CO$_2$ reforming of coke oven gas over a Ni/γAl$_2$O$_3$ catalyst to produce syngas for methanol synthesis

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A R T I C L E   I N F O

A B S T R A C T

The CO$_2$ reforming of coke oven gases (COG) was carried out over a Ni/γAl$_2$O$_3$ catalyst in order to obtain a suitable syngas for methanol synthesis. The influence of different operating conditions, such as temperature and volumetric hourly space velocity (VHSV), was studied. It was found that the H$_2$ present in the feed gas promotes the Reverse Water Gas Shift reaction (RWGS), which produces water. Nevertheless, the Ni/γAl$_2$O$_3$ catalyst showed a high selectivity to the CO$_2$ reforming reaction and it was possible to avoid the RWGS under certain operating conditions. Moreover, a part of the reaction could take place via a different path (RWGS followed by the steam reforming of methane instead of the direct dry reforming of methane). The deactivation of the Ni/γAl$_2$O$_3$ catalyst was also studied. Both the methane and the carbon dioxide conversions remained steady for 50 h without showing any sign of deactivation. However, the sinterization of the nickel particles and the presence of carbon deposits seemed to indicate that the catalyst would eventually loose catalytic activity.

1. Introduction

Methanol is a raw material of primary importance for the chemical industry, for which there is a growing demand due mainly to its use in the production of biodiesel and as an alternative fuel [1–5]. Methanol is an excellent fuel in its own right or it can be blended with gasoline, although it has half the volumetric energy density of gasoline or diesel [1,3–5]. In addition, one of the most important attractions of methanol is that it can be used as a good hydrogen carrier, since it can be handled more easily and safely than raw hydrogen, as a direct fuel in some kinds of fuel cells (DMFC) or in internal combustion engines [1,3–6]. This gives methanol an important role to play in the emerging 'Hydrogen Economy'.

Nowadays, methanol is almost exclusively produced from synthesis gas [4,5], a raw material, consisting mainly of hydrogen and carbon monoxide, that is used in the large-scale production of hydrogen and a wide variety of organic products in industry [7,8]. Syngas is mainly produced from natural gas and oil, but increasing awareness about climate change and the emissions of greenhouse gases is promoting research into alternative processes for syngas production [7,9–11].

One of these alternative technologies is the CO$_2$ reforming of coke oven gas (COG). COG can be considered as a by-product from coking plants, consisting mainly of H$_2$ (∼55–60%), CH$_4$ (∼23–27%), CO (∼5–8%) and N$_2$ (∼3–5%) along with other hydrocarbons, H$_2$S

and NH$_3$ in small proportions [12,13]. This gas is used as fuel in the coke ovens, but usually there is a surplus of gas which is used in other processes of the plant, or is simply burnt away in torches, giving rise to environmental problems, e.g. CO$_2$ emissions [13,14]. Only a few studies have focused on the production of syngas from COG by partial oxidation [12], steam reforming [15,16] or CO$_2$ reforming [13]. Dry reforming, or CO$_2$ reforming, offers certain advantages over the other methods, such us energy saving and CO$_2$ consumption. However, the most interesting characteristic of this alternative is the possibility of producing, in just one step and without the need for a conditioning stage, a syngas with a H$_2$/CO ratio close to 2, which is the most suitable ratio for methanol synthesis [9,17], provided that the process is carried out under stoichiometric conditions of CH$_4$ and CO$_2$ [13]. Furthermore, this method can be considered as a way of partially recycling CO$_2$ since it consumes, at least theoretically, half of the CO$_2$ produced when methanol is consumed (see Fig. 1). Another interesting aspect of the CO$_2$ reforming of COG is that the energy consumed by the endothermic reactions can be obtained from some of the exothermic processes that take place in the steelmaking plant. For instance, the blast furnace, which high temperature exhaust gases (1600 °C) could be used as heat source [18].

The dry reforming of methane is a catalytic process, and so a critical factor for its performance is the development of appropriate catalysts. A great deal of research has been focused in this direction over recent years. Nickel is commonly used in this reaction as active metal for the catalyst, due to its low cost and wide availability that make it a more preferable choice than other metals which have shown higher conversions and better resistance to

