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Steam reforming of phenol as biomass tar model compound over Ni/Al_2O_3 catalyst

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Abstract

Catalytic steam reforming of phenol over Ni/Al_2O_3 catalyst with 10 wt% of Ni loading was carried out in a fixed bed reactor. The effect of temperature (650-800 ºC), reaction time (20-80 min) and catalyst amount (0-2 g corresponding to 0-4.5g_{cat} h g_{phenol}^{-1}) on carbon conversion, H_2 potential and catalyst deactivation was studied. High efficiency of Ni/Al_2O_3 catalyst in steam reforming of phenol is observed at 750 ºC for a reaction time of 60 min when 1.5 g of catalyst (3.4 g_{cat} h g_{phenol}^{-1}) is used, with carbon conversion and H_2 potential being 81 and 59 %, respectively. An increase in temperature enhances phenol reforming reaction as well as coke gasification, minimizing its deposition over the catalyst. However, at high temperatures (800 ºC) an increase in Ni crystal size is observed indicating catalyst irreversible deactivation by sintering. As catalyst time on stream is increased the coke amount deposited over the catalyst increases, but no differences in Ni crystal size are observed. An increase in catalyst amount from 0 to 1.5 g increases H_2 potential, but no further improvement is observed above 1.5 g. It is not observed significant catalyst deactivation by coke deposition, with the coke amount deposited over the catalyst being lower than 5 % in all the runs.

Keywords: Ni/Al_2O_3 catalyst, biomass gasification, tar model compound, phenol, steam reforming

1. Introduction

Biomass is considered as a potential renewable energy source in order to decrease our current dependence on fossil fuels [1,2]. Its abundance, renewability, carbon-neutrality and low sulphur content make biomass especially interesting to replace fossil fuels as energy source [3,4]. Among the different technologies, gasification is a promising one in which biomass is converted into a syngas stream that can be combusted in an internal combustion engine for power generation or in a furnace for heat generation [5,6]. Besides, the syngas produced can be used as a raw material for production of fuels and chemicals by Fischer-Tropsch synthesis method [7].

The main drawback of biomass gasification process and its large scale implementation is the formation of unwanted byproducts together with syngas, such as particulates, alkali metals, fuel-bound nitrogen, sulphur, chlorine and tar [7,8]. These byproducts cause several problems in process equipment (corrosion, clogging…) as well as environmental pollution. Tar is a complex mixture of condensable hydrocarbons with molecular weight higher than benzene and its elimination has raised significant concern in literature [3,5,8-10]. The concentration and the composition of the tar in the gas stream produced in biomass gasification depend on the raw material, the operating conditions and the gasification technology used [11]. Tar lead to several operational problems in process equipment, such as metal corrosion, clogging filters and valves or condensing in cold spots plugging them. Besides, tar concentration limits the application of the produced syngas in internal combustion engines (<100 mg/Nm^3) as well as gas turbines (<5 mg/Nm^3) due to the clogging of pipelines and injectors in engines and turbines [8]. Furthermore, tar compounds make the produced gas useless for applications such as Fischer-Tropsch process for chemical production, in which tar presence leads to serious coke deposition over the catalyst.

Tar removal methods can be classified in primary and secondary methods, where the gas cleaning treatment is carried out inside or downstream the gasifier respectively [10,12]. Several technologies have been studied for a downstream tar removal, generally divided into physical methods, catalytic cracking or thermal treatment [8]. Among them, downstream catalytic steam reforming is widely studied in order to convert tar compounds into useful fuel gas, thus obtaining high purity gas and increasing fuel value. Natural minerals, such as natural calcite, olivine and dolomite [13-16], nickel based catalyst [11,17,18] or non-nickel metal catalyst [4] have been extensively studied in order to find a catalyst that is inexpensive, effective in tar reduction, resistant to deactivation and easily regenerated.

Tar model compounds are widely used in order to deeply study the catalyst performance and the process operating conditions. Toluene, benzene, naphthalene and phenol are usually identified as the principal biomass gasification tar model compounds [3] and they are the commonly chosen tar model compounds to study its steam reforming over supported metal catalysts [4,19-22]. Ni commercial steam reforming catalyst has been widely studied for biomass tar reforming [8,11], given that it allows obtaining high tar conversion and improving the quality of the syngas, since light hydrocarbons are also reformed and higher H_2 yields are obtained. Besides, several supports (Al_2O_3, SiO_2, ZrO_2, MgO, olivine…) [20,23-25] and promoters (CeO_2, Co, La…) [22,26] for Ni metal have been studied in the literature in order to improve the activity, stability, coking resistance and regenerability of the catalyst.

In this work phenol has been used as a model compound of biomass gasification tar, given that it is an oxygenated aromatic compound that is more refractory to reforming than non-aromatic compounds and causes faster deactivation than non-oxygenated compounds. Phenol steam reforming over Ni/Al_2O_3 catalyst has been studied in order to

optimize the experimental conditions (temperature, reaction time, catalyst amount) for maximizing the phenol conversion and minimizing the catalyst deactivation by coke deposition as well as sintering. This study has been conducted with the aim of optimizing operating conditions for a future detailed study of the steam reforming process in which different model compounds or catalysts will be assayed. It should be noted that steam reforming of phenol over Ni metal catalyst has also been studied in order to obtain information about bio-oil steam reforming considering phenol as bio-oil model compound [27,28].

