

Syngas from CO₂ Reforming of Coke Oven Gas: synergetic effect of activated carbon / Ni- γ -Al₂O₃ Catalyst

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Abstract

The CO₂ reforming of coke oven gas for the production of synthesis gas has been studied over an activated carbon, an in-lab prepared Ni/Al₂O₃ catalyst and physical mixtures of both materials in different proportions (AC+Ni) at 800 °C. It was found that there are two possible coexisting reaction pathways: the direct dry reforming of methane (decomposition of methane followed by gasification of the carbon deposits) and the reverse water gas shift reaction followed by the steam reforming of methane. If the process is carried out with the physical mixtures AC+Ni, there is a synergetic effect between both materials. The experimental conversions are higher than the conversions predicted by the law of mixtures, whereas the production of water is lower, resulting in a higher selectivity. The mixtures also showed a lower loss of porosity than when the activated carbon and the in-lab prepared Ni/Al₂O₃ were used individually. Therefore, the combination of these materials may produce catalysts that are more resistant to deactivation. The synthesis gas obtained was analyzed and it was found suitable for the production of methanol.

Keywords

CO₂ reforming; Coke oven gas; Synthesis gas; Activated carbon; Ni/Al₂O₃ catalyst

1. Introduction

The CO₂ reforming of methane (reaction 1), or dry reforming, has been shown to be a promising alternative to steam reforming in recent years [1-4]. This is mainly due to environmental factors, since in the CO₂ reforming two greenhouse gases (methane and carbon dioxide) are consumed, giving rise to synthesis gas, a raw material consisting mainly of H₂ and CO, which is widely used in the chemical industry [3; 5]. This process is also attractive because it produces a synthesis gas with a low H₂/CO ratio, suitable for the production of higher hydrocarbons and oxygenated derivatives [4].



The vast majority of the studies in this area have focused on the dry reforming of just methane alone, since it is the main component of natural gas, but there are other methane sources which could be adapted for this reaction. An interesting example is that of coke oven gas (COG) [6-9]. COG can be considered as a by-product of coking plants, which mainly consists of H₂ (~55-60 %), CH₄ (~23-27 %), CO (~5-8 %) and N₂ (~3-5 %) along with other hydrocarbons, H₂S and NH₃ in small proportions [6; 10]. COG is mostly used as fuel in the coking plant or in the associated steel industry, but sometimes it is produced in excess. This situation gives rise to environmental problems, in the form of greenhouse gases emissions [6; 11]. When this gas is upgraded via CO₂ reforming under stoichiometric conditions of methane and carbon dioxide, it is possible to obtain a syngas with a H₂/CO ratio close to 2, which is the ratio suitable for methanol synthesis [12]. This process can be considered as a partial recycling of carbon dioxide, since half of the carbon dioxide produced in the combustion of the methanol is consumed [6].

Research efforts have so far been focused on the development of catalysts suitable for the process, since the most important drawback of the dry reforming of methane is that there are no commercial catalysts able to resist deactivation caused by carbon deposition [1; 3; 13-15]. Almost all of the metals in Group VIII have been tested over different supports, resulting in catalysts with a good catalytic activity, although nickel has captured most attention on this matter [13-14; 16-17]. Nickel is more susceptible to deactivation by carbon deposits than noble metals, but its low cost and high availability

compensate for this drawback [13-14]. The support used also exerts great influence on the catalytic activity and deactivation of the catalyst, so different materials have been tested as Ni supports for the CO₂ reforming of methane, e.g. inorganic oxides or carbon materials [13-15]. Moreover, carbon materials, especially activated carbons, have been successfully used as catalysts in their own right in methane reforming, offering advantages such as low cost, a high mechanical resistance, a high surface area, the possibility of modifying pore size distribution, good reductive properties and the possibility of easily modifying surface chemistry [18-19]. In addition, some carbon materials can be heated by microwave energy, giving rise to hot spots (or microplasmas) which improve their catalytic activity [20-21]. Furthermore, it has been reported that mixtures of activated carbon with nickel-based catalysts can give rise to a synergetic effect in the dry reforming of methane [22]. In the case of COG, there are a few works which have studied the process using carbons or Ni/Al₂O₃ as catalyst [6-7; 9; 23].

The aim of the present work is to study the catalytic performance of different mixtures of an activated carbon and an in-lab prepared Ni/Al₂O₃ catalyst in the CO₂ reforming of coke oven gas, in an effort to determine whether the synergetic effect observed between both fractions in the CO₂ reforming of CH₄ also takes place when coke oven gas is used. Although this synergetic effect has been proved in the case of the dry reforming of methane [22], it has never been studied with COG. In this case, the presence in the feeding gases of two reaction products (H₂ and CO) may promote other reactions or change the conversions, having an effect on this synergetic effect. Thus, the influence of composition of COG has been studied. The possibility of using the resulting synthesis gas for the production of methanol has also been considered.

2. Experimental

2.1. Preparation and characterization of the Catalyst

A series of physical mixtures of grains (0.5-2 mm) of a commercial activated carbon FY5 (supplied by CPL Carbon Link) and cylindrical pellets (2 mm in diameter and 3 mm in height) of an in-lab prepared Ni/Al₂O₃ were used as catalyst. The catalysts composed exclusively of FY5 or exclusively of Ni/Al₂O₃ were labeled 100AC and

100Ni respectively, while the mixtures of both these materials were labeled as XXAC/YYNi, where XX and YY are the weight percentages of the activated carbon and Ni/Al₂O₃ respectively.

