All data was obtained from using a standard configuration: syringe pump, temperature controller connected to an electric resistance evolved onto alumina tubes (catalytic reactor), airflow meter and gas chromatography (GC). Outlet gases were analyzed in GC connected to the reactor outlet to quantify and qualify the combustion products.

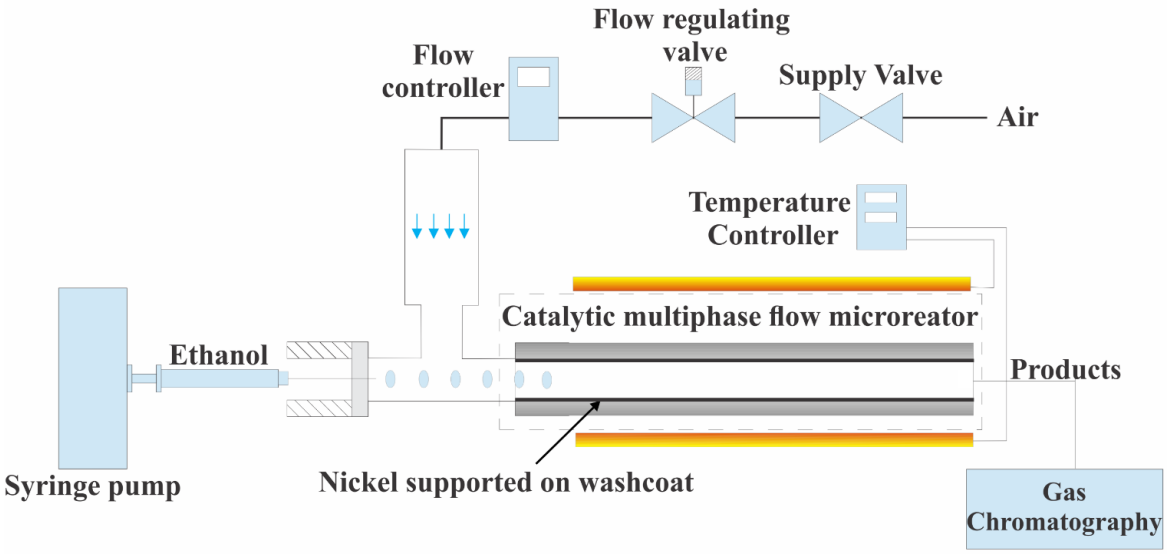

Figure 1. Schematic experimental apparatus.

Metal reduction was carried out before the catalytic reaction due to the metal oxide formed by calcination process (Laosiripojana, et al., 2007). Flow rate of 50 $cm^3.min^{-1}$ of 5% H_2/N_2 at 300 ºC for 1h was done to the reduction. Then, N_2 flow rate of 50 $cm^3.min^{-1}$ was applied for 20 minutes to guarantee the programmed temperature stabilization. Tests were performed varying temperature from 400 to 600 ºC in order to find out the ignition temperature. Sutton and Biblarz (2001) suggested a fuel-rich mixture containing a portion of low molecular mass reaction products. For this

reason, oxidant to fuel mass ratio (O/F_{real}) was defined as 8.24 after simulations on GASEQ software evaluating equilibrium constant and previous experimental tests. After the reaction, tubes were regenerated at 500 ^{o}C with airflow rate of 100 $cm^3.min^{-1}$ for 1h30min.

3. RESULTS AND DISCUSSION

3.1 Washcoated tubes characterization

Washcoat layer was examined in order to evaluate its thickness and morphology. Table 2 details the loading percentage of each tube obtained from the washcoating process, calculated from Eq. (1) where m_f is the mass after immersions and m_i is the initial mass. Slurry with 40% alumina content achieved higher loading content when compared with 30%. Agrafiotis and Tsetsekou (2000) observed that slurries of higher viscosity produced higher loading percentage. Besides, they affirmed that successive immersions achieved higher loading percentages as presented in Tab. 2. However, SEM images were analyzed to identify the relation between %wt and apparent dispersion on the surface.

Table 2. Weight percentage of each tube after the washcoating process.