2. Experimental

2.1. Catalyst preparation and characterization

A nickel alumina catalyst (Ni/Al_2O_3) with a nickel loading of 10 wt.% was prepared by a simple impregnation method, and tested in the catalytic steam reforming of phenol. Approximately 11 g of nickel nitrate hexahydrate ($Ni(NO_3)_2 \bullet 6H_2O$, Sigma-Aldrich) were dissolved in 20 ml of deionised water and mixed with approximately 20 g of aluminium oxide (γ-Al_2O_3, 96% Alfa Aesar). The precursor was stirred at 100 °C for around 30 minutes to ensure homogeneous mixture of components and promote water evaporation. Subsequently, the resulting semi-solid mixture was further dried overnight at 105 °C, and calcined at 750 °C with 20 °C min^{-1} heating rate in an air atmosphere for 3 hours. The resulting catalyst was crushed and sieved to obtain finer particles with a size in the 0.18-0.24 mm range. The prepared catalyst was not reduced, since during the process some of the pyrolysis gases, such as H_2 and CO, have the capability to reduce the catalyst itself [29].

The physical or structural properties of the catalyst (BET surface area, pore volume and pore size distribution) were measured using Micromeritics TriStar 3000. These

properties were determined by the adsorption-desorption of N_2 at -192 ºC. The experimental procedure consists in degassing the sample for approximately 8 h at 150 °C to remove all possible impurities, followed by adsorption-desorption of N_2. The surface area was calculated using the BET method and the average pore diameter was calculated using the BJH method, with the calculated values being 116.5 m^2/g and 24 Å, respectively.

X-Ray diffraction (XRD) analyses of the catalyst were carried out using Bruker D8 instrument with a CuKα radiation for a qualitative phase analysis (fresh catalyst) and crystal size determination (used catalyst). The samples were ground to less than 75 μm size and loaded into the 20 mm aperture of an aluminium sample holder. Concerning the fresh catalyst, 3 different phases corresponding to NiO, Al_2O_3 and $NiAl_2O_4$ have been identified. The determinations of Ni crystal size for used catalysts were carried out using Scherrer equation.

Temperature programmed oxidation (TPO) of used catalysts were carried out to determine the amount and nature of the coke deposited over the catalyst for which the thermogravimetric analyzer Shimadzu TGA-50 was used. About 20 mg of sample was heated in air atmosphere at 15 ºC min^{-1} to a final temperature of 800 ºC and maintained for 10 min at this temperature. Besides, high resolution scanning electron microscopy (SEM, Hitachi SU8230) was used to identify the nature of the coke deposited over the catalyst.

2.2. Experimental equipment and procedure

Figure 1 shows the experimental equipment used to study the steam reforming of phenol over Ni/Al_2O_3 catalyst with 10 wt% of Ni loading. Phenol was dissolved in water at a steam/carbon molar ratio of 13, and they were fed continuously by means of a syringe pump using a flow rate of 6.64 ml min^{-1}. The first furnace was maintained at 250 ºC to

evaporate the feedstock before entering the second reactor. Besides, 80 ml min^{-1} of nitrogen was fed to sweep the volatiles formed in the reactor. Both reactors were 16 cm length with an internal diameter of 2.2 cm and each was separately heated externally by an electrical furnace. The influence of the reforming reactor temperature was studied in the 650-800 ºC range, using 1 g of Ni/Al_2O_3 catalyst for a reaction time of 40 min. As aforementioned, the catalyst has not been reduced before use because H_2 and CO are present in the reaction medium and, as concluded in a previous work [30], they are capable of reducing the catalyst. Therefore, the effect of the reaction time (20-80 min) was studied to analyze the evolution of catalyst activity by using 1 g of Ni/Al_2O_3 at a reforming temperature of 750 ºC. Moreover, the influence of the catalyst amount on phenol conversion was analyzed in the 0-2 g range (corresponding to space-times in the 0-4.5 g_{cat} h g_{phenol}^{-1} range) at 750 ºC for 60 min.

Figure 1

The volatile stream formed goes to a condensation system which is formed by two condensers cooled with dry-ice. The non-condensable gases are collected in a 10 L Teldar™ gas sample bag. The gases are collected for 20 min subsequent to the end of each run to ensure that all the produced gases are collected. The gases collected in the gas sample bag were analysed off-line by gas chromatography. Hydrocarbon gases (from C_1 to C_4) were determined by a Varian 3380 chromatograph with a flame ionisation detector (GC/FID), 80-100 mesh Hysep column and using nitrogen as carrier gas. Permanent gases, i.e., CO, O_2, N_2 and H_2, were determined by a Varian 3380 chromatograph with a 60-80 mesh molecular sieve column and argon as carrier gas with a thermal conductivity detector, whereas CO_2 was analysed by another Varian 3380 GC provided with a Hysep 80-100 mesh column and using argon as carrier gas and a thermal conductivity detector.

The condensers were weighed before and after each run to measure the liquid amount obtained and N_2 was used as internal standard to calculate the gas yield. Each run was repeated at least twice to verify the reproducibility of the results and the mass balance closure was between 95-105 % in all the runs.