The main chemical characteristics of the activated carbon FY5 can be found elsewhere [15]. Proximate analysis (moisture, ash and volatile matter content) and elemental analysis (C, H, O, N, S) were carried out in a LECO TGA-601 thermo-balance and in a LECO CNHS-932 apparatus, respectively. The oxygen content was calculated by difference. Textural characterization was carried out by means of N₂ adsorption-desorption isotherms at -196 °C in the pressure range of 2·10⁻⁶–1 bar in a Micromeritics Tristar 3000. The Dubinin–Raduskevich method and BET equation were applied to the N₂ adsorption isotherms in order to determine the volume of micropores (V_{mic}) and BET surface area (S_{BET}), respectively. The total pore volume (V_t), i.e., the contribution of mesopores and micropores, was calculated from the quantity adsorbed at the saturation point of the N₂ adsorption-desorption isotherms, in accordance with the Gurvistsh rule .

The Ni/Al₂O₃ pellets were prepared in the lab as follows: a weighed amount of nickel nitrate was dissolved in distilled water and then the appropriate amount of γ Al₂O₃ (commercial pellets provided by Alfa Aesar GmbH & Co) was added and sonicated for 7 hours in an ultrasonic bath. The mixture was then dried overnight at 100 °C. Finally, it was reduced at 400 °C in a flow of H₂ for 2 hours. The Ni content of the catalyst was analyzed using an AA-6300 Shimadzu spectrometer, which showed the amount of Ni loaded to be 4.20 wt. %. The characterization of the Ni/Al₂O₃ has been described in detail in previous works of this group [22].

2.2. CO₂ reforming experiments

The CO₂ reforming experiments were conducted in a fixed-bed quartz tube reactor heated up by an electric furnace. The reaction temperature was monitored and controlled in the middle of the catalyst bed using a thermocouple.

The experiments were carried out in a gaseous stream composed of 54 % H₂, 23 % CH₄ and 23 % CO₂ (which will be referred to as gas ternary mixture, GTM). This mixture

maintains the H₂/CH₄ ratio of the COG and ensures the stoichiometric conditions of CH₄ and CO₂ for the dry reforming of the methane. The effect of the carbon monoxide present in the coke oven gas was also studied by adding it to the gas feed. This results in a mixture (which will be referred to as gas quaternary mixture, GQM) composed of 52 % H₂, 21 % CH₄, 21 % CO₂ and 6 % CO, which also maintains the H₂/CH₄/CO ratio of the coke oven gas and the stoichiometric conditions of CH₄ and CO₂ for the dry reforming of methane.

Tests were performed at atmospheric pressure, 800 °C and at two different volumetric hourly space velocities, VHSV (1.00 and 3.75 L g⁻¹ h⁻¹). Before the reaction, the system was drained with N₂ for 15 minutes at a flow rate of 60 mL/min under room temperature. Then it was heated up to the reaction temperature. Once at 800 °C, the N₂ flow was cut off and the reactant gases were introduced to start the reaction. A condenser was placed at the outlet of reactor in order to collect the water produced in the experiments. The gaseous products were analyzed in an Agilent Technologies 3000A micro gas chromatograph.

With the water recovered and the product gaseous stream compositions, the CH₄ and CO₂ conversions were calculated using an iterative method and closing the mass balances to within a ± 5 % margin of error. These parameters were calculated as follows:

$$\text{CH}_4 \text{ conversion, \%} = 100 \cdot (\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out}) / \text{CH}_4 \text{ in} \quad (\text{Eq. 1})$$

$$\text{CO}_2 \text{ conversion, \%} = 100 \cdot (\text{CO}_2 \text{ in} - \text{CO}_2 \text{ out}) / \text{CO}_2 \text{ in} \quad (\text{Eq. 2})$$

$$\text{H}_2 \text{ selectivity, \%} = 100 \cdot (\text{H}_2 \text{ out} - \text{H}_2 \text{ in}) / (2 \cdot (\text{CH}_4 \text{ in} - \text{CH}_4 \text{ out})) \quad (\text{Eq. 3})$$

where CH_{4 in}, CO_{2 in} and H_{2 in}, are moles of each gas at the inlet of the reactor and CH_{4 out}, CO_{2 out} and H_{2 out} are moles of each gas at the outlet.

3. Results and discussion

The results of the CO₂ reforming of GTM experiments conducted at 800 °C and a total VHSV of 1 L g⁻¹ h⁻¹ at 800 °C are shown in Figure 1.

