Dry reforming of biogas in fluidized bed: Process intensification

P. Ugarte, P. Durán, J. Lasobras, J. Soler, M. Menéndez*, J. Herguido

Catalysis, Molecular Separations and Reactor Engineering Group (CREG), Aragon Institute of Engineering Research (I3A), University of Zaragoza, Spain

ABSTRACT

Biogas is a renewable resource obtained mainly from the anaerobic fermentation of agro-industrial and anthropogenic residues. The production of hydrogen by dry reforming of methane represents a potential application for this renewable energy carrier. This could play a positive contribution towards meeting the challenge of providing a global supply of energetically sustainable and environmentally friendly energy. This work combines a catalytic reaction, a separation and the catalyst regeneration in a single reactor. To this end, a two zone fluidized bed reactor (TZFBR) with hydrogen selective membranes has been employed (TZFBR + MB). The operating conditions for the process of dry reforming of biogas have been optimized experimentally, both in TZFBR and TZFBR + MB. Several catalysts were prepared (Ni/Al_2O_3, $Ni-Ce/Al_2O_3$, $Ni-Co/Al_2O_3$), characterized and tested in reactions in both TZFBR and in TZFBR + MB. Finally, the influence of using oxygen or carbon dioxide as regenerating gases in the process has been studied. Experimental results show the feasibility of using CO_2 for *in situ* catalyst regeneration, avoiding the potential problems associated with the use of O_2.

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Introduction

The world today requires an energy system based on clean renewable energy sources, and the use of hydrogen as an energy vector would be advantageous in terms of reducing both greenhouse gas emissions and our dependence on fossil fuels [1].

This work aims to upgrade biogas by producing hydrogen by means of dry reforming of methane (DRM) (reaction 1). DRM is an alternative to the traditional process of steam reforming of methane, since it avoids the energy consumption associated with steam production. We aim to counteract the possible disadvantages (coke formation and a lower H_2/CO ratio in the product stream) by the use of a novel reactor that will allow the catalyst regeneration and the separation of pure hydrogen to take place in the same vessel. This process uses as a reactant biogas formed mainly by the two gases that are the most important contributors to the greenhouse effect, namely CO_2 and CH_4, thus making a contribution to the global challenge of residue minimization.

Several reactions are involved in this process, such as water gas shift (WGS, reaction 2), methane decomposition (reaction 3) and the Boudouard reaction (reaction 4).

- Dry reforming of methane (DRM)

$$CH_4 + CO_2 \leftrightarrow 2H_2 + 2CO \tag{r.1}$$

- Water gas shift (WGS)

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{r.2}$$

- Methane decomposition

$$CH_4 \leftrightarrow C + 2H_2 \tag{r.3}$$

- Boudouard reaction

$$2CO \leftrightarrow C + CO_2 \tag{r.4}$$

In this case the reverse water gas shift reaction would be undesirable, since it would consume the target product (H_2). Reactions 3 and 4 are also undesirable, since they would cause a loss of catalyst activity by coke deposition over its surface. In fact, coke formation is one of the main disadvantages of this process, and thus a large number of research projects have aimed to obtain catalysts that would reduce the activity loss by coke poisoning. The aim of these studies was to achieve catalysts able to maintain a good level of activity over a long period of time, by decreasing the coke formation rate [2]. Although noble metal (Pd, Pt, Rh, Ru) catalysts could avoid coke formation [3,4], they are considerably more expensive than catalysts based on more common metals. Nickel metal catalysts are employed in the present work since they have good activity in this process [5—7]. Otherwise, to reduce coke formation the catalyst will be doped with other metals, in particular with Ce [8] and Co [9]. The chosen support was alumina because of its low cost, high specific surface area and good mechanical properties, in particular its resistance to attrition which is critical for its use in a fluidized bed reactor.