The overall reaction of catalytic steam reforming of phenol is defined as follows:

$$C_6H_6O + 11\ H_2O \rightarrow 6\ CO_2 + 14\ H_2 \qquad (1)$$

In order to analyze the effect of operating conditions on the steam reforming of phenol, carbon conversion and H_2 potential was defined. The carbon conversion was defined as the moles of carbon in the gaseous products divided by the moles of carbon fed and H_2 potential as percentage of the potential stoichiometric H_2 yield, where stoichiometic H_2 moles were calculated according to eq. 1.

$$\text{C conversion (\%)} = \frac{\text{moles of carbon in the product gas}}{\text{moles of carbon in the feed}} 100 \qquad (2)$$

$$\text{H}_2\text{ potential} = \frac{\text{moles of H}_2\text{ in the product gas}}{\text{moles of H}_2\text{ in stoichiometric potential}} 100 \qquad (3)$$

The yield of gas compounds was calculated as follows,

$$\text{Yield (\%)} = \frac{\text{g of the compound in the product gas}}{\text{g of phenol fed}} 100 \qquad (4)$$

3. Results

3.1. Effect of temperature

Figure 2 shows the effect of temperature on carbon conversion and H_2 potential obtained in the steam reforming of phenol over Ni/Al_2O_3 catalyst (1 g of catalyst corresponding to a space time of 2.25 g_{cat} h g_{phenol}^{-1}). It can be seen that temperature has

great influence on phenol reforming, increasing the carbon conversion from 8 % at 650 ºC to 57 % at 800 ºC. Likewise, H_2 potential increases as reforming temperature is increased, reaching a value of 47 % at 800 ºC. This increase in carbon conversion and H_2 potential can be attributed to the endothermic nature of oxygenated compound reforming reaction, which is enhanced as temperature is increased.

Figure 2

The same trend of carbon conversion and H_2 yield with temperature was observed in the literature on steam reforming of phenol over Ni/Al_2O_3 catalyst [28,31]. Wang et al. [28] studied the steam reforming of different bio-oil model compounds, in which phenol has been identified as the most refractory compound due to its stable structure with an aromatic ring.

Figure 3 displays the effect of temperature on the yield of the gas compounds. It can be seen that an increase in temperature increases the yield of all gas compounds due to the enhancement of reforming reaction, reaching a maximum CO_2, CO and H_2 yield at 800 ºC, 66, 55 and 14 wt%, respectively. Phenol steam reforming reaction on nickel surface is explained by two possible mechanisms [32], which are initiated with the dissociation of O-H followed by: i) a ring opening caused by C-H scission and C=C rupture in positions 2 and 6; ii) C-O bond dissociation followed by C-H and C=C rupture. Both decomposition mechanisms give way to H_2, CO and light hydrocarbon formation. The low values of light hydrocarbon yields obtained (lower than 1 wt% in all the temperature range studied) shows that its reforming is almost complete even at low temperatures. The low CH_4 yield obtained can be attributed to the absence of methyl group in the phenol structure.

Figure 3

Nevertheless, it can be observed that the ratio between CO and CO_2 is significantly changed as temperature is increased, showing that an increase in temperature increases the phenol reforming reaction and causes thermodynamic equilibrium displacement in the water gas shift exothermic reaction.

Figure 4 shows the temperature programmed oxidation (DTG-TPO) curves for the coke deposited over Ni/Al_2O_3 catalyst used in the steam reforming of phenol at different temperatures. Ni/Al_2O_3 catalyst deactivation by coke deposition has been widely studied in the literature [33,34] for which two types of coke have been identified: i) amorphous coke, which is burnt at low temperatures (around 450 ºC) since its combustion is activated by Ni metal on which the coke is deposited causing its encapsulation; ii) filamentous coke, which is not adsorbed over Ni sites and it is combusted at high temperatures (above 450 ºC).

Figure 4

The coke deposited over the catalyst used at 650 ºC (4.6 wt%) is combusted in a wide temperature range, between 350 and 600 ºC. Although a main peak at 480 ºC is observed, several shoulders can be observed at different temperatures (370, 410 and 460 ºC), which evidence the heterogeneous nature of the coke deposited. This heterogeneity reveals the existence of nascent coke (the shoulder at 370 ºC), which is formed by phenol condensation and adsorbed as phenate species over Ni sites [35] and its combustion is catalyzed by Ni metal sites. This coke evolves into more condensate structures by multilayer growing and it is separated progressively from Ni sites, requiring higher temperatures for its combustion.

Furthermore, the composition of the coke deposited in steam reforming depends on the operating conditions used (temperature, steam/carbon ratio and space-time) since coke deposition is a result of a balance between its formation and its elimination by

gasification [36]. Consequently, the coke deposited at 750 ºC is significantly affected by gasification, which is faster for the less condensed coke. Thus, at 750 ºC the coke amount deposited is lower (2.1 wt%) and more evolved, with the peak being moved at higher temperatures. Coke gasification rate is higher at 800 ºC, decreasing the amount of coke deposited until 1.1 wt%.

Figure 5 shows SEM images for the fresh (a) and used catalyst (at 650 (b), 750 (c) and 800 (d)). It can be seen that SEM imagines do not show the presence of high structured filamentous coke. It should be noted that the catalyst with the highest coke amount is that used at the lowest temperature, for which an amorphous coke deposited between catalyst particles is observed.

Figure 5

XRD analysis for the catalyst used in the reforming of phenol at 650 ºC, 750 ºC and 800 ºC have been carried out in order to study the influence of the reforming temperature on the Ni crystal size. The catalyst used at 650 ºC does not present a peak representative of Ni metal, indicating that 650 ºC is not high enough to reduce the catalyst. The catalyst used at 750 ºC presents a peak representative of the Ni metal with a crystal size of 45 Å. Likewise, for the catalyst used at 800 ºC a peak characteristic of Ni metal is observed with a crystal size of 72 Å, showing that reforming temperature causes catalyst irreversible deactivation by Ni metal sinterization.