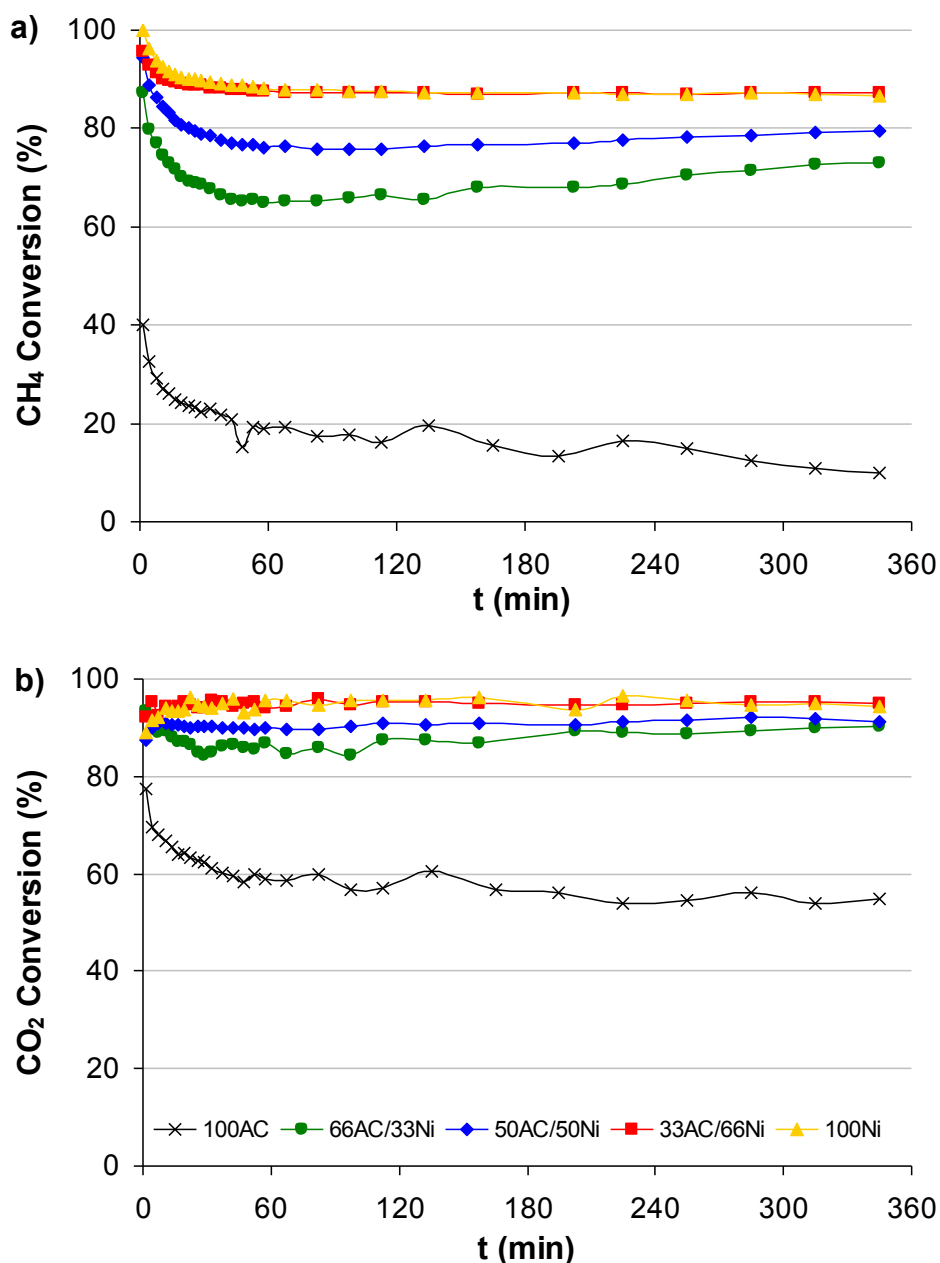


Figure 1. (a) CH₄ and (b) CO₂ conversions, in the CO₂ reforming of GTM with different mixtures used as catalysts (800 °C, CH₄/CO₂ = 1:1, 1 atm)

In all of the experiments, the conversion of methane initially achieved its highest values. Then, when the catalyst contained Ni/Al₂O₃, it quickly decreased for a period of

approximately 60 minutes. This behavior is the consequence the Ni/Al₂O₃ undergoing a reduction process. When the catalyst is heated up under a N₂ atmosphere, the Ni and the Al₂O₃ interact to give a spinel (NiAl₂O₄). Once the reaction begins, the spinel is reduced to Ni⁰ under the strongly reducing atmosphere of the reaction. This process, which yields very small Ni⁰ particles, has been described in detail in previous works [22].

After this, the 100Ni catalyst shows stable conversions (about 87 % for methane and 93 % for carbon dioxide) throughout the experiment while the conversions with the 100AC catalyst continuously decrease (from 25 % to 10 % in the case of methane and from 65 % to 55 % in the case of carbon dioxide). What is more, when the 100Ni catalyst is used, a small amount of water is produced (approximately 1 % vol. of the products) while with the 100AC catalyst a much higher amount of water remains in the condenser (approximately 10 % vol. of the products). The mechanism proposed to describe the dry reforming of methane is the decomposition of methane (reaction 2) to produce hydrogen and carbon deposits followed by the gasification of these deposits with carbon dioxide due to the Boudouard equilibrium (reaction 3).



However in the case of the CO₂ reforming of the coke oven gas, the presence of water after the experiments, suggests that a different mechanism is accompanying that of the dry reforming. This second probable mechanism is the reverse water gas shift reaction (RWGS, reaction 4) followed by steam reforming (reaction 5).



Finding the preferential mechanism is not straightforward, since the combination of so many different reactions makes this very difficult. Nevertheless, the smaller amount of water obtained when the 100Ni catalyst is used suggests that this catalyst is able to

transform, via steam reforming, almost all the water that is produced through the RWG, whereas the 100AC catalyst is unable to do this.

The mixtures show a different behavior. When the mixtures are used, the conversions seem to rise during the experiment, especially that of methane. This phenomenon appears to be more pronounced as the percentage of activated carbon present in the catalyst increases. This situation could be a consequence of the synergetic effect that these mixtures show in the dry reforming of methane [22]. This effect can be observed in the closeness of the conversions achieved by the mixtures to those of 100Ni. Even when the highest proportion of activated carbon is present in the catalyst, the conversions are closer to the conversions achieved with 100Ni than with 100AC. This phenomenon is especially accentuated in the case of the 33AC/67Ni catalyst. This catalyst reaches almost the same values as 100Ni for both methane and carbon dioxide conversions. The synergetic effect can be clearly observed in Figure 2. Here, the theoretical conversions predicted by the law of mixtures (continuous line) are plotted against the experimental conversions (squares) after 6 hours of reaction. As can be seen, the experimental conversions achieved with the mixtures are much better than the theoretically predicted ones. This means that the loss of catalytic activity due to the replacement of the Ni catalyst (much more active than the activated carbon) by the activated carbon is not as great as one would have expected. This synergetic effect has interesting economic implications in this kind of processes, since the replacement of part of the expensive catalyst (Ni/Al₂O₃) by a cheaper material (activated carbon or other carbon materials) while at the same time achieving almost the same conversions could lead to lower process costs.