One way to deal with catalyst deactivation is to use a reactor with periodic regeneration [10]. However, several re-actors would be needed and the system would operate in unsteady state. The two zone fluidized bed reactor (TZFBR) has been successfully employed to offset catalyst deactivation in several processes [11—15], achieving steady state operation. In a TZFBR there are two gas feeding points. The hydrocarbon (or organic compound in general) is introduced through a quartz rod in an intermediate point of the catalytic bed, whereas an oxidizer is fed through a distributor located at the bottom of the bed. The DRM reaction takes place in the upper zone of the bed, forming carbon deposits (reducing zone). The oxidizing gas is used to burn or gasify coke, regenerating the catalyst in the lower bed zone (oxidation zone). Since in a fluidized bed there is a continuous mixing of solid by the ac-tion of gas bubbles, the catalyst that is deactivated by coke in the upper part is transported to the lower part and regener-ated. Simultaneously, the regenerated catalyst is transported to the upper part of the bed.

An additional factor of process intensification is the incorporation into the fluidized bed of Pd/Ag membranes that are permselective towards H_2. The use of these membranes inside the fluidized bed reactor allows extracting H_2 "in situ". The removal of H_2 increases the achievable conversion,

therefore allowing a greater production of hydrogen, which is the desired product. Although the removal of H_2 through a membrane during a reaction to increase the conversion has been frequently reported [16], most studies have employed fixed bed membrane reactors and only a few research groups have used fluidized beds [17—19]. Only a few papers from our group [20—22] have reported the use of hydrogen selective membranes in TZFBR (i.e. TZFBR + MB), and never for DRM.

This work will cover two aspects: A comparison of the performance of four different catalysts in DRM and the improvement of the DRM process by means of process intensification using a novel two zone fluidized bed reactor with hydrogen selective membranes (TZFBR + MB). This pro-cess intensification attempts to achieve several targets: a) to counteract catalyst deactivation by coke, b) to increase the achievable conversion at a given temperature, therefore allowing practical operation at lower temperatures, c) to pro-duce a stream of high purity hydrogen.

Experimental

Reaction system

Gases are fed to the reactor using mass flow controllers (Alicat Scientific). The reactor, whose scheme is shown in Fig. 1, is quartz-made, with a 2.8 cm internal diameter and 30 cm in height. A porous quartz plate, with pores smaller than 90 μm, supports the catalyst bed and acts as the gas distributor. The system can be operated as a conventional fluidized bed (FBR) or as a TZFBR. When the reactor is operated as a FBR, all the reactants are fed through the porous plate, while if operated as a TZFBR the reactants (CH_4 and part of the CO_2) are fed through a quartz tube (4 mm external diameter) with a "T" shape at the end. This point is located in a central position of the fluidized bed. In addition, in the TZFBR configuration, a regenerating gas is introduced through the porous plate.

The reactor exit stream is condensed in an ice-salt bath to remove water, and the remaining gases are analyzed on-line by gas chromatography (Varian CP3800). The GC is equipped with a molecular sieve (MolSieve 13X) to analyze permanent gases (H_2, CO, N_2, CH_4 and O_2) and a micropacked column (HayeSep® Q) to detect CO_2. When the reactor is operated as a TZFBR + MB, a vacuum pump which provides a low pressure in the permeate side (c.a. 6 mbar) is employed. This stream is also analyzed by GC.

Two Pd/Ag commercial membranes (REB Research [23]) were employed, with a total length of 15.2 cm, external diameter of 0.32 cm and a thickness of the Pd/Ag layer of 76 μm.