Tube	%wt after 1st immersion	%wt after 2nd immersion	%wt after 3rd immersion
A	0.1130	-	-
B	0.2165	-	-
C	0.1202	0.4120	-
D	0.1223	0.3913	0.4158

$$\%wt = \frac{m_f - m_i}{m_i} \tag{1}$$

Figure 2 shows SEM images of tubes fragments immersed once into the 30% slurry concentration and Figure 3 shows images of tubes fragments immersed once into the 40%, both without nickel impregnation. Images from Fig. 2 shows smaller particles of alumina coating over the surface. Conversely, Fig.3 shows that only a part of the surface was coated by the alumina slurry. For this reason, apparent dispersion was better on 30% if compared with 40% slurry loading content. Pakdehi *et al.* (2015) related no difference in washcoat homogeneity of nanoparticles of Al_2O_3 with concentration up to 30% wt. However, slurry with concentration over 30% might cause cracks and become a nonhomogeneous surface.

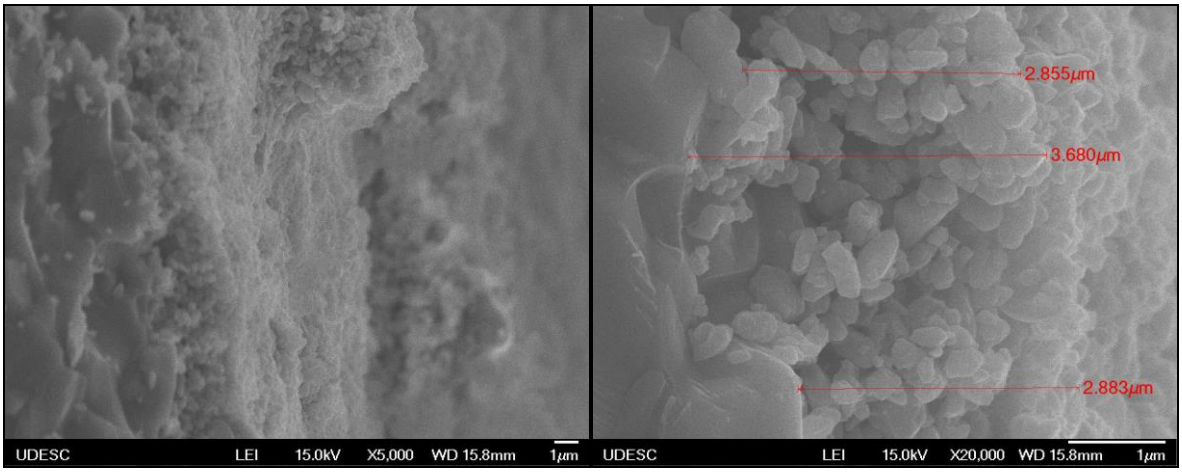

Figure 2. SEM images from the after one immersion into the 30% slurry concentration.