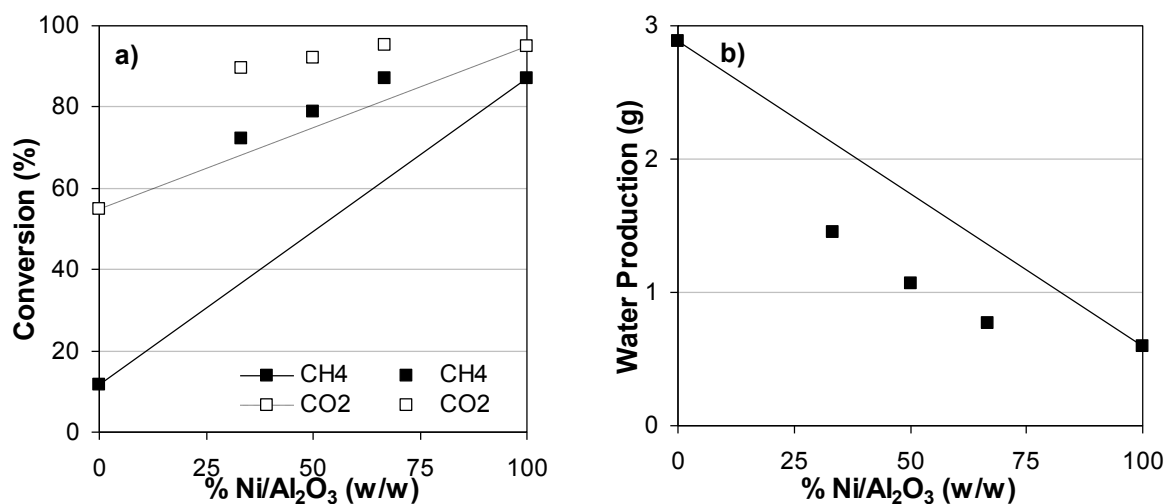


Figure 2. Comparison of the results predicted by the law of mixtures (continuous line) with those achieved in the experiments (squares) for the: (a) conversions of CH₄ and CO₂; and (b) water production, after 6 hours of reaction in the CO₂ reforming of GTM.

If the same analysis is applied to the production of water, it can be seen that the synergetic effect not only affects the direct dry reforming mechanism [22], but also the alternative mechanism, i.e., the RWGS followed by steam reforming. Figure 2 shows the amount of water collected in the condenser after 6 hours of reaction with the different catalysts. The continuous line represents the predicted amount of water by the law of mixtures and the squares the experimental results. As can be seen, when the mixtures are used, the amount of water produced is less than the theoretically predicted amount. This could mean either that less water is produced through the RWGS or that more water reacts through the steam reforming reaction. Either way, the most important conclusion from this is that the mixtures are able to increase the conversions and decrease the formation of byproducts such as water.

In order to study the presence of this synergetic effect with higher flows and its long term persistence, a series of experiments was carried out at 800 °C and at 3.75 L g⁻¹ h⁻¹ of VHSV for 50 hours with the same catalysts. The results are shown in Figure 3.