3.2. Effect of time on stream

Figure 6 displays the effect of reaction time on carbon conversion and H_2 potential obtained in the catalytic reforming of phenol over Ni/Al_2O_3 catalyst at 750 ºC (1 g of catalyst corresponding to a space time of 2.25 g_{cat} h g_{phenol}^{-1}). It can be seen that an increase in time on stream until 60 min gives way to a linear increase in carbon

conversion, increasing from 35 % for 20 min to 56 % for 60 min. Above 60 min no change in carbon conversion is observed. As aforementioned, the catalyst is not reduced before use because H_2 and CO present in the reaction medium will reduce it [37]. It can be seen that an initial period of catalyst activation is necessary and the catalyst is reduced completely for the run carried out for 60 min, maintaining its activity above this reaction time. Similarly, H_2 potential increases as time on stream increased, reaching a maximum value of 39 % for the run carried out for 40 min and maintaining this value for longer reaction times.

Figure 6

Figure 7 shows the effect of reaction time in the catalytic reforming of phenol over Ni/Al_2O_3 catalyst at 750 ºC on the individual gas compounds yields obtained. It can be seen that an increase in reaction time until 40 min gives way to an increase in CO, CO_2 and H_2 yield (47, 58, 11 %) due to the enhancement of reforming reaction as the catalyst is reduced. An increase in reaction time from 40 to 60 min shows a significant increase in CO_2 yield (form 58 % to 73 %) and a slight increase in H_2 yield (form 11 % to 12 %). However, an increase in reaction time from 60 to 80 min gives way to a decrease in CO_2 (form 73 % to 63 %) and H_2 yield (form 12 % to 11 %), but an increase in the yield of CO (form 49 % to 57 %). The trend observed can be attributed to water gas shift reaction, which is enhanced when time on stream increases form 40 to 60 min due to the complete reduction of the catalyst and an increase in its activity. However, it seems that an increase in reaction time above 60 min reduces the catalyst activity for water gas shift reaction since coke deposition over the catalyst decrease its activity for this reaction.

Figure 7

DTG-TPO results for the Ni/Al_2O_3 catalyst used in phenol steam reforming at 750 ºC for different reaction times (Figure 8) show that the coke amount increases as reaction time is increased, from 2.1 % for 20 min to 3.8 % for 80 min. It can be seen that the coke deposited over all the catalysts studied is combusted between 350-600 ºC and they present a prevailing peak around 500 ºC. Nevertheless, the nature of the coke deposited over the catalyst is different depending on the reaction time. The catalyst used for 60 min presents a significant shoulder at low temperatures (400 ºC) and a main peak at intermediate temperatures (500 ºC). Although the coke amount does not increase significantly, an increase in reaction time until 80 min gives way to a higher degree of structuring of the carbonaceous material deposited, which decreases the shoulder at low temperatures (400 ºC) and increases the main peak at higher temperatures (500 ºC).

Figure 8

SEM analysis for the fresh (Figure 9a) and the catalyst used for different reaction times, 40 (Figure 9b), 60 (Figure 9c) and 80 min (Figure 9d), have been carried out in order to gain knowledge about the coke nature and position. Regarding the SEM images, no significant differences are observed for low times on stream due to the low coke amount deposited over the catalyst. However, for long reaction times (Figure 11d), an amorphous coke deposited is clearly observed over catalyst particles. XRD analysis has also been used to calculate the Ni crystal size and analyze the influence of the reaction time over catalyst deactivation by sintering. The catalysts used for 40, 60 and 80 min have been analyzed and no influence of reaction time over catalyst sinterization is observed, with the Ni crystal size being around 45 Å for all the catalysts studied. This evidences that there is no Ni particle dragging, which is consistent with the absence of filamentous coke.

Figure 9

3.3. Effect of catalyst amount

Figure 10 displays the effect of the catalyst amount used (0, 1, 1.5 and 2 g of catalyst corresponding to space times of 0, 2.25, 3.4 and 4.5 g_{cat} h g_{phenol}^{-1}) on carbon conversion and H_2 yield obtained at 750 ºC and for a reaction time of 60 min (a steam/carbon molar ratio of 13 and a flowrate of 6.64 ml min^{-1}). The run without catalyst was carried out using 1 g of sand. As observed, the catalyst used is highly efficient, given that it increases carbon conversion from 9 to 56 % and H_2 yield from 4 to 38 % when 1 g of catalyst is added. An increase in the catalyst amount used from 1 to 1.5 g leads to a significant increase in carbon conversion as well as H_2 potential, reaching values of 81 and 59 %, respectively. However, an increase in catalyst amount above 1.5 g does not show a notable influence in phenol reforming, maintaining carbon conversion and H_2 yield almost constant when catalyst amount is increased to 2 g. Wang et al. [28] obtained similar results studying the steam reforming of bio-oil model compounds over Ni/Al_2O_3 catalyst.

Figure 10

Figure 11 shows that an increase in catalyst amount from 0 to 1.5 g gives way to a increase in the yield of CO, CO_2 and H_2 from 10, 9.9 and 1.4 wt.% to 72, 111 and 17 wt.%, respectively. However, an increase in space-time above this value lead to an increase in the yield of CO_2 (118 wt.%) and a decrease in the yield of CO (68 wt.%), indicating that water gas shift reaction is favoured when a large amount of catalyst is used. Swierczynski et al. [38] have also seen the enhancement of water gas shift reaction when space-time is increased. They study toluene steam reforming over Ni/olivine catalyst at 800 and 650 ºC showing that an increase in space-time led to an increase in CO_2 selectivity and a decrease in CO selectivity.