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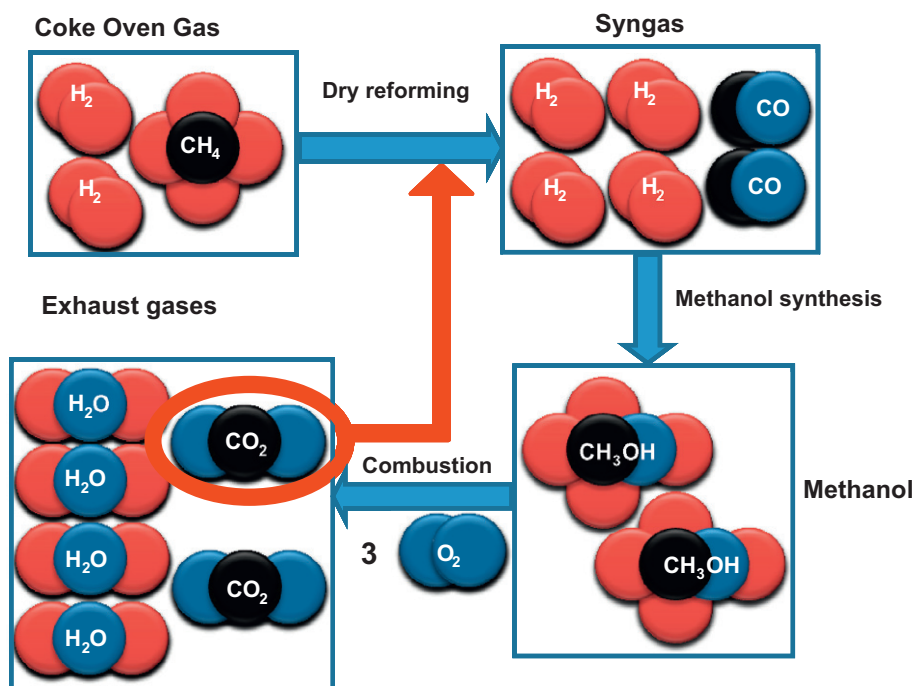 E-mail address: angelmd@incar.csic.es (J.A. Menéndez).

Coke Oven Gas

Syngas

Dry reforming

Methanol synthesis

Exhaust gases

Combustion

Methanol

Fig. 1. CO_2 partial recycling scheme by means of the CO_2 reforming of COG for methanol production.

coke formation (like Rh, Pt, Ru or Ir) [19–24]. The choice of the support is also important in the preparation of a catalyst, because it can have a strong influence on the activity and deactivation of a catalyst [19–22,25]. A variety of materials have been tested as Ni supports in the reaction of dry reforming of CH_4, e.g. inorganic oxides [19,22] and carbon materials [20–22,25]. One of the most commonly used materials as support is Al_2O_3 (mainly α and γ species), due to its chemical and physical stability and high mechanical resistance [19,23,24].

The objective of this work is to gain further insight into the CO_2 reforming of COG over $Ni/\gamma Al_2O_3$ in order to produce a syngas suitable for methanol production and to study the influence of different parameters (such us temperature, volumetric hourly space velocity and H_2 present in the feed) on the process, conversions and selectivity.

2. Experimental

2.1. Preparation and characterization of the Catalyst

Ni supported on a γAl_2O_3 catalyst ($Ni/\gamma Al_2O_3$), containing 5 wt.% Ni, was prepared by the direct impregnation method using $Ni(NO_3)_2 \cdot 6H_2O$ as metal precursor. The characteristics of the γAl_2O_3 used as support have been described in previous works [26]. A weighed amount of nickel nitrate was dissolved in a beaker with distilled water. Once the salt was completely dissolved, the appropriate amount of support (γAl_2O_3) was added and then sonicated in an ultrasonic bath for 7 h. After that, the mixture was dried overnight at 100 °C. Finally, it was reduced at 400 °C in a flow of 100 mL/min of H_2 for 2 h.

The Ni content of the catalyst was analyzed using an AA-6300 Shimadzu spectrometer, in order to check the amount of Ni deposited on the catalyst. The analysis showed that the amount of Ni loaded was 4.20 wt.%.

The $Ni/\gamma Al_2O_3$ species were determined by means of X-ray diffraction and the Ni particle size was evaluated by X-ray diffraction and Scherrer's equation.

The presence of carbonaceous deposits was determined by total organic carbon analysis, consisting in the IR measuring of the CO_2 formed in a catalytic oxidation at 900 °C, using a TOC V-CPH E200V instrument.

2.2. CO_2 reforming experiments

The CO_2 reforming of COG was carried out under atmospheric pressure in a fixed-bed quartz tube reactor which was heated up inside an electric furnace. The reaction temperature was monitored and controlled by means of a thermocouple located in the middle of the catalyst bed.

For comparative purposes, a test was carried out using a gaseous stream of CH_4 and CO_2 at a ratio of 1:1. For the rest of the experiments, H_2 was added in order to study its effect on the process of the CO_2 reforming of methane. This gas mixture gives way to a stream composed of 54% H_2, 23% CH_4 and 23% CO_2 (which will be referred to as gas ternary mixture, GTM), which keeps the H_2/CH_4 ratio of the COG (2–2.7) and the stoichiometric conditions of CH_4 and CO_2 for the dry reforming of the methane. The effect of the carbon monoxide present in the coke oven gas is outside the scope of this work and will be studied in due course.