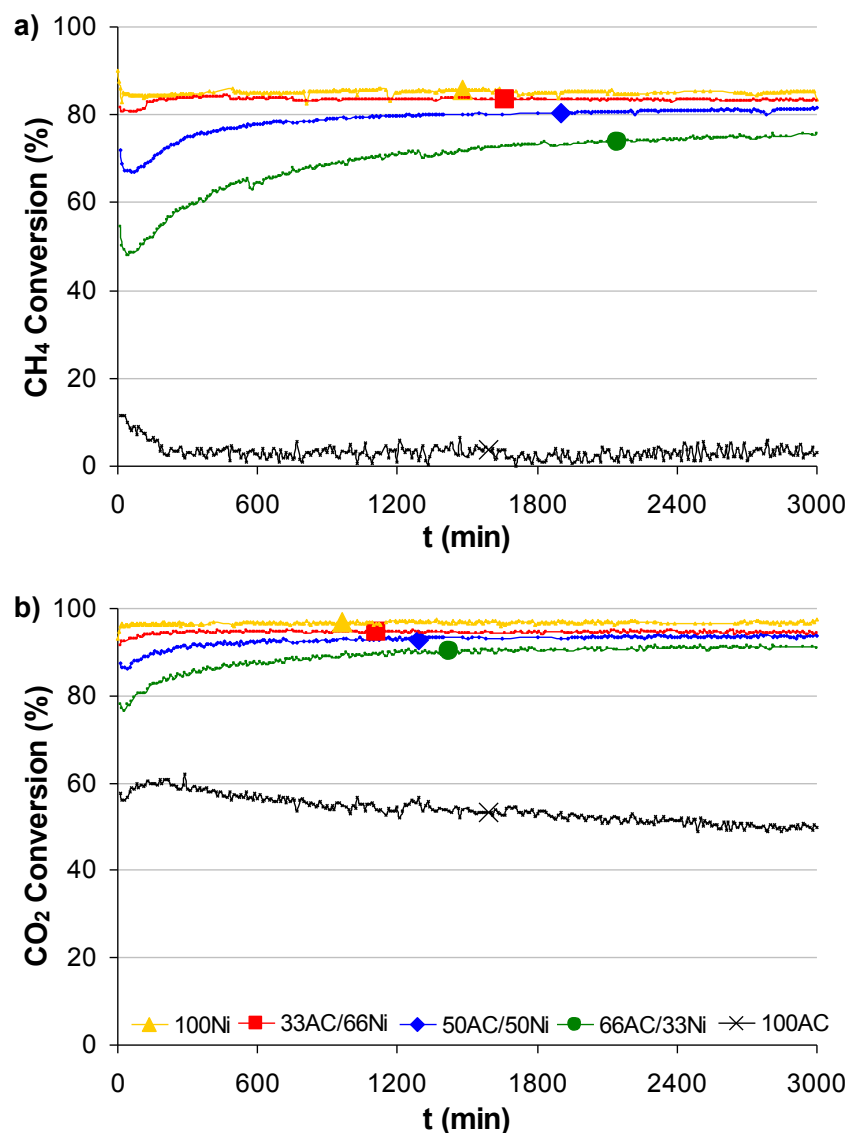


Figure 3. (a) CH₄ and (b) CO₂ conversions, in the CO₂ reforming of GTM with the different mixtures used as catalysts during 50 hours of reaction (800 °C, CH₄/CO₂ = 1:1, VHSV_{tot} = 3.75 L g⁻¹ h⁻¹, 1 atm).

These results confirm the presence of the synergetic effect. Working at a VHSV of 3.75 L g⁻¹ h⁻¹, the activated carbon appears to be inactive in the dry reforming or the steam reforming reactions. Almost none of the methane is transformed and all of the carbon dioxide reacts through the RWGS, as the amount of water collected in the condenser indicates. In the case of the Ni catalyst, the conversion of methane drops slightly compared to the experiments carried out at 1.00 L g⁻¹ h⁻¹. However, it is important to point out that, at the end of the 50 hours, the catalysts with 50 % or more of Ni/Al₂O₃ achieved practically the same conversion of methane (approximately 4 % difference between the highest value and the lowest value). In the case of the conversion of carbon

dioxide the results were similar to the ones achieved working at a $1.00 \text{ L g}^{-1} \text{ h}^{-1}$. In addition, the conversion of CO_2 was practically the same for all the mixtures and for the 100Ni catalyst (about 5 % difference between the highest value and the lowest value). When the mixtures are used as catalyst, again it is possible to appreciate that the conversions of both gases are nearer to the conversions achieved with the 100Ni catalyst than to the conversions achieved with the 100AC catalyst. From Figure 3 it can also be seen that when the mixtures are used as catalysts, the conversions, and therefore the synergetic effect, continuously improve throughout the entire experiment. This phenomenon is specially marked in the case of the 67AC/33Ni catalyst, with conversions of just 10 % and 5 % lower for methane and carbon dioxide respectively than in the case of the 100Ni catalyst after 50 hours. Figure 4 compares, after six and fifty hours of reaction, the experimental and the theoretically predicted values by the law of mixtures for methane and carbon dioxide conversions and water production.

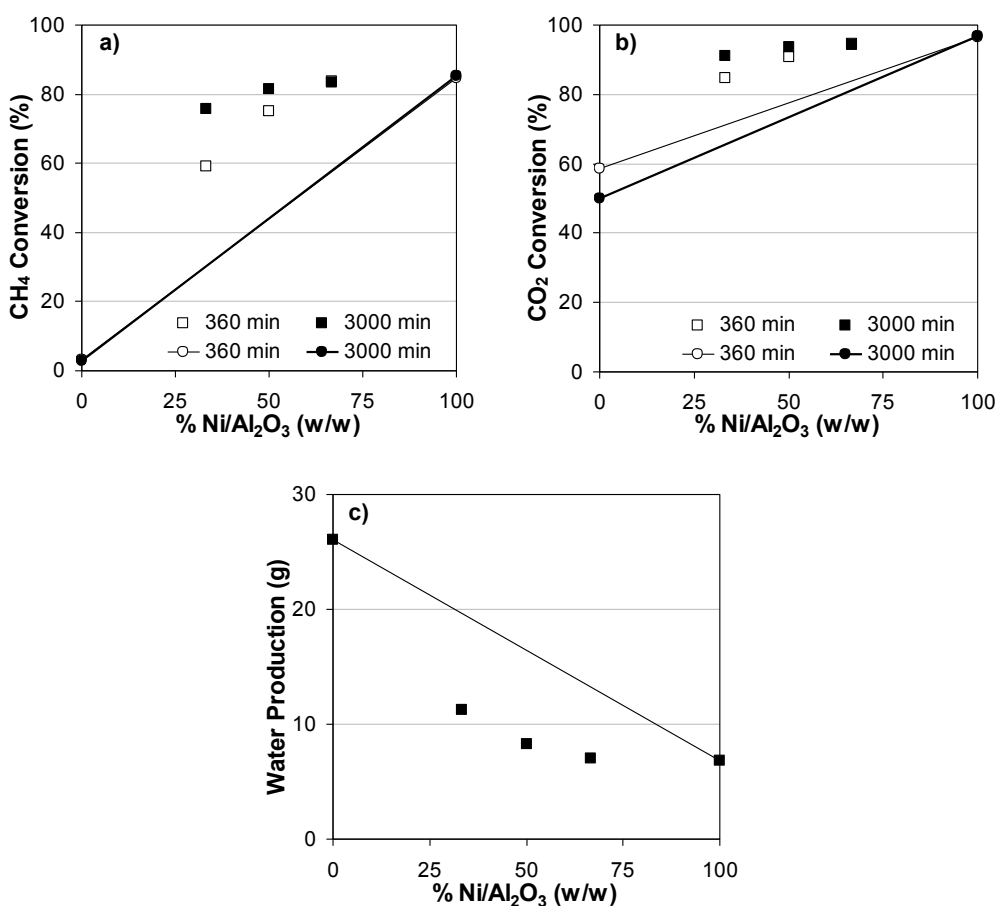


Figure 4. Comparison of the results predicted by the law of mixtures (continuous lines) with those achieved in the experiments (squares) for the: (a) conversion of CH₄; (b) conversion of CO₂ after 6 hours of reaction (open symbols) and 50 hours of reaction (closed symbols); and (c) water production after 50 hours of reaction.