Figure 11

Figure 12 displays TPO curves of the coke deposited over Ni/Al_2O_3 catalyst in the steam reforming of phenol when different amounts of catalyst are used at 750 ºC for 60 min. It can be observed that the amount of catalyst used does not affect significantly the nature of the coke deposited but it does the amount of coke deposited over the catalyst. All the TPO curves present a main peak at 500 ºC with a shoulder at 400 ºC which evidences that the coke deposited over the catalyst has a similar degree of graphitization and similar location over the catalyst. Furthermore, as the amount of catalyst (catalytic bed length) is increased, the amount of coke deposited on the catalyst decreases. Consequently, based on the evolution of phenol concentration with catalyst amount, the role of phenol should be noted as coke precursor by phenate species adsorbed as intermediates [35].

Figure 12

4. Conclusion

High carbon conversion and H_2 potential has been obtained in the steam reforming of phenol over Ni/Al_2O_3 catalyst, reaching a value of 81 and 59 %, respectively, at 750 ºC for a reaction time of 60 min and using 1.5 g of catalyst. The coke deposited over the catalyst is mainly of low degree of graphitization and its amount has been lower than 5 % in the whole operating range studied.

An increase in temperature gives way to an increase in carbon conversion and H_2 potential due to the enhancement of phenol reforming reaction. Besides, coke gasification rate increases as temperature is increased, and the amount of coke deposited over the catalyst significantly decreases (from 4.6 % to 1.1 %) when temperature is increased from 650 to 800 ºC. However, a high reforming temperature (800 ºC) causes an increase in Ni crystal size and, therefore, catalyst deactivation by sintering.

It is concluded that an initial period of NiO reduction is required to activate the catalyst. Thus, an increase in time on stream increases the carbon conversion and H_2 potential until 60 min of time on stream, from which the catalyst activity is maintained constant. Regarding coke deposition, an increase in time on stream influences the amount of coke deposited but also the nature of the coke, whose amount and graphitization degree is higher as reaction time increases.

The amount of the catalyst used has great influence on phenol steam reforming, with carbon conversion increasing linearly, as well as H_2 potential, with the amount of catalyst used. However, phenol conversion seems to have a ceiling value in the steam reforming, whereas a further enhancement of water gas shift reaction is observed.

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Figure captions

Figure 1. Experimental equipment used for steam reforming of phenol.

Figure 2. Effect of temperature on carbon conversion and H_2 potential (40 min; 1 g of catalyst).

Figure 3. Effect of temperature on gas compounds yield (40 min; 1 g of catalyst).

Figure 4. DTG-TPO curves of the coke deposited over the catalyst used at different temperatures (40 min; 1 g of catalyst).

Figure 5. SEM imagines of the fresh catalyst (a) and used catalyst at 650 (b), 750 (c) and 800 ºC (d) (40 min; 1 g of catalyst).

Figure 6. Effect of reaction time on carbon conversion and H_2 potential (750 ºC; 1 g of catalyst).

Figure 7. Effect of reaction time on gas compounds yield (750 ºC; 1 g of catalyst).

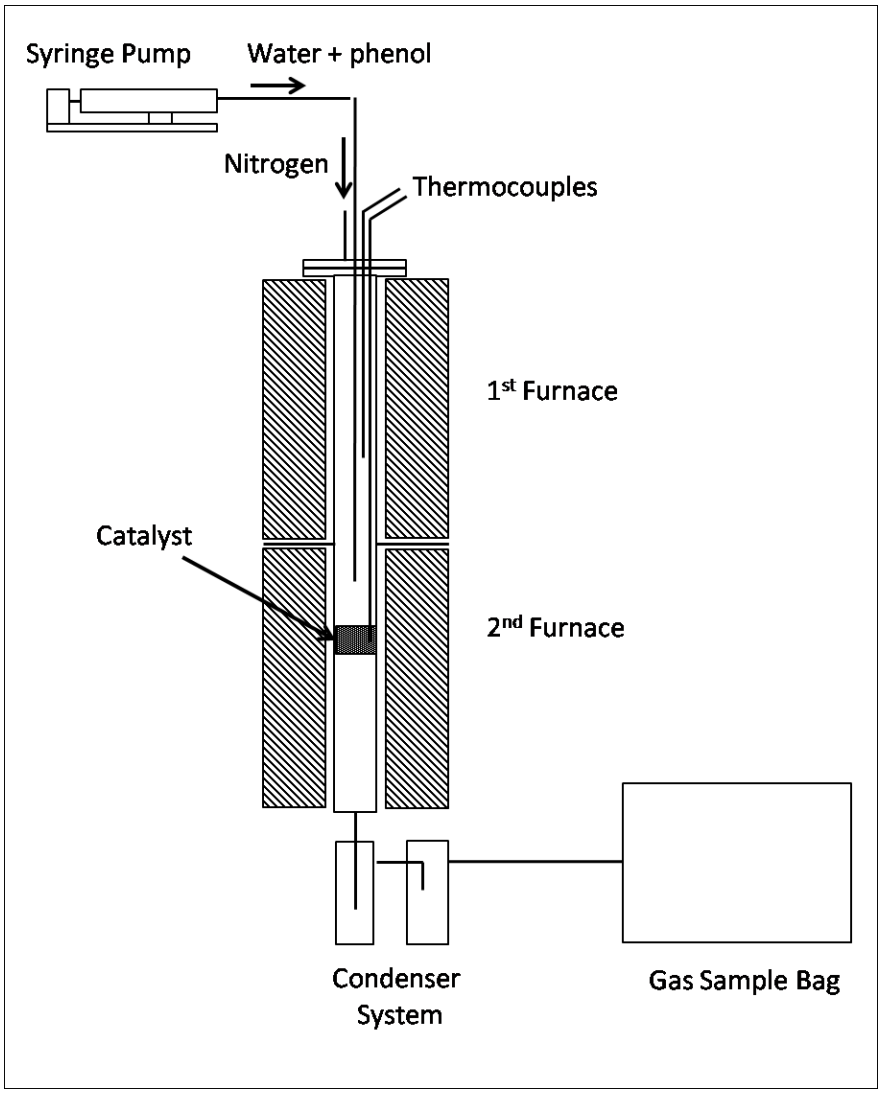
Figure 8. DTG-TPO curves of the coke deposited over the catalyst used for different reaction times (750 ºC; 1 g of catalyst).