Tests were performed at atmospheric pressure, at three different temperatures (800, 900 and 1000 °C) and at different volumetric hourly space velocities, VHSV (0.75–9.30 L g^{-1} h^{-1}) [13]. The gas product was collected in Tedlar® sample bags in the course of the experiment at different times. A condenser was used to collect water that had formed before it reached the bags. Before starting the reaction, the system was flushed with N_2 for 15 min at a flow rate of 60 mL/min under room temperature. Then, using the same N_2 flow rate, the reactor was heated up until the catalyst bed reached reaction temperature. At that point the N_2 flow was cut off and the reactant gases were introduced into the reactor to start the reaction. Samples of the outlet gases were analyzed in a Varian CP-3800 gas chromatograph.

In order to study the deactivation of the catalysts, two additional tests were carried out at 800 and 900 °C and 3.75 L g^{-1} h^{-1}

Table 1
Operating conditions of the experiments.

Temperature (°C)	VHSV$_{CH4}$ (L g^{-1} h^{-1})	VHSV$_{total}$ (L g^{-1} h^{-1})	Time (min)
800	0.16	0.75	360
800	0.51	2.25	360
800	0.84	3.75	360
800	0.84	3.75	3000[a]
800	1.38	6.15	360
800	1.80	8.00	360
800	2.09	9.30	360
900	0.16	0.75	360
900	0.84	3.75	3000[a]
900	2.09	9.30	360
1000	0.16	0.75	360

[a] Experiments carried out in the micro-reactor.

in a micro-reactor, consisting of a catalyst bed of diameter 10 mm and length 35 mm over a period of 50 h. Samples of the outlet gases were analyzed in an Agilent Technologies 3000A micro-gas chromatograph.

Table 1 summarizes the results of the experiments and the operating conditions.

The CH$_4$ and CO$_2$ conversions and selectivity to H$_2$ were calculated from the amount of water recovered and the product gaseous stream compositions, by means of an iterative method, based on the Newton method for nonlinear equations using Solver Microsoft Excel® tool and closing the mass balances to within a ±5% error margin. Selectivity to hydrogen gives an approximate idea of the amount of methane transformed into H$_2$ or into other species (such as light hydrocarbons, ⩾C2, or water). These parameters were calculated as follows:

$$CH_4 \text{ conversion, } \% = 100 \cdot (CH_{4 \text{ in}} - CH_{4 \text{ out}})/CH_{4 \text{ in}} \qquad \text{(Eq.1)}$$

$$CO_2 \text{ conversion, } \% = 100 \cdot (CO_{2 \text{ in}} - CO_{2 \text{ out}})/CO_{2 \text{ in}} \qquad \text{(Eq.2)}$$

$$H_2 \text{ selectivity, } \% = 100 \cdot (H_{2 \text{ out}} - H_{2 \text{ in}})/[2 \cdot (CH_{4 \text{ in}} - CH_{4 \text{ out}})] \qquad \text{(Eq.3)}$$

where CH$_{4 \text{ in}}$, CO$_{2 \text{ in}}$ and H$_{2 \text{ in}}$, are moles of each gas at the inlet of the reactor and CH$_{4 \text{ out}}$, CO$_{2 \text{ out}}$ and H$_{2 \text{ out}}$ are moles of each gas at the outlet.

3. Results and discussion

3.1. Effect of the presence of H$_2$ in the feed gases

The results of the CO$_2$ reforming of methane (reaction 1) over the Ni catalyst are shown in Fig. 2. As can be seen, at 800 °C, working at atmospheric pressure, under stoichiometric conditions of methane and carbon dioxide and with a VHSV$_{CH4}$ of 0.16 L g^{-1} h^{-1} (0.32 L g^{-1} h^{-1} for the global feed) it is possible to achieve conversions of more than 90% over a period of 6 h for both gases.

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \quad \Delta H = 247.3 \text{ kJ/mol} \qquad \text{(reaction1)}$$
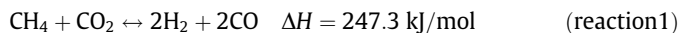
When the process is carried out with COG, the high amount of hydrogen present in the feed can give rise to two different phenomena: (i) the equilibrium may be shifted to the side of the reactants (see reaction 1), resulting in lower CH$_4$ and CO$_2$ conversions, and (ii) the Reverse Water Gas Shift reaction (RWGS) (reaction 2) may have more influence on the process, leading to the increase in the conversion of CO$_2$, the production of water, the consumption of hydrogen and a decrease in the H$_2$/CO ratio and selectivity [27,28].