Catalyst synthesis

Four catalysts were synthetized, in all cases over Al_2O_3 as a support, with different metal contents: Ni (5 wt%), Ni (10 wt%), Ni/Ce (5/10 wt%) and Ni/Co (5/10 wt%). The metal was added by the incipient wetness method. First, the Al_2O_3 support (Sasol, Puralox® SCCa-150/200) was sieved to a size between 106 and 180 μm, and calcined in a muffle furnace (Nabertherm, B180) with a heating rate of 1 °C/min until 950 °C, maintaining
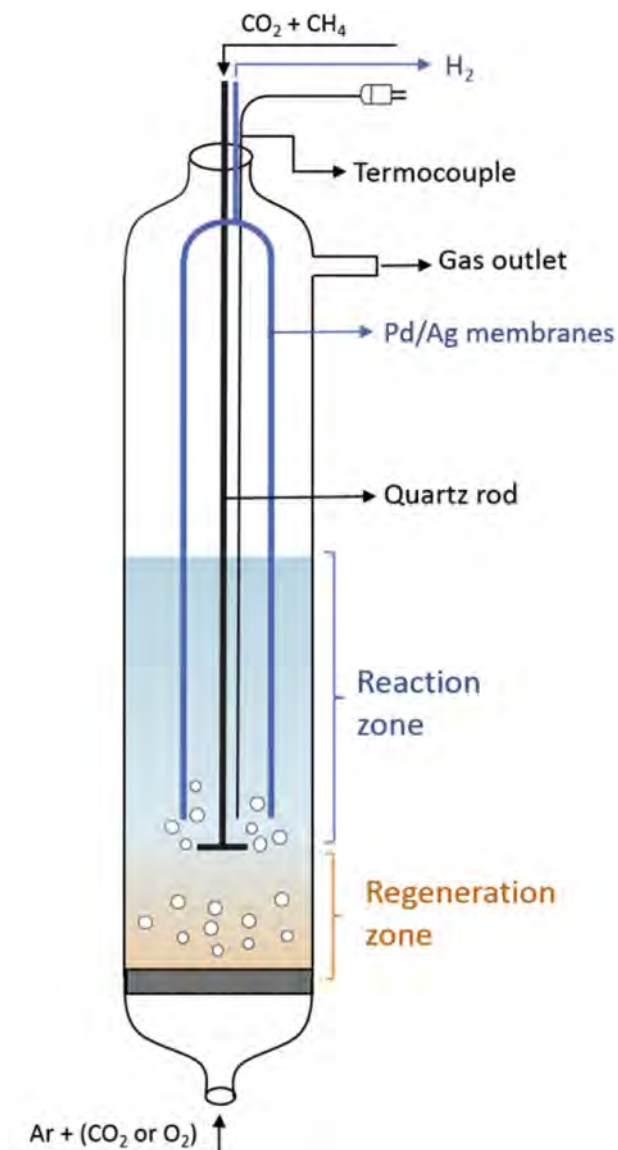
Fig. 1 − Reactor scheme for biogas dry reforming using TZFBR + MB for hydrogen production.

this temperature for 1 h. The support was then impregnated with a solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, *Sigma Aldrich*, 99.999 wt%) with an appropriate concentration to achieve the desired metal load. The resulting product was dried at 120 °C and calcined at 950 °C. When a second metal is present, the procedure was repeated with a second solution. In these cases, the precursors employed were $Co(NO_3)_2 \cdot 6H_2O$ (*Sigma Aldrich*, >98 wt%) and $Ce(NO_3)_3 \cdot 6H_2O$ (*Sigma Aldrich*, 99.999 wt%). Finally, the product was dried and calcined, applying the same procedure as used with the first precursor.

Experimental conditions

The experiments performed can be classified in three groups, depending on the reactor configuration. The first group was a comparison of the catalysts' performance using a conventional fluidized bed reactor. In these experiments the

composition of the feed was an equimolar mixture of methane and carbon dioxide (representing biogas [24]), mixed with argon, in such way that biogas constituted 25 or 80% of the feed. Experiments were done at three temperatures (500, 600 and 700 °C). This series of experiments was repeated for the four catalysts prepared.

In a second group of experiments, the Pd/Ag membranes for hydrogen separation were placed inside the reactor. Experiments were started without vacuum in the permeate side (and thus without hydrogen permeation), and then, after some reaction time, hydrogen was extracted through the membrane. This operation mode allows monitoring the effect of hydrogen extraction and also checking whether there is any effect of the previous history of the catalyst on the process performance. Experiments were done with various time lengths before hydrogen extraction and at several temperatures.