Figure 9. SEM imagines of the fresh catalyst (a) and used catalyst for 40 (b), 60 (c) and 80 (d) min (750 ºC; 1 g of catalyst).

Figure 10. Effect of catalyst amount on carbon conversion and H_2 potential (750 ºC; 60 min).

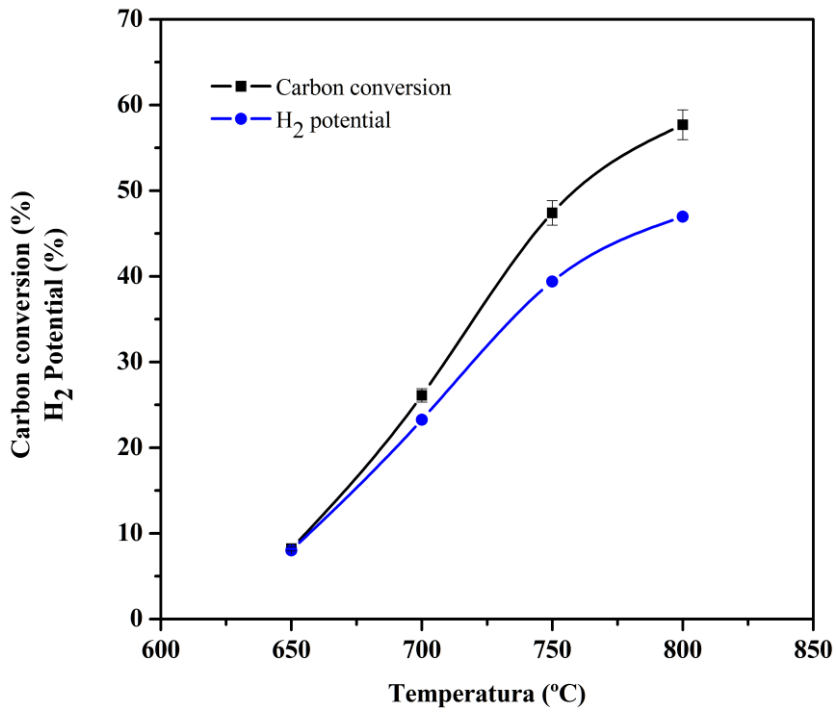
Figure 11. Effect of catalyst amount on gas compounds yield (750 ºC; 60 min).

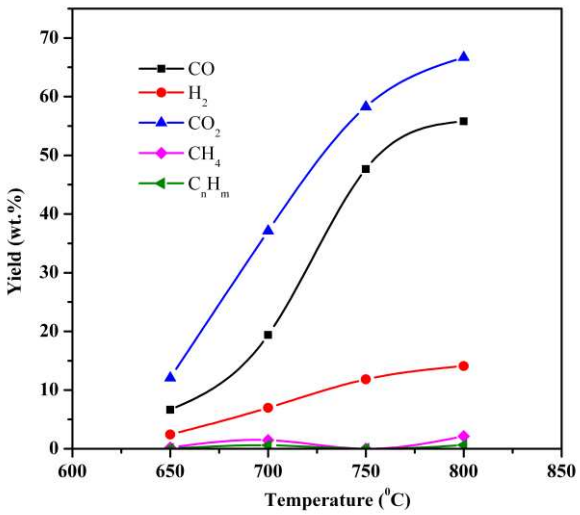
Figure 12. DTG-TPO curves of the coke deposited over the catalyst used for different catalyst amounts (750 ºC; 60 min).


Syringe Pump
Water + phenol
Nitrogen
Thermocouples
1st Furnace
Catalyst
2nd Furnace
Condenser System
Gas Sample Bag

491

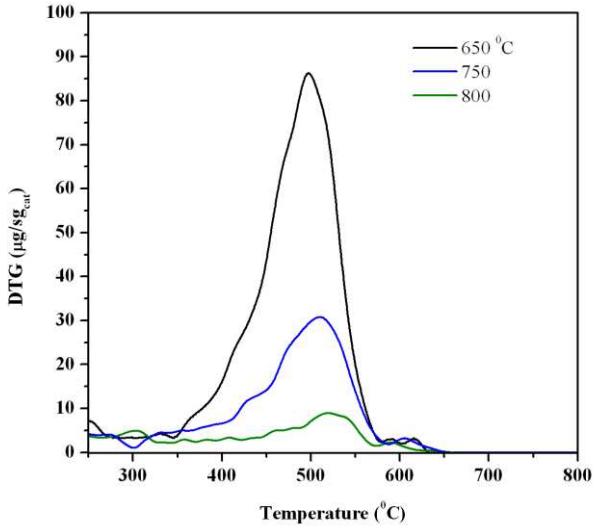
492


Carbon conversion
H2 potential
Carbon conversion (%)
H2 Potential (%)
Temperatura (ºC)
0
10
20
30
40
50
60
70
600
650
700
750
800
850