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad \Delta H = 41.2 \text{ kJ/mol} \qquad \text{(reaction2)}$$
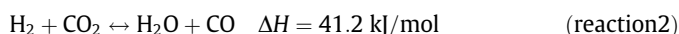
The most important consequence of these two effects is the decrease in hydrogen production. Thus, as can be seen in Fig. 3, at
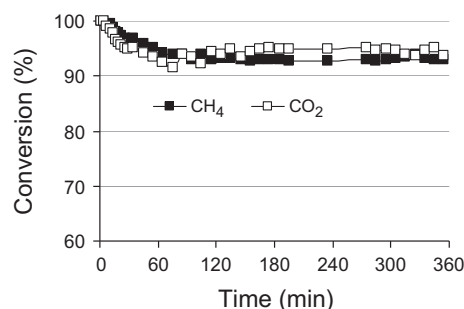

Fig. 2. CH$_4$ and CO$_2$ conversions in the CO$_2$ reforming of CH$_4$ (800 °C, CH$_4$/CO$_2$ = 1, VHSV$_{CH4}$ = 0.16 L g^{-1} h^{-1}, VHSV = 0.32 L g^{-1} h^{-1}, 1 atm).

800 °C both phenomena take place when the GTM is used instead of methane, as a result of which changes in the conversions occur. The conversion of methane initially reaches 100%, but after a few minutes this drops to 87%, a value which is maintained throughout the experiment. This initial change in conversion is due to the amount of time necessary to reach the stationary state and to the reduction experienced by the catalyst in the presence of hydrogen, which will be discussed in Section 3.5. Compared with the dry reforming of methane, in the CO$_2$ reforming of GTM there is a decrease of approximately 6% in the conversion of methane. In the case of carbon dioxide, conversion is about 86% at the beginning but this gradually increases to 93%, a value which is maintained throughout the experiment and is practically the same as in the dry reforming of methane (Fig. 2). This suggests that the RWGS has the same influence on the process as the shift in the equilibrium. This is supported by the amount of water collected in the condenser. The water represents approximately 1 vol.% of the reaction products which indicates that about the 6% of the carbon dioxide has reacted through the RWGS. Also significant is the fact that the amount of water produced is very low, as water could be a problem in the synthesis of methanol, due to the deactivating effect which it has on the Cu/ZnO/Al$_2$O$_3$ catalyst used in this reaction [29]. The tiny amount of water produced in this experiment might be low enough to avoid this problem.

3.2. Effect of temperature

Fig. 4 shows the results of the CO$_2$ reforming of GTM at 900 °C. As can be seen, both conversions increased with respect to the CO$_2$ reforming experiment of GTM at 800 °C (Fig. 3), a value of over 90% being retained throughout the experiment. Especially marked were the increase in methane conversion and the decrease in the production of water, to a value 3.5 times lower than in the experiment at 800 °C. These results suggest that the dry reforming reaction has been enhanced versus the RWGS reaction. This idea is
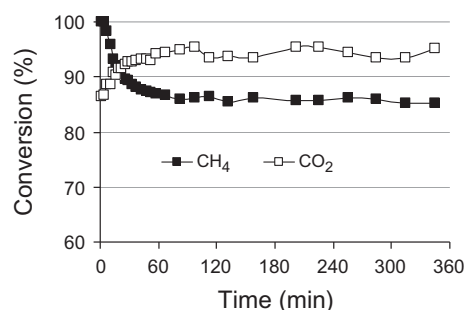

Fig. 3. CH$_4$ and CO$_2$ conversions in the CO$_2$ reforming of GTM (800 °C, CH$_4$/CO$_2$ = 1, VHSV$_{CH4}$ = 0.16 L g^{-1} h^{-1}, VHSV = 0.75 L g^{-1} h^{-1}, 1 atm).

thermodynamically consistent, since the dry reforming of methane reaction is more endothermic than RWGS and so any increase in temperature should enhance the former and will give rise to a higher degree of methane conversion, a greater production of hydrogen and a reduction in the amount of water produced. It is also possible that the water produced via the RWGS reaction reacts through the steam methane reaction (reaction 3) with the unreacted methane. However, this path is essentially the same as the one proposed for the dry reforming reaction because the sum of reactions 2 and 3 results in reaction 1.

$$H_2 + CO_2 \leftrightarrow H_2O + CO \quad \Delta H = 41.2 \text{ kJ/mol} \qquad \text{(reaction2)}$$

$$H_2O + CH_4 \leftrightarrow 3H_2 + CO \quad \Delta H = 206.1 \text{ kJ/mol} \qquad \text{(reaction3)}$$

$$CH_4 + CO_2 \leftrightarrow H_2 + CO \quad \Delta H = 247.3 \text{ kJ/mol} \qquad \text{(reaction1)}$$
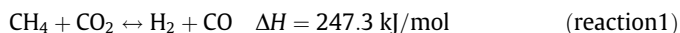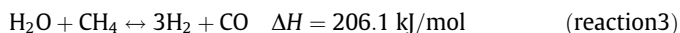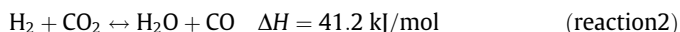
Fig. 5 shows the results of the test carried out at 1000 °C. If these results are compared with those shown in Figs. 3 and 4, it can be seen that, as the temperature increases, the conversions of methane and carbon dioxide also increase, achieving values of 100%. Interestingly after the experiment no water was found in the condenser. Therefore, by working at this temperature it is possible to avoid the RWGS and so maximize hydrogen production and selectivity. Similar results have also been achieved with other catalysts, such us activated carbon [13].