In a third group of experiments, the reactor was operated as a TZFBR + MB. Thus, methane and CO_2 were fed at an intermediate point of the bed, while a regenerating gas was fed to the bottom of the bed. In each experiment, the reactor was operated alternately as a TZFBR and as a TZFBR + MB (i.e. without or with hydrogen extraction). In some experiments the regenerating agent was O_2 while in other experiments it was CO_2.

In all cases the catalyst was regenerated with 8% oxygen after the reaction experiment. The resulting gases from this combustion were analyzed by gas chromatography. The total coke content in the catalyst after the reaction experiment was calculated from the amount of CO and CO_2 formed (Eq. (1)).

$$Yield\ to\ coke = \frac{mg\ C_{regeneration}}{mg\ C_{feed}} \tag{1}$$

Results and discussion

Catalyst characterization

The surface area and the composition of the catalysts were measured before and after reaction (c.a. 40 h of time-on-stream), in order to check for changes in the catalyst. The results are shown in Table 1. A small decrease in surface area was observed, which was smaller in the case of catalysts doped with Co or Ce. The results of the chemical composition, measured by X-ray Fluorescence, were quite similar in the fresh and the used samples. A small loss of metal was

Table 1 − Catalyst characterization before and after reaction.

Catalyst	BET (m²/g)		XRF	
	Fresh	Used	Fresh	Used
5%Ni/Al₂O₃	128	108	4.9%Ni	4.0%Ni
10%Ni/Al₂O₃	112	92	9.4%Ni	7.9%Ni
5%Ni−10%Co/Al₂O₃	92	88	4.8%Ni	4.4%Ni
			8.9%Co	8.0%Co
5%Ni−10%Ce/Al₂O₃	91	88	4.6%Ni	4.6%Ni
			8.9%Ce	8.9%Ce

observed in the catalysts containing only nickel or cobalt-nickel, while this was not appreciated in the catalyst doped with ceria. The changes could be explained by some loss of active phase to the gas phase during the regeneration of the catalyst in the lower part of the bed, because of the combustion of carbon whiskers [25] which had a metal crystallite at their tops. Fig. 2 shows TEM images of a carbon whisker over the catalyst after reaction. EDS analysis corroborated that the material in the top of the whisker was a nickel particle. In spite of the small loss of surface area or metal load, a decrease in catalyst activity was not observed. The conversion values were consistent in all the experiments.

A study of crystalline species over the four fresh catalysts was made using X-ray diffraction. The data was taken at room temperature using a diffractometer Rigaku©, model D/max 2500. 2 theta interval measured was from 10 to 85°; step = 0.03°, t = 1 s/step. The spectra are shown in Fig. 3.

In catalyst samples subjected to only one impregnation process of nickel precursors, peaks corresponding to high-temperature alumina were found [26,27]. In addition, a mixed oxide of aluminum and nickel was observed (Al_2O_4Ni). Due to the active phase load, the intensity of diffraction pattern is bigger in the sample with 10% of Ni in comparison with the sample with a 5% of Ni. Nickel oxide (NiO) structure was not detected.

In order to improve Ni catalyst performance, a second impregnation process was made to introduce a second metal.

These catalysts 5%Ni/10%Ce and 5%Ni/10%Co show the presence of nickel aluminum oxide, formed previously in first impregnation process. A second oxide was detected in the case of 5%Ni + 10%Ce/Al_2O_3 CeO_2 pattern and in the case of 5%Ni + 10%Co/Al_2O_3 Co_3O_4 pattern.