CO
H2
CO2
CH4
CnHm
Yield (wt.%)
Temperature (0C)
0
10
20
30
40
50
60
70
600
650
700
750
800
850

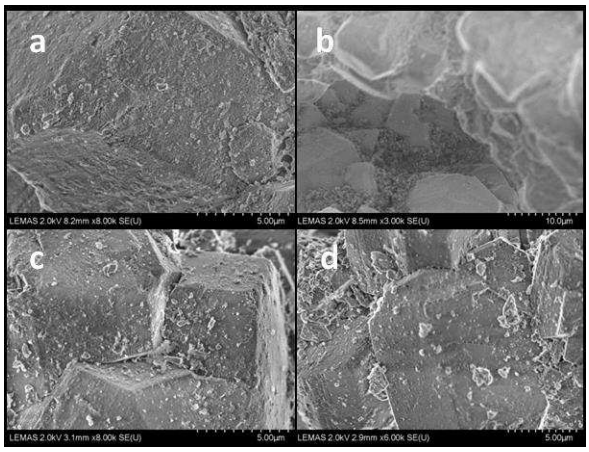
495

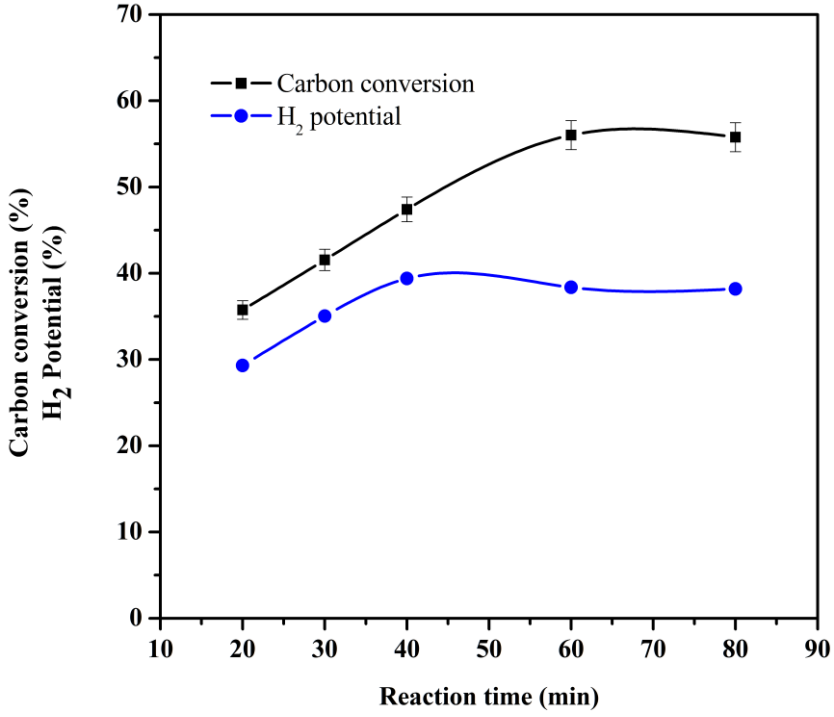
496


100
90
80
70
60
50
40
30
20
10
0
DTG (μg/sg$_{cat}$)
300
400
500
600
700
800
Temperature (^{0}C)
650 ^{0}C
750
800

497

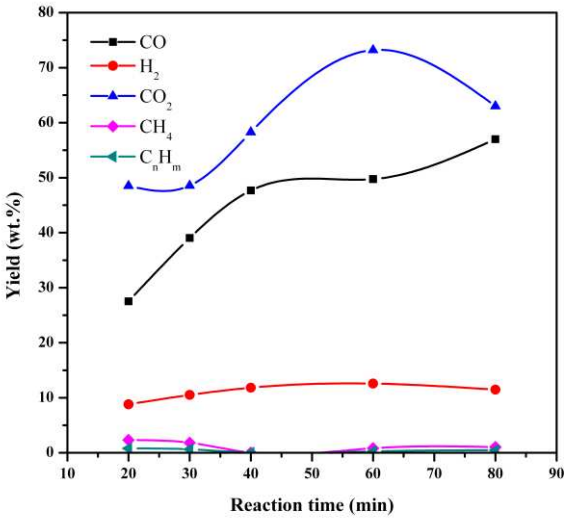
498


a
b
c
d
LEMAS 2.0kV 8.2mm x8.00k SE(U)
5.00µm
LEMAS 2.0kV 8.5mm x3.00k SE(U)
10.0µm
LEMAS 2.0kV 3.1mm x8.00k SE(U)
5.00µm
LEMAS 2.0kV 2.9mm x6.00k SE(U)
5.00µm


Carbon conversion
H2 potential
Carbon conversion (%)
H2 Potential (%)
Reaction time (min)
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90