3.3. Effect of the volumetric hourly space velocity (VHSV)

The effect of the VHSV on the process was also studied at 800 °C and 900 °C. The procedure selected was to increase the VHSV at 800 °C until the conversion of methane (which was always lower than the conversion of carbon dioxide) reached values below 70%. The same VHSV was then used at 900 °C, in order to see if the influence of this parameter is affected by the change in temper-

ature. The results of these series of experiments are presented in Figs. 6–8.

As can be seen, the CH_4 and CO_2 conversions were affected by the VHSV, but the conversion of methane decreased sharply. A possible explanation for this could be the overlapping of two different effects: the decrease in CH_4 and CO_2 reacted via the dry reforming reaction and the increase in CO_2 reacted via the RWGS reaction. The decreases in conversion in both compounds due to a worsening of the dry reforming reaction are similar, but the increase in the amount of carbon dioxide reacted via the RWGS reaction, leads to the divergence in the decreasing conversions. This result, presented in Fig. 7, suggests that the RWGS is enhanced as the VHSV is increased. This could be due to the rise in CO_2 concentration inside the reactor, since, due to the high amount of H_2 present, the CO_2 could be the species which limits the RWGS reaction. High conversions of CO_2 are therefore necessary to avoid this side reaction. Another possible explanation is that the RWGS could be a quicker reaction than dry reforming, so it is more far-reaching. Some of the water produced then reacts with the methane through the steam reforming reaction. As the VHSV increases, the RWGS reaction proceeds whereas the steam reforming reaction does not have sufficient time to react in the same extent. This supports the idea that the second path (sum of reactions 2 and 3 to give rise to reaction 1) is the principal one.

The results obtained by increasing the VHSV at 900 °C are shown in Fig. 8. As can be seen, at this temperature the variation in conversions is much lower than at 800 °C. The conversion of carbon dioxide shows the same value while the decrease in the conversion of methane is about 4%. Also worthy of note is the fact that the increase in the water production is really low. This is due either to an improvement of the first path (direct dry reforming of the methane present in the feed) over the second path (sum of reactions 2 and 3 to give rise to reaction 1) or to an improvement of the reaction rate of the steam reforming, resulting in higher conversions in shorter periods of time. Thus, it can be concluded that temperature has a greater effect on the process than the VHSV.
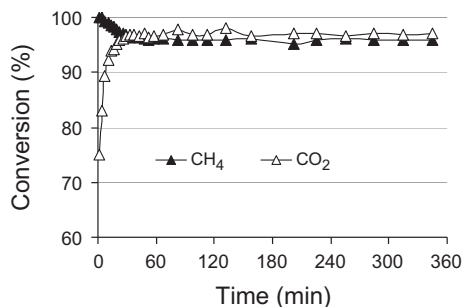

Fig. 4. CH_4 and CO_2 conversions in the CO_2 reforming of GTM (900 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.16 \text{ L g}^{-1} \text{ h}^{-1}$, VHSV = 0.75 L g^{-1} h^{-1}, 1 atm).
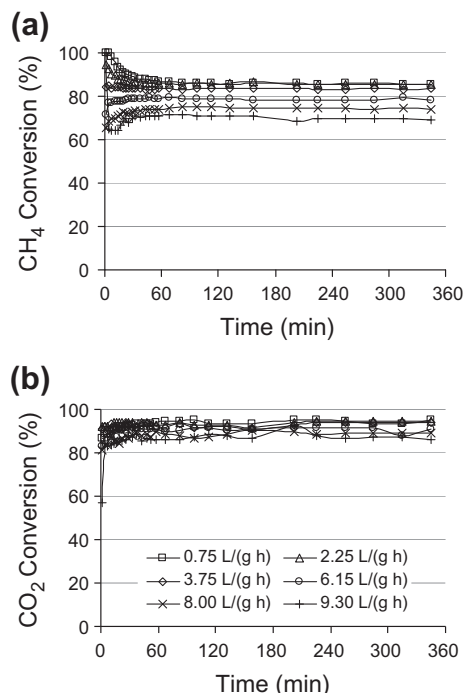

Fig. 6. Influence of the VHSV on the (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM (800 °C, $CH_4/CO_2 = 1$, 1 atm).