Comparison of the performance of the catalysts (FBR)

Preliminary experiments were carried out to study the effect of diluting the biogas in a FBR with 15 g of catalyst (5%Ni/Al_2O_3), with a gas velocity of twice the minimum fluidization velocity (u_{mf} = 10 cm^3 (STP)/(cm^2·min)) and a ratio of $CH_4:CO_2$ = 1:1. The effect of varying the biogas concentration (25 or 80% of the total feed) can be seen in Fig. 4. The conversion obtained was smaller in the more concentrated feed, as may be expected since the number of moles in the reaction products (r.1) is larger than in the reactants. In addition, the CO_2 conversion was found to be always higher than the methane conversion, because CO_2 is also transformed to CO by the reverse water gas shift reaction (r.2). On spite of this result, from the application point of view it is desirable to work with concentrated feeds and thus to introduce less inert. Hereafter, the experiments were performed with 80% of biogas in the feed.

The effect of the reaction temperature was studied for each catalyst. As an example, the results obtained with the 5%Ni + 10%Co/Al_2O_3 catalyst at 500, 600 and 700 °C are shown in
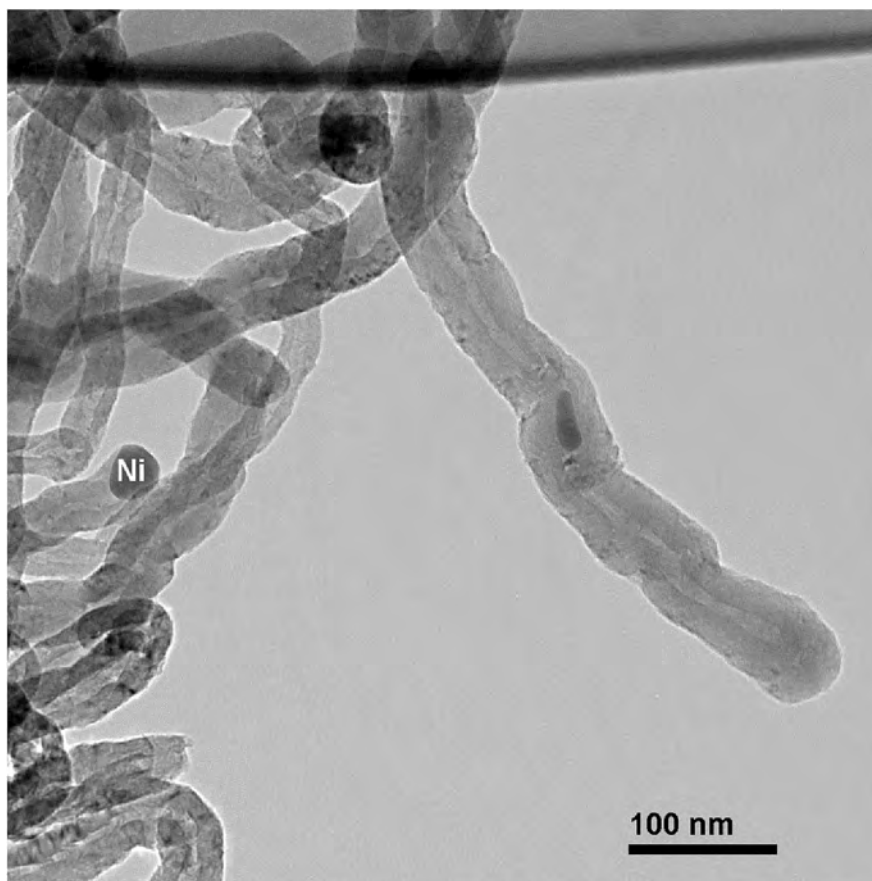