As can be seen, after six hours and after fifty hours the experimental conversions are above the predicted conversions, confirming the presence of the synergetic effect at a high VHSV and its long term persistence. After six hours, the differences between the experimental and the predicted conversions are lower than in the case of the experiments carried out at $1.00 \text{ L g}^{-1} \text{ h}^{-1}$ of VHSV. But after 50 hours, the differences between the experimental and predicted conversions increase, reinforcing the idea that the synergetic effect improves as the experiment proceeds.

Variation in the porous textural properties during the experiments was also studied. In previous works it was found that, in the case of activated carbons, the CO_2 reforming of CH_4 occurs mainly in the micropores [18]. Thus, a large volume of micropores is necessary to obtain good CH_4 and CO_2 conversions. During the reaction, CH_4 decomposition leads to the blockage of the micropores. This process, known as Chemical Vapor Deposition (CVD) [24], is one of the main reasons for the loss of catalytic activity in the activated carbons. The results for the porous textural properties of the activated carbon and the $\text{Ni}/\text{Al}_2\text{O}_3$ catalyst before and after the experiments are shown in Table 1. Analysis of these results provides further evidence of the synergetic effect that take place between both materials. When the activated carbon or the $\text{Ni}/\text{Al}_2\text{O}_3$ are used alone, they experience a decrease in their porous textural properties, mainly due to the carbon deposits. This decrease is especially pronounced in the case of the activated carbon, which after the experiment of 50 hours and at a VHSV of $3.75 \text{ L g}^{-1} \text{ h}^{-1}$ with the 100AC catalyst, reduced its BET surface to almost a third of the initial surface area and its microporosity to less than the half. In the case of $\text{Ni}/\text{Al}_2\text{O}_3$ this reduction in porous textural properties was lower. These differences can be attributed to the different active centers of both materials. The activated carbon has a very high BET surface area (about $1000 \text{ m}^2/\text{g}$) and its active centers are mainly located in the micropores. The methane diffuses into the micropores, reacts and gives rise to the carbon deposits which block the access to the active centers. The carbon dioxide regenerates some of these deposits, but cannot regenerate them all because part of the carbon dioxide reacts with the carbon from the initial activated carbon. The reaction with the carbon from the initial activated carbon is more rapid than with the carbon deposits located in the micropores, since the CO_2 does not need to diffuse into the micropores. On the other hand, the $\text{Ni}/\text{Al}_2\text{O}_3$ has a low BET surface area (about $100 \text{ m}^2/\text{g}$) but its active centers are located on the external surface, not inside the

micropores. The active centers blocked by the carbon deposits are easy to regenerate since the carbon dioxide does not need to diffuse in order to reach them and there is no other carbon which can compete with them to react with the carbon dioxide. In contrast, when the mixtures/blends are used this decrease is much lower for both materials. When the 50AC/50Ni catalyst is used, although the conversions are much higher than in the case of 100AC, there is a reduction in the BET surface of about 15 % and the microporosity at the end of the experiment is twice as high as that achieved with 100AC. Thus, the catalysts showed a greater resistance to the loss of BET surface area and microporosity when they were used in the mixtures/blends than when used alone. This is an interesting finding since it means that the mixtures/blends may be more resistant to the deactivation produced by carbon deposits than when the activated carbon or the Ni/Al₂O₃ are used alone.

Table 1. Porous textural properties of the activated carbon FY5 and the Ni/Al₂O₃ catalyst before and after the experiments

| | | FY5 | | | Ni/Al ₂ O ₃ | | |
|----------------------|-----------|--|---|---|--|---|---|
| | | S _{BET} ^a (m ² /g) | V _t ^b (cm ³ /g) | V _{mic} ^c (cm ³ /g) | S _{BET} ^a (m ² /g) | V _t ^b (cm ³ /g) | V _{mic} ^c (cm ³ /g) |
| Before | | 1153 | 0.51 | 0.44 | 166 | 0.53 | 0.06 |
| 1.00 L/(g h) 6 h | 100AC | 953 | 0.42 | 0.35 | n.a | n.a | n.a |
| | 50AC/50Ni | 998 | 0.44 | 0.37 | 162 | 0.53 | 0.06 |
| | 100Ni | n.a | n.a | n.a | 159 | 0.51 | 0.06 |
| 3.75 L/(g h) 50 h | 100AC | 473 | 0.24 | 0.18 | n.a | n.a | n.a |
| | 50AC/50Ni | 968 | 0.48 | 0.35 | 149 | 0.51 | 0.06 |
| | 100Ni | n.a | n.a | n.a | 138 | 0.50 | 0.05 |

a. BET surface area obtained from the N₂ adsorption isotherms at -196 °C.

b. Total specific pore volume, defined as the liquid volume adsorbed at $p/p^0 = 0.95$ from the isotherm of nitrogen at -196 °C.

c. Specific volume of micropores (pores of internal width <2 nm), calculated from the isotherm of nitrogen at -196 °C.

3.1. Effect of carbon monoxide

Apart from hydrogen and methane, carbon monoxide is the third gas in the composition of the coke oven gas. Carbon monoxide normally appears in concentrations between 5 and 8 % vol. The presence of carbon monoxide could affect the CO₂ reforming of COG in several ways. It could shift the equilibrium of the dry reforming (reaction 1) to the side of the reactants, in the same way as the presence of H₂ does [6; 25]. This would

have negative consequences, since it would decrease the conversion of methane and carbon monoxide. It could also shift the equilibrium of the RWGS to the side of the reactants. This would decrease the production of water, thereby increasing the selectivity of the process. However, seeing that this water could react with the methane through the steam reforming reaction, it could also have a negative effect, by partially preventing the second path of the process. The most probable situation is a combination of both effects leading to several different results. To determine the influence of the presence of CO on the process, experiments in which carbon monoxide was added to the feed were conducted, the results of which are shown in Figure 5.