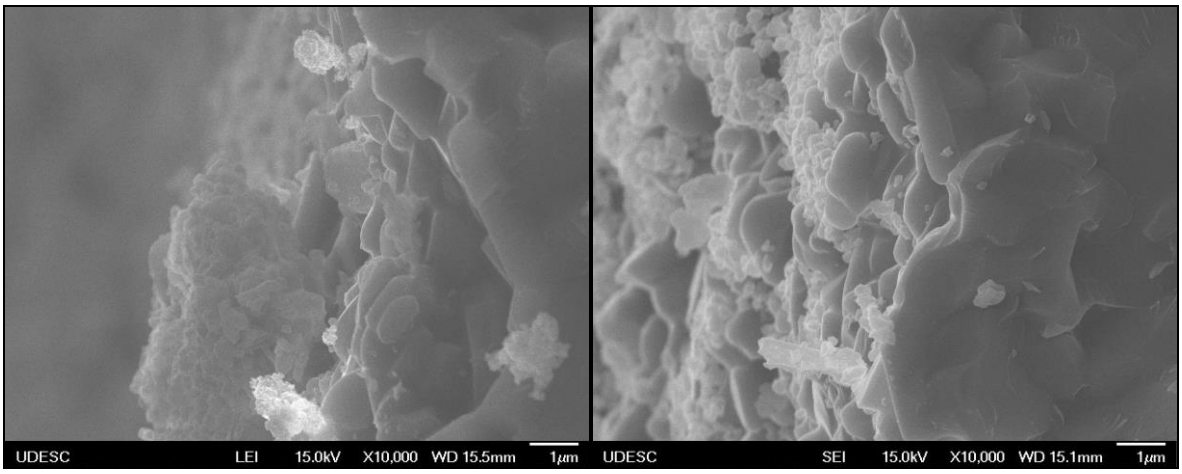

Figure 3. SEM images from the tubes after one immersion into the 40% slurry concentration.

Figure 4 presents SEM images from tubes fragments after 2nd immersion and Figure 5 shows SEM images from tubes fragments after 3rd immersion into slurry with 30% alumina content. Thickness average obtained was 2.43 µm with standard deviation of 0.64 µm. However, it was observed small variation of thickness despite weight percentage had increased between once and twice immersions. The interconnection between surface irregularities and slurry particles had filled some empty spaces. Agrafiotis and Tsetsekou (2000) related that washcoat layers adhesion depends on how good particles were deposited and interconnected. Besides, the slurry adhesion onto the support by mechanical mechanisms was defined as "anchoring".

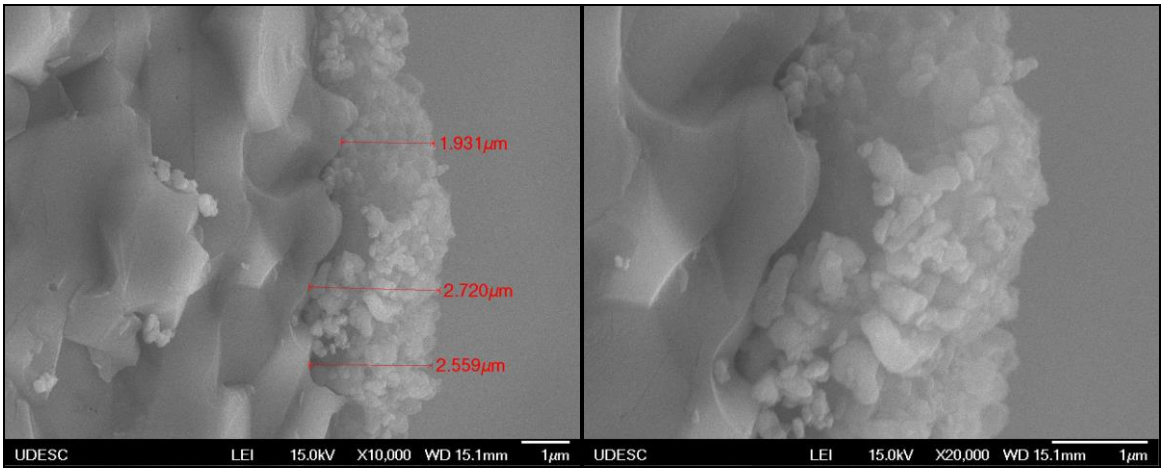

Figure 4. SEM images from tubes after two immersions into 30% slurry concentration.