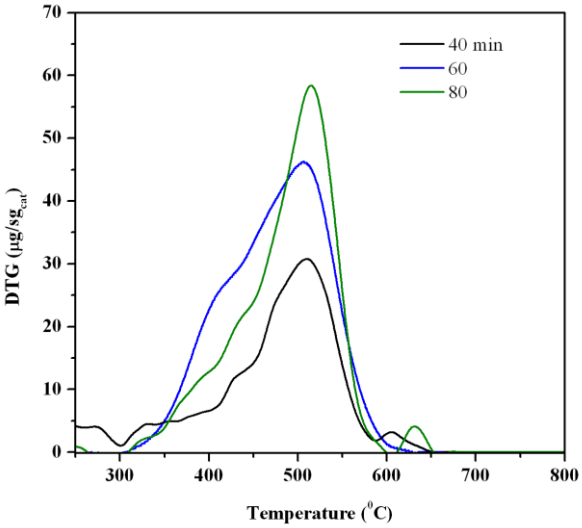
501

502


CO
H2
CO2
CH4
CnHm
Yield (wt.%)
Reaction time (min)
0
10
20
30
40
50
60
70
80
90

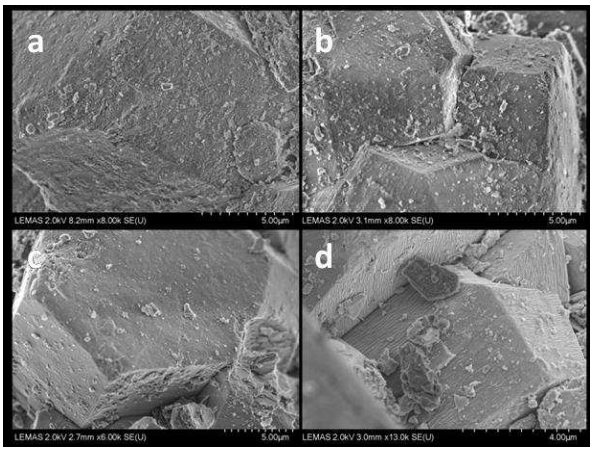
503

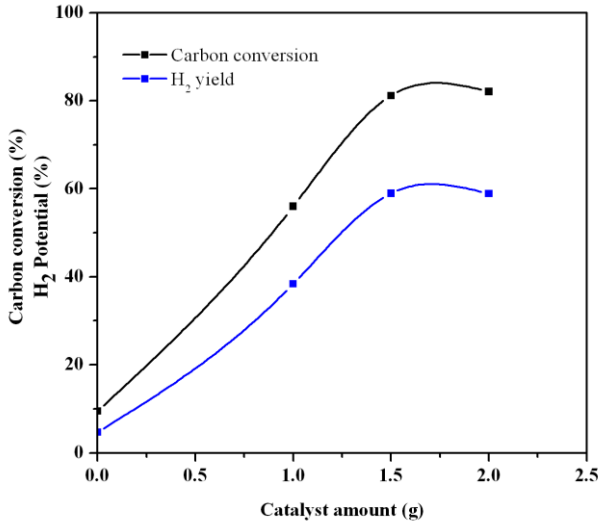
504

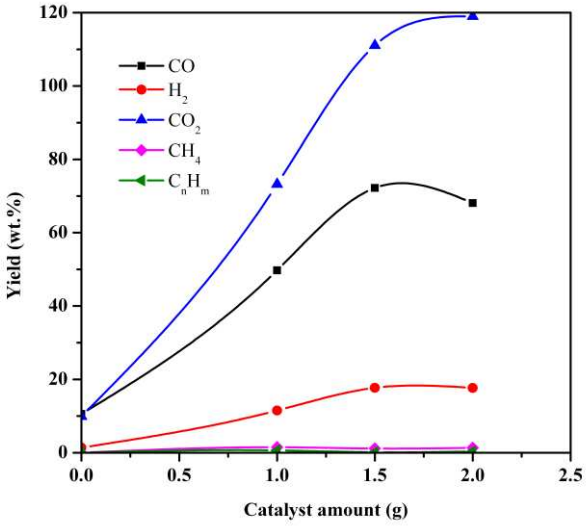

40 min
60
80
DTG (μg/sg$_{cat}$)
Temperature (^{0}C)
0
10
20
30
40
50
60
70
300
400
500
600
700
800

505

506

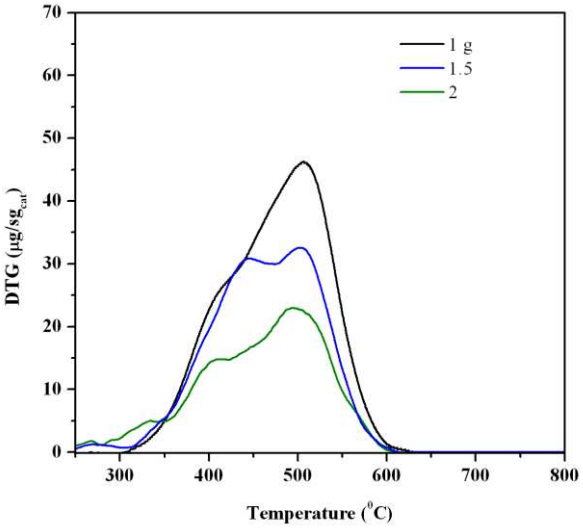

a
b
c
d
LEMAS 2.0kV 8.2mm x8.00k SE(U)
5.00µm
LEMAS 2.0kV 3.1mm x8.00k SE(U)
5.00µm
LEMAS 2.0kV 2.7mm x6.00k SE(U)
5.00µm
LEMAS 2.0kV 3.0mm x13.0k SE(U)
4.00µm


Carbon conversion
H2 yield
Carbon conversion (%)
H2 Potential (%)
Catalyst amount (g)
0
20
40
60
80
100
0.0
0.5
1.0
1.5
2.0
2.5


120
100
80
60
40
20
0
Yield (wt.%)
0.0
0.5
1.0
1.5
2.0
2.5
Catalyst amount (g)
CO
H2
CO2
CH4
CnHm

511

512


1 g
1.5
2
DTG (μg/sg$_{cat}$)
Temperature (^{0}C)
0
10
20
30
40
50
60
70
300
400
500
600
700
800

513

514

515