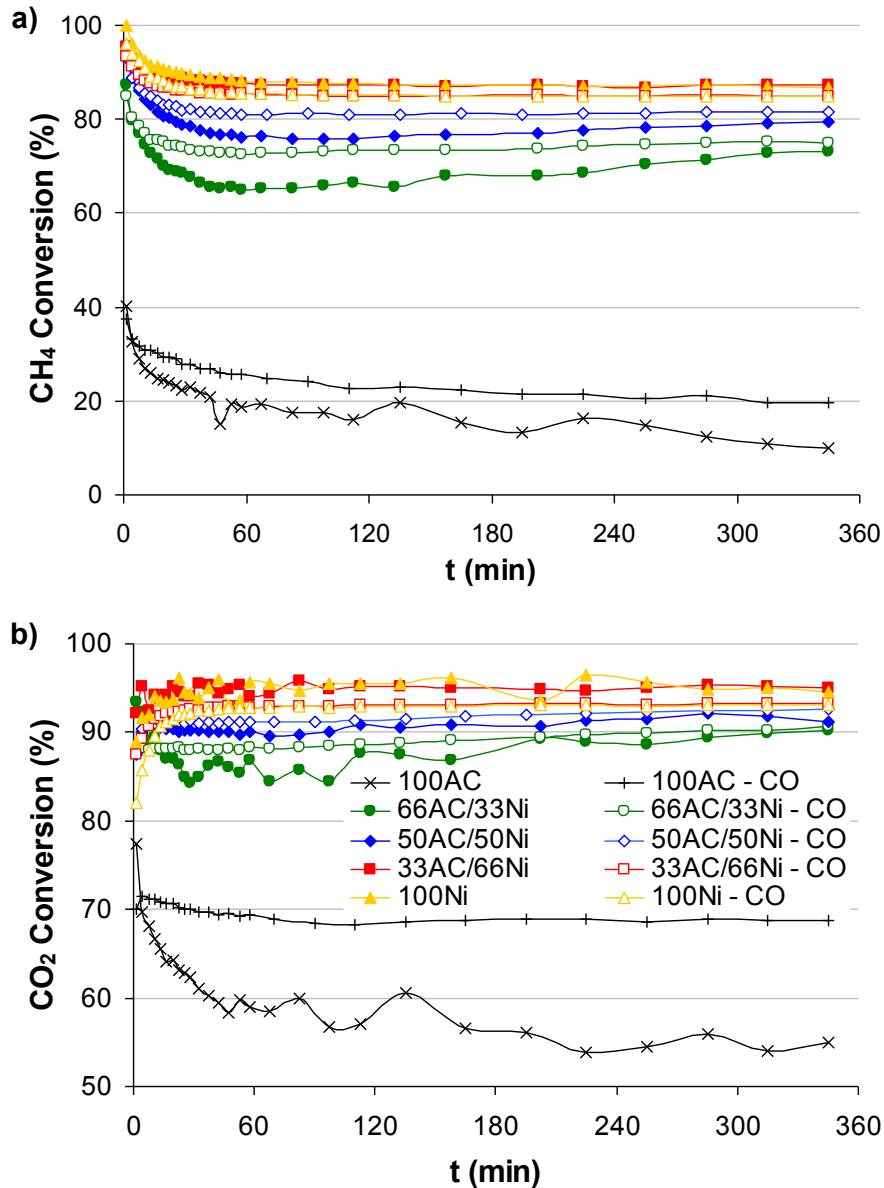


Figure 5. (a) CH₄ and (b) CO₂ conversions, in the CO₂ reforming of GTM and the GQM with the different mixtures used as catalysts (800 °C, CH₄/CO₂ = 1:1, 1 atm)

As can be seen, the results of these experiments show only minor differences in comparison to the case when no CO is added to the feed. If only the activated carbon is used as catalyst, the presence of CO clearly has a positive effect. Both the methane and carbon dioxide conversions increase and show more stable values. The increase in the conversions is 8 % for the methane and 14 % for the carbon monoxide. In contrast, when the Ni/Al₂O₃ is used, the conversions decrease. However, the effect is much lower than in the experiment with activated carbon used as catalyst, because the conversions are only 2 % lower than in the experiments without CO. When the physical mixtures are used, whether the effect is negative or positive, depends on the percentage of activated carbon used. When catalysts 67AC/33Ni and 50AC/50Ni are employed, the conversions increase, whereas in the case of 33AC/67Ni catalyst, the conversions decrease. As in the case of the experiments with no CO, the behaviors of 100Ni and 33AC/67Ni are practically the same. In any case, the differences between the experiments carried out with and without CO using the physical mixtures as catalyst are insignificant. It seems that in the case of the Ni/Al₂O₃ catalysts both effects (the shift in the equilibriums of dry reforming and RWGS) are taking place, but their influence is almost negligible. In the case of the activated carbon, a possible explanation for the rise in the conversions is a combination of both effects. The presence of carbon monoxide shifts the Boudouard equilibrium to the side of the reactants. This will give rise to an increase in the carbon dioxide concentration, the positive effect of which would outweigh the negative effect of the presence of CO over the RWGS. As a result of these shifts in equilibriums, the conversion of CO₂ and the production of water are higher than in the case of the experiments without CO. In the case of the conversion of CH₄ there is also an enhancement, but it is lower than in the case the conversion of CO₂. The presence of more water probably increases the amount of methane transformed through steam reforming, though not to the same extent as in the case of carbon dioxide. This hypothesis is supported by the higher amount of water produced when carbon monoxide is introduced into the feed (approximately 15 % higher). Another possible explanation is that the higher amount of carbon deposits formed due to carbon dioxide disproportionation leads to a decrease in the catalytic activity of the catalyst for the transformation of methane [26].