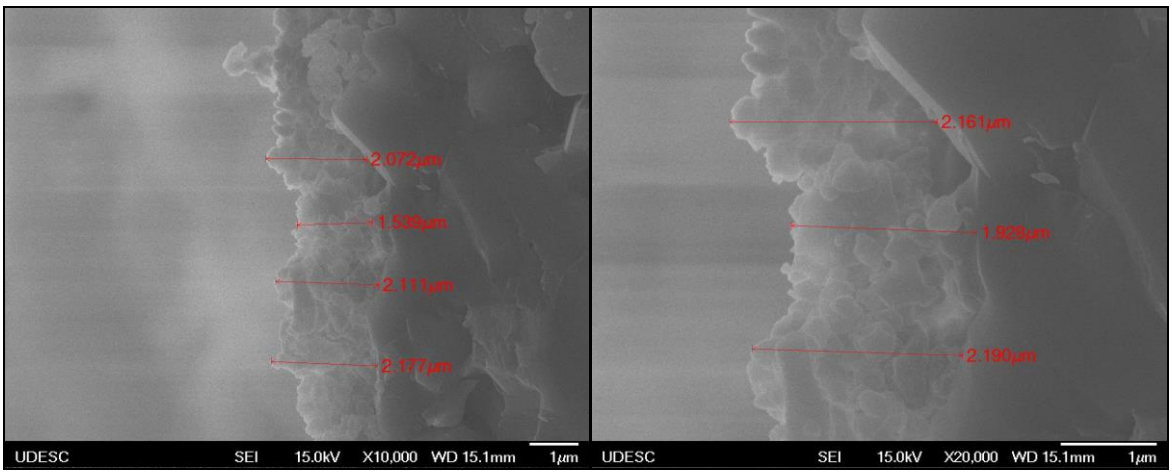

Figure 5. SEM images from tubes after three immersions into 30% slurry concentration.

Figure 6 shows SEM images from tubes immersed twice into 30% slurry concentration with nickel impregnated onto washcoat surface. It was not possible to identify the nickel dispersion onto washcoat surface due to the metallic film formed, but it could be possible to observe cracks on the surface due to metal oversaturation. Degenstein et al. (2006) explained that metal excess is presented as film over the surface with considerable cracked layers. In addition, difference between thermal expansion coefficient of film and substrate might result in that behavior (Ohring, 2002).