Fig. 5. CH_4 and CO_2 conversions in the CO_2 reforming of GTM (1000 °C, $CH_4/CO_2 = 1$, $VHSV_{CH4} = 0.16 \text{ L g}^{-1} \text{ h}^{-1}$, VHSV = 0.75 L g^{-1} h^{-1}, 1 atm).
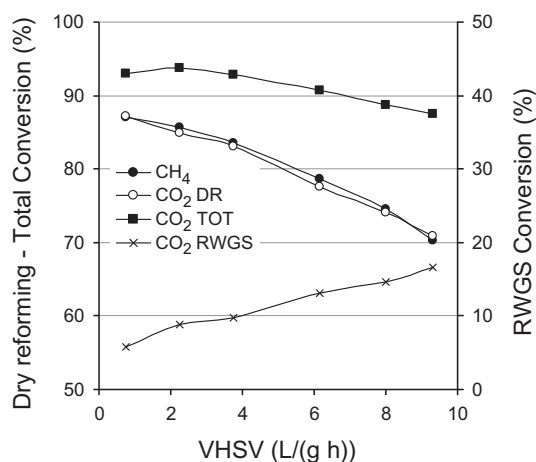
Fig. 7. Influence of the VHSV on the conversions of methane and carbon dioxide through the Reverse Water Gas Shift reaction (RWGS), the Dry Reforming reaction (DR) and total conversion (TOT) (800 °C, $CH_4/CO_2 = 1$, 1 atm).
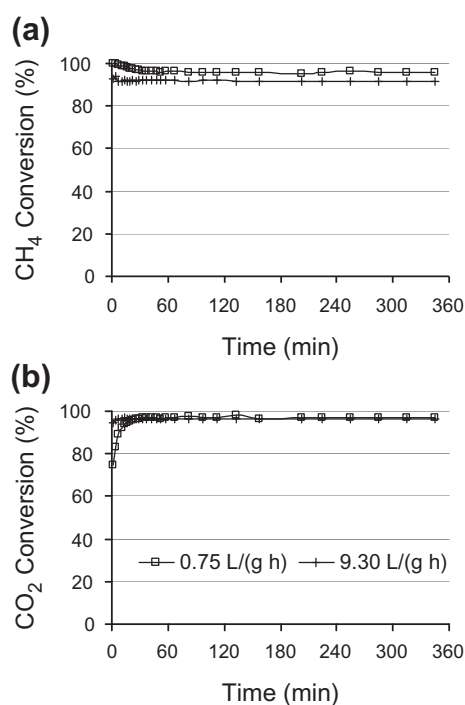

Fig. 8. Influence of the VHSV on the (a) CH_4 and (b) CO_2 conversions, in the CO_2 reforming of GTM (900 °C, $CH_4/CO_2 = 1$, 1 atm).
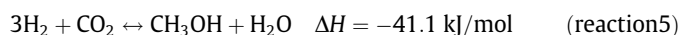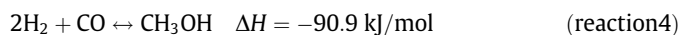
3.4. Analysis of the syngas

The application for which the synthesis gas is intended will determine the different proportions of hydrogen and carbon monoxide needed. To produce methanol, it is necessary to have a H_2/CO ratio of 2. However, the parameter most commonly used to study the suitability of the syngas for this purpose is the R parameter (Eq. (4)), which expresses the relation between the concentrations of hydrogen, carbon monoxide and carbon dioxide [17,30].

$$R = (H_2 - CO_2)/(CO + CO_2) \qquad (Eq.4)$$

In this case, it is necessary to take into account carbon dioxide, because the synthesis of methanol takes place through two different reactions (reactions 4 and 5) and, as can be seen, carbon

dioxide appears in reaction 5 as one of the reactants. Moreover, carbon dioxide acts as a promoter of reaction 4 and helps to maintain the activity of the catalyst [17].

$$2H_2 + CO \leftrightarrow CH_3OH \quad \Delta H = -90.9 \text{ kJ/mol} \qquad (reaction4)$$

$$3H_2 + CO_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H = -41.1 \text{ kJ/mol} \qquad (reaction5)$$

In order to optimize the process, the R parameter must have a value equal to or slightly higher than 2 [17,30]. If R takes on values lower than 2, there is an increase in the by-products formed during the synthesis of methanol. On the other hand, if R takes on values much higher than 2, it is necessary to increase the recycling rate due to the excess of hydrogen, which leads to a less efficient and more expensive process [30].

Table 2 summarizes both the H_2/CO ratio and R parameter for the different tests carried out for GTM reforming at different temperatures and VHSV.

As can be seen, in all the experiments the H_2/CO ratio takes on values over 2. It is noticeable that the temperature has a very slight influence on this parameter (less than 0.5% of variation from 800 °C to 1000 °C) while the VHSV has a grater influence (about 5% of variation from 0.75 to 9.3 L g^{-1} h^{-1}). This suggests that, in order to obtain a suitable synthesis gas, VHSV is a more critical factor than temperature. As the VHSV increases, the H_2/CO ratio increases because the conversions of methane and carbon dioxide decrease. This reinforces the influence of the high amount of H_2 present in the feed upon this parameter.