With regard to the synergetic effect, the experiment carried out with the GQM show only minor differences with the experiments carried out with the GTM. First of all it

should be noted that, in the experiments carried out adding CO to the feed and using the mixtures as catalysts, the conversions are stable. Therefore, there is no increase in the synergetic effect as the experiment proceeds. When CO is added to the feed, the synergetic effect is not as strong as in the experiments with no addition of CO. This is mainly due to the significant improvement in methane and carbon dioxide conversions in the case of the 100AC catalysts (+8 % and +14 % respectively), whereas in the other cases the improvement is not as great (+2 % for methane and +1 % for carbon dioxide when the 67AC/33Ni and the 50AC/50Ni catalysts are used) or there is even a worsening (-2 % for the methane and -2 % for the carbon dioxide when the 33AC/67Ni and the 100Ni catalysts are used).

3.2. Analysis of the synthesis gas

The use of the synthesis gas to produce different organics products depends on its H₂/CO ratio [5]. When the ratio is near to 1 it can be used to synthesize higher hydrocarbons and oxygenated derivatives, such as acetic acid, whereas if it takes on values of 3 or higher it may be used to produce H₂ or CH₄ [5]. Probably the most interesting application of the CO₂ reforming of COG is the production of a syngas suitable for the synthesis of methanol, which requires a H₂/CO ratio of 2 [6]. In order to be suitable for methanol production, the syngas produced must also satisfy the R parameter (Equation 4). The R parameter is an expression that relates the proportions of H₂, CO and CO₂ in the syngas which must take on values slightly higher than 2 [27-28]. In the production of methanol it is necessary to bear in mind that the CO₂ takes part in the process (reactions 6 and 7). It appears in reaction 6 and acts as a promoter of reaction 7.

$$R = (H_2 - CO_2) / (CO + CO_2) \quad (\text{Eq. 4})$$



Given that the GQM composition is more or less the average composition of a typical COG, the H₂/CO ratio and R parameter of the different experiments carried out with the GQM are shown in Table 2.

Table 2. H₂/CO ratio, R parameter and selectivity in the CO₂ reforming of GQM with the different catalysts

| Catalyst | H ₂ /CO (dimensionless) | R (dimensionless) | Selectivity (%) |
|-----------|---------------------------------------|----------------------|------------------------------|
| 100AC | 2.14 ± 0.02 | 1.44 ± 0.02 | (-10) – (-60) ^(*) |
| 67AC/33Ni | 2.00 ± 0.01 | 1.835 ± 0.009 | 76 |
| 50AC/50Ni | 2.008 ± 0.006 | 1.888 ± 0.001 | 80 |
| 33AC/67Ni | 2.004 ± 0.002 | 1.905 ± 0.001 | 85 |
| 100Ni | 2.01 ± 0.02 | 1.906 ± 0.001 | 85 |

^(*) Results of the selectivity at the beginning and at the end of the experiment

As can be seen, in all of the experiments the H₂/CO ratio took on values of about 2, and the syngas obtained can be considered as suitable for the synthesis of methanol. However, the values of the R parameter also have to be taken into account. The results of the R parameter reveal that it is possible to use this synthesis gas for the production of methanol when the catalysts 50AC/50Ni, 33AC/67Ni and 100Ni are used. In fact, the R parameter took on values a little bit lower than two, but in the production of methanol this situation is usually corrected by adding the H₂ that has not reacted in the methanol synthesis stage, and which is recovered at the end of the process.

It is also productive to study the selectivity of the process. This parameter (Equation 3) gives an idea of the amount of reactants transformed into products or byproducts. Table 2 also shows the results of selectivity achieved over the different catalysts. The results for the 100CA catalyst are specially striking, since they are negative values. This means that, not only is all of the hydrogen from the methane transformed into water (this is the only byproduct detected), but part of the hydrogen present in the feed is also transformed into water. For the rest of the catalysts the results of selectivity are much higher, so they are able to transform most of the methane to produce hydrogen. Close examination of the values achieved with the different catalysts provides further evidence of the synergetic effect, since the selectivity values of the 67AC/33Ni,

50AC/50Ni and 33AC/67Ni catalysts are much nearer to the value of the 100Ni catalysts than to the value of the 100AC catalyst.

4. Conclusions

There are two different possible paths for the CO₂ reforming of COG: the direct dry reforming of methane and the reverse water gas shift reaction followed by the steam reforming of methane. As a consequence of this second path some water is produced as a byproduct.

The use of the physical mixtures of activated carbon and Ni/Al₂O₃ gives rise to a synergetic effect. Thus, the conversions achieved are significantly higher than those predicted by the law of mixtures, whereas the amount of water produced is lower. The loss of BET surface area and microporosity experienced by the materials when they are used in the mixtures is much lower than when they are used by themselves.

The presence of CO in the COG leads to a considerable increase in the conversions when the activated carbon is used as catalyst and to a slight decrease when Ni/Al₂O₃ is used. In the case of the mixtures, when the percentage of activated carbon is higher than that of Ni/Al₂O₃ there is a small increase in the conversion, while an excess of Ni/Al₂O₃ produces a decrease. Such variations undermine the strength of the synergetic effect.

In sum, the use of mixtures of activated carbon and Ni/Al₂O₃ as catalysts for the CO₂ reforming of COG is preferable than using them separately.

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