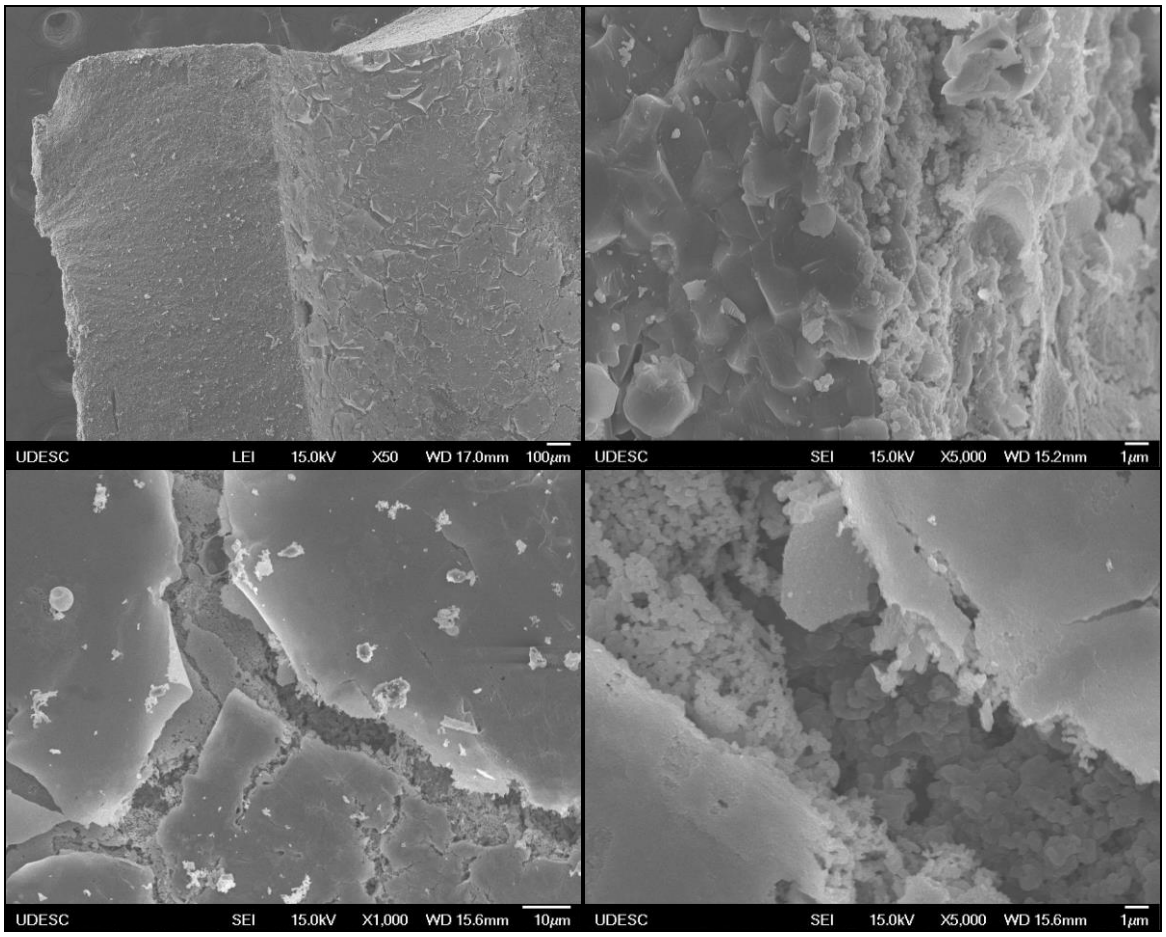

Figure 6. SEM images from tubes after two immersions into slurry with 30% alumina content with posterior nickel impregnation.

3.2 Performance of the catalytic tubular reactor

Catalytic performance of the tubular reactor was carried out in order to find out the ignition temperature of ethanol over nickel supported on alumina. Range temperature represents the operation temperature evaluated and it was determined based on Mukai et al. (2015). Figure 7 shows the majority product components obtained from the catalytic reaction whereas Fig. 8 represents minority product components. Acetone and ethene were not represented because their molar fraction were less than 1%. Water could not be detected in GC so it was estimated through hydrogen balance, considering all reminiscent hydrogen had converted to water. All tests were carried out duplicates and Fig. 7 and Fig. 8 represent the mean data with their standard deviation. Ethanal (C_2H_4O) was the main component until 500 ºC produced via ethanol dehydrogenation according to Eq. (2) and Fig. 7.

$$C_2H_5OH \rightarrow C_2H_4O + H_2 \qquad \Delta H^o_{298} = 46\ kJ.mol^{-1} \qquad (2)$$

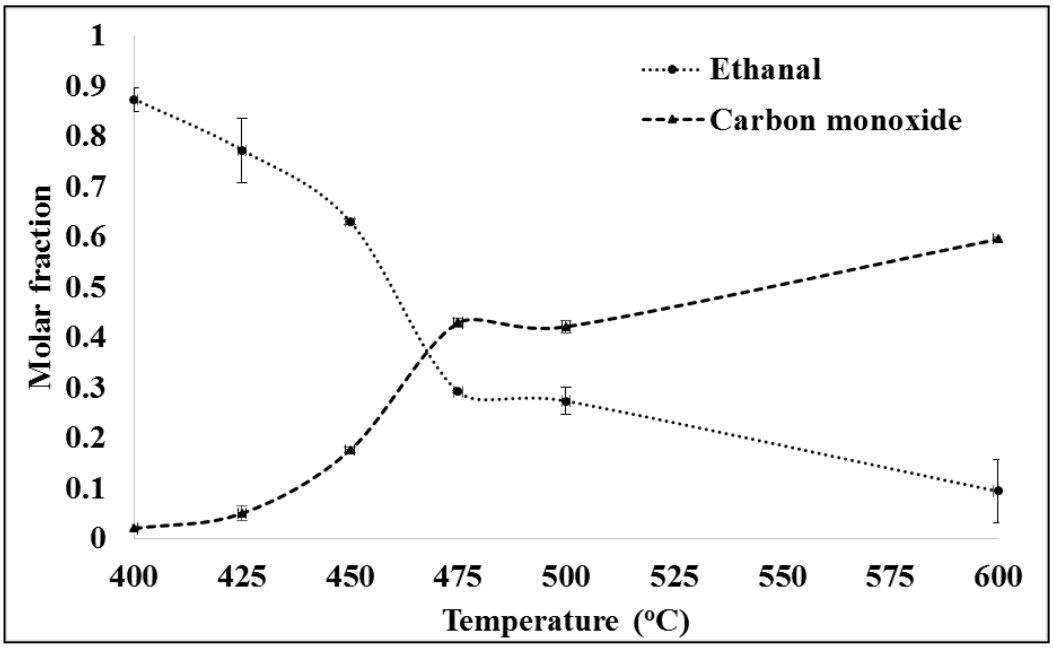

Figure 7. Majority product components from the catalytic reaction.