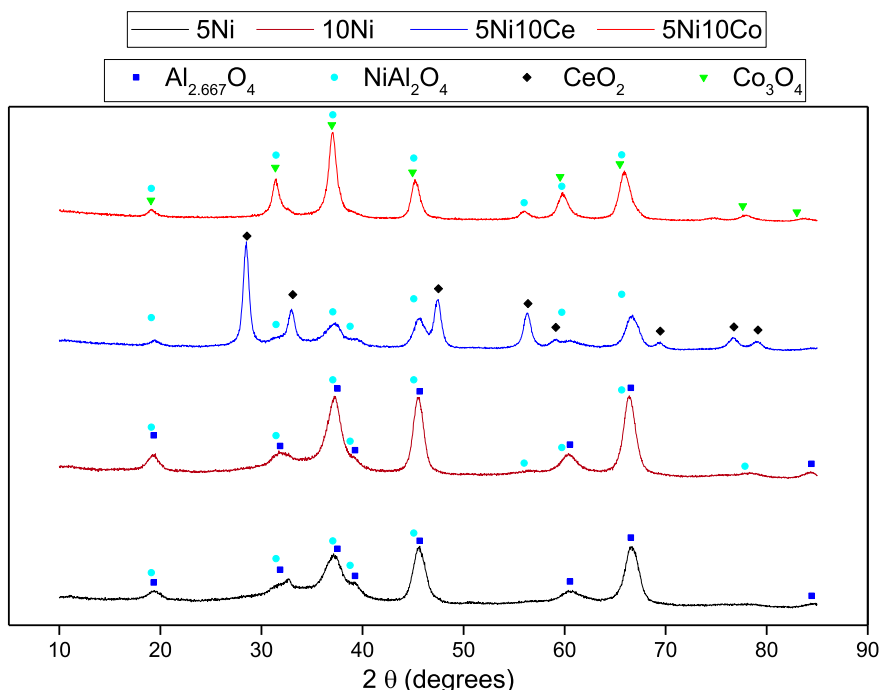**Fig. 2 — TEM image of the catalyst (10%Ni/Al_2O_3) after reaction.**

Fig. 3 − X-ray diffractogram of the four catalyst.

Fig. 5. As can be seen in this figure, an increase in the reaction temperature leads to higher conversion, the results being close to the thermodynamic equilibrium.

A comparison between the results of the four catalysts at 500 °C is shown in Fig. 6. In addition to methane conversion, other parameters, such as those shown in Table 2, are important for measuring the performance of the catalysts. The yield to hydrogen was very similar in the experiments with the four catalysts. However, the H_2/CO ratio was quite different. If hydrogen production is the desired target, a high value of H_2/CO is preferable. In this case, the highest ratio was obtained with a $10\%Ni/Al_2O_3$ catalyst.

Another result shown in Table 2 is that the catalysts on which the largest amounts of coke were formed were those in which nickel was the only metal. The catalyst with the lowest coke formation was the sample containing ceria.

Although the four catalysts tested gave similar yields to hydrogen, two catalysts were selected for the subsequent experiments: a) The catalyst containing Ce ($5\%Ni-10\%Ce/Al_2O_3$) because it provided the lowest yield to coke; b) The catalyst with the highest Ni content ($10\%Ni/Al_2O_3$) because it provided the highest H_2/CO ratio.
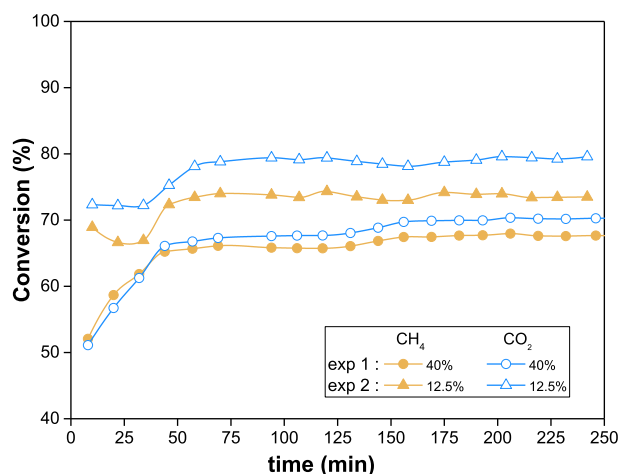