Temperature and VHSV affect the R parameter in different ways. When the temperature increases, the R parameter also increases whereas when the VHSV increases, the R parameter falls. This behavior can be explained in terms of variations of both conversions. When the temperature increases, the rise in methane conversion is greater than the rise in carbon dioxide conversion. This results in a greater increase in hydrogen concentration versus the increase in the carbon monoxide concentration. In the case of VHSV, the decrease in methane conversion is greater than the decrease in carbon dioxide conversion. This leads to a greater drop in the concentration of hydrogen versus the drop in carbon monoxide concentration. In all of the experiments, the R parameter takes on values higher than 2, and in some cases higher than 2.2. This problem could probably be corrected if carbon monoxide were added to the feed (since in COG there is 5–8% of CO which has not been added to the GTM).

As explained above, selectivity can be used to determine how much of the hydrogen present in the CH_4 is transformed into H_2 or other species. Table 2 also shows the selectivity to H_2 in the different experiments. The results lower than 100% are due to the production of water, since no hydrocarbons other than CH_4 (e.g. C_2H_2 and C_2H_6) were detected. The best results were obtained when the temperature was increased, a selectivity value of 100% being achieved at 1000 °C. This also shows that the RWGS reaction

Table 2
H_2/CO ratio, R parameter and selectivity in the CO_2 reforming of GTM at different temperatures and VHSV.

Temperature(°C)	VHSV (L g^{-1} h^{-1})	H_2/CO (adim.)	R (adim.)	Selectivity (%)
800	0.75	2.25 ± 0.01	2.176 ± 0.004	91
800	2.25	2.29 ± 0.02	2.173 ± 0.006	83
800	3.75	2.29 ± 0.02	2.161 ± 0.006	83
800	6.15	2.31 ± 0.01	2.140 ± 0.005	80
800	8.00	2.33 ± 0.02	2.117 ± 0.007	78
800	9.30	2.35 ± 0.02	2.093 ± 0.008	75
900	0.75	2.24 ± 0.02	2.208 ± 0.007	94
900	9.30	2.27 ± 0.01	2.207 ± 0.001	90
1000	0.75	2.24 ± 0.01	2.228 ± 0.001	100

is handicapped against dry reforming reaction when the temperature is increased, since a lower percentage of hydrogen from the reacted methane is transformed into water. However, when the VHSV increases, the opposite occurs. In this case, selectivity decreases as VHSV increases, showing that the RWGS reaction is favored against the dry reforming reaction when VHSV is increased.

3.5. Deactivation of the catalyst

Figs. 9 and 10 show the results of the CO_2 reforming of GTM at 800 and 900 °C during 50 h at a medium total VHSV ($3.75 \, L \, g^{-1} \, h^{-1}$). As can be seen, the catalyst did not show signs of deactivation in any of the experiments, since the conversions of methane and carbon dioxide were steady over the reaction time. Two main effects may lead to deactivation in the dry reforming of methane: (i) carbon deposits from the decomposition of methane may block the access of the reactants to the active centers [31]; and (ii) the sintering of nickel particles on the catalyst surface. The second effect has only a slight influence on the activity of the catalyst, compared to the carbon deposition, but it may nevertheless promote the coking effect [32,33].

The XRD patterns of the catalyst at different stages of the experiments revealed the species present in the catalyst. These XRD spectrums were obtained at the beginning of the reaction, when the conversions reached a constant value (after 60 min at 800 °C and 30 min at 900 °C) and at the end of the experiments (50 h). The diffractograms obtained for the catalyst used in the experiment at 900 °C are shown in Fig. 11. As can be seen, at the beginning of the experiment, when the catalyst has been heated in an inert atmosphere, the reduced nickel from the $Ni(NO_3)_2$ deposited on the γAl_2O_3 reacts with the latter to give rise to a spinel ($NiAl_2O_4$). After several minutes under the reaction atmosphere, which is strongly reducing, this spinel is reduced to Ni^0, and from this moment the conversions remain stable throughout the experiment.
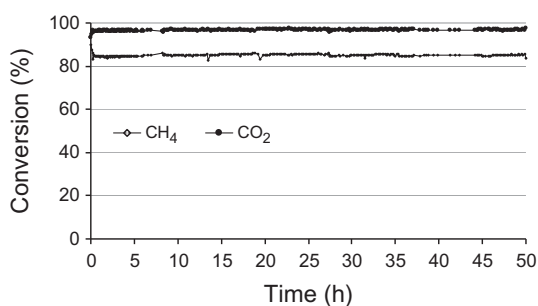