Figure 8 shows accentuated increase in methane (CH_4) and hydrogen (H_2) molar fractions related to catalytic ignition which had occurred between 450 and 475 ºC as described by Durão (2017). Fatsikostas and Verykios (2004) described that CH_4 and CO production was related to C_2H_4O decomposition as shown in Eq. (3). Besides, they found no nickel activity in methane partial oxidation below 450 ºC. Mukai et al. (2015) observed ignition occurred at 450 ºC, which was observed in this report as well. However, they suggest the addition of cobalt to Ni/Al_2O_3 catalyst to improve low temperature ignition.

$$C_2H_4O \rightarrow CO + CH_4 \qquad \Delta H^o_{298} = -132\ kJ.mol^{-1} \tag{3}$$

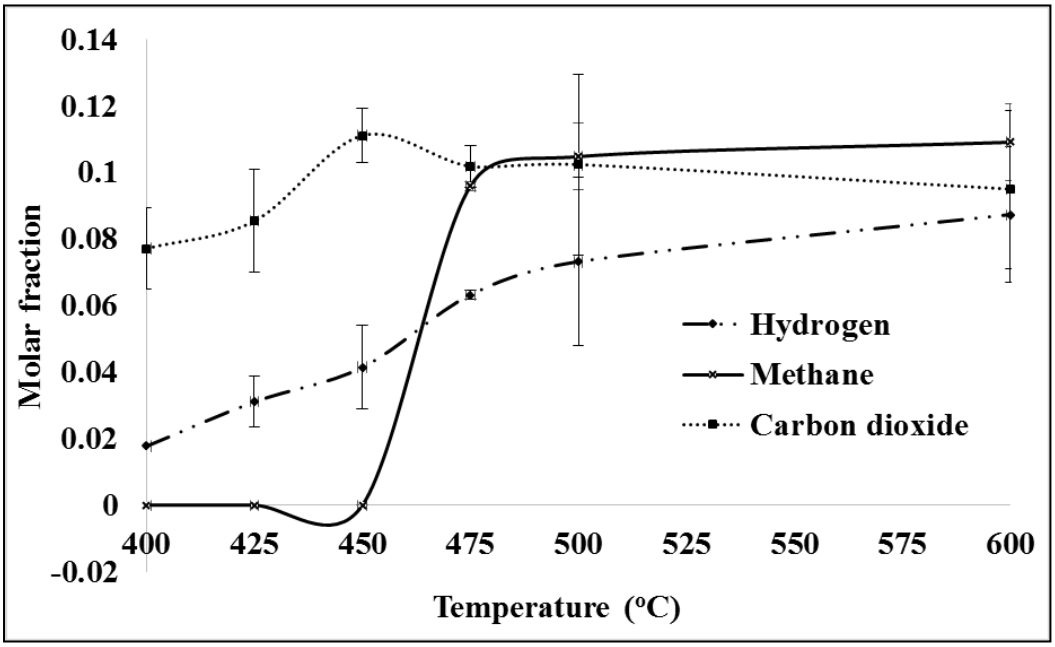

Figure 8. Minority product components from the catalytic reaction.

4. CONCLUSION

Wall-impregnated catalyst tubular reactor was fabricated and analyzed by SEM. Preliminary results from SEM showed a washcoat thickness of 2.43 µm (± 0.64 µm). Number of immersions did not influence on washcoat thickness.

However, each immersion had filled empty spaces between tube irregularities and washcoat layer as long as the tubes were immersed. Cracks on metal surface were formed due to over limit metal saturation. Accentuated increase in methane (CH_4) and hydrogen (H_2) molar fractions was related to catalytic ignition which had occurred between 450 and 475 ºC. High ignition temperature of Ni suggests that further studies should be carried out using platinum as catalyst or other noble metal.

5. ACKNOWLEDGEMENTS

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