Fig. 9. CH_4 and CO_2 conversions in the CO_2 reforming of GTM for 50 h (800 °C, $CH_4/CO_2 = 1$, VHSV$_{CH4}$ = 0.84 L g^{-1} h^{-1}, VHSV = 3.75 L g^{-1} h^{-1}, 1 atm).
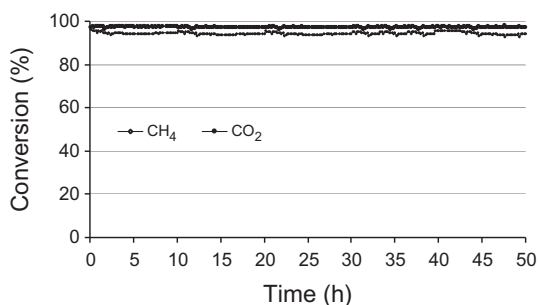
Fig. 10. CH_4 and CO_2 conversions in the CO_2 reforming of GTM for 50 h (900 °C, $CH_4/CO_2 = 1$, VHSV$_{CH4}$ = 0.84 L g^{-1} h^{-1}, VHSV = 3.75 L g^{-1} h^{-1}, 1 atm).
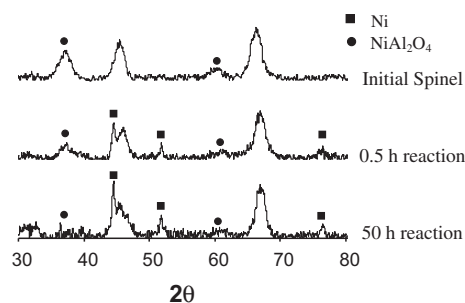

Fig. 11. XRD patterns of the catalyst at the beginning of the experiment (initial spinel), after 30 min in the reaction stream (0.5 h) and at the end of the experiment (50 h).

Table 3
TOC analysis results from the experiments carried out for 50 h.

Temperature (°C)	TC (mg C/g cat)	IC (mg C/g cat)	TOC (mg C/g cat)
800	1.0	1.0	0.0
900	4.4	1.0	3.4

After 50 h the XRD spectrum shows the same species as after 30 min, which may explain the steady conversions obtained throughout the experiment.

After the experiments, the catalysts were again subjected to XRD to compare the Ni^0 particle sizes. The Ni^0 particle size has increased from around 17 nm to around 24 nm after 50 h of reaction at both temperatures, which qualitatively indicates that the sintering process is taking place and that coke deposition is favored as time passes. In order to study the presence of these carbon deposits, the catalysts used in the experiments were subjected to total organic carbon (TOC) analysis. The results, which are summarized in Table 3, shows that the coking effect is also taking place. In the case of the experiment carried out at 800 °C, 1 mg of carbon/g of catalyst was found compared to 4.4 mg of carbon/g of catalyst at 900 °C. This shows that not only is the coking effect taking place but also that temperature has a critical influence on the process, since at 900 °C the amount of carbon is four times higher than at 800 °C. It is also noticeable that, at 800 °C all the carbon deposited on the catalyst is inorganic (IC), probably nickel carbide, since it has been previously reported that this species may appear in such processes [34]. Nevertheless, when the reaction was carried out at 900 °C, the same amount of IC was found, while the rest of the carbon deposited (3.4 mg C/g catalyst) was organic carbon (TOC), probably deposited as amorphous or graphitic carbon [34].

To conclude, although after 50 h of reaction the conversions of methane and carbon dioxide still show high and stable values, if the reaction goes on for a longer period of time, the catalyst may eventually lose its catalytic activity.

4. Conclusions

Upgrading coke oven gases via CO_2 reforming followed by methanol synthesis, could be an effective way to partially recycle the CO_2 produced when methanol is burnt.

The hydrogen present in the COG shifts the equilibrium to the reactants (reducing the conversions of methane and carbon dioxide) and promotes the reverse water gas shift reaction, with part of the hydrogen being consumed to produce water. Nevertheless the $Ni/\gamma Al_2O_3$ catalyst shows a high selectivity to the CO_2 reforming, which minimizes this problem. However, as the reaction temperature increases, it is possible to increase the conversions of methane and carbon dioxide and so reduce the amount of water

produced, it being possible to achieve conversions of 100% for both gases.

When the volumetric hourly space velocity is increased, the conversions of both gases decrease. In this case the decrease in the conversion of methane is greater than that of the carbon dioxide. This could be due to a worsening of the dry reforming reaction accompanied by an enhancement of the RWGS reaction. Another possible explanation is that part of the process takes place through a different path, composed of the RWGS reaction followed by the steam reforming of the methane. Via this path, the RWGS takes place completely, while the steam reforming does not has sufficient time to react in the same extent as the VHSV is increased.

Whereas the H_2/CO ratio of the syngas is almost unaffected by the variation in temperature, it is affected by VHSV, giving rise to an increase in its values. In the case of the R parameter, a rise in temperature leads to an increase in the R parameter values whereas an increase in the VHSV causes the R values to fall. Another important parameter of the process is selectivity, which has also been shown to be affected by temperature and VHSV. The selectivity values increase with temperature (to values of 100% at 1000 °C) while selectivity falls as VHSV is increased.

After 50 h there were no signs of deactivation in the catalyst. Nevertheless, analysis of the used catalyst revealed that both sintering and coke deposition had taken place. Therefore, deactivation may eventually take place if the reaction proceeds beyond 50 h.

Acknowledgments

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