Fig. 4 − Influence of reactants ratio over biogas conversion in FBR (Exp 1 → CH_4:CO_2:Ar = 1.25:1.25:7.5 and Exp 2 → CH_4:CO_2:Ar = 4:4:2). Operating conditions: Catalyst. 5% Ni/Al_2O_3; W_{cat} = 15 g; WHSV = 0.8 h^{-1}; T = 600 °C; u = 2u_{mf}.
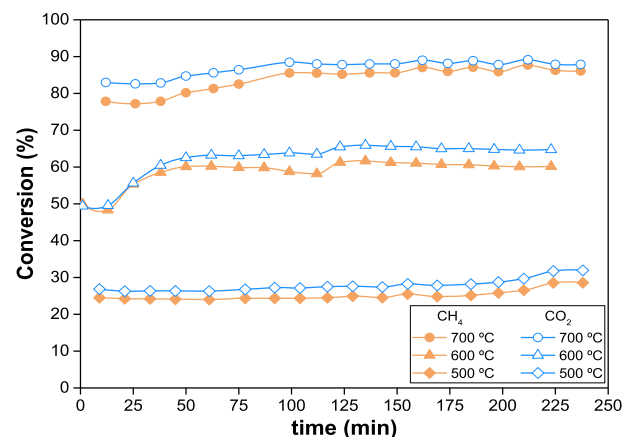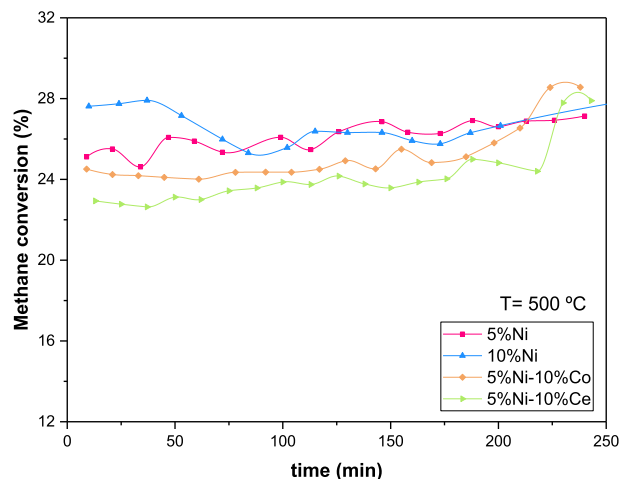

Fig. 5 − Evolution in biogas conversion (CH_4 and CO_2) at different temperatures in FBR. Operating conditions: Catalyst, $5\%Ni/Al_2O_3$; W_{cat} = 15 g; WHSV = 0.8 h^{-1}; u = 2u_{mf}, and CH_4:CO_2:Ar = 4:4:2.

Fig. 6 — Comparison of catalysts tested in the evolution of conversion in FBR experiments. Operating conditions: $W_{cat} = 15$ g; WHSV $= 0.8$ h^{-1}; T $= 500$ °C; u $= 2u_{mf}$ and CH$_4$:CO$_2$:Ar $= 4$:4:2.

Fig. 7 — Evolution in conversion of reactants for DRM experiments using fluidized bed reactor and membranes. Operating conditions: Catalyst: 5%Ni—10%Co/Al$_2$O$_3$; $W_{cat} = 15$ g; WHSV $= 0.8$ h^{-1}; T $= 500$ °C; u $= 2u_{mf}$ and CH$_4$:CO$_2$:Ar $= 4$:4:2.

Table 2 — Yield to H$_2$, H$_2$/CO ratio and yield to coke of DRM in FBR at 500 °C for the four catalysts tested. Time-on-stream: 4 h.

Catalyst	Yield to H$_2$ (%)	H$_2$/CO ratio	Yield to coke (%)
5%Ni/Al$_2$O$_3$	18	1.02	7.8
10%Ni/Al$_2$O$_3$	18	1.14	9.6
5%Ni—10%Co/Al$_2$O$_3$	17	0.80	4.4
5%Ni—10%Ce/Al$_2$O$_3$	16	0.81	4.0

Experiments in the FBR + MB system

The aim of this series of experiments was to analyze the behavior of the membranes in the reaction system (FBR). The operating conditions in these experiments were the same as in the above section. In some preliminary experiments hydrogen was extracted during the first minutes of reaction. In these experiments the selectivity quickly decreased, which can be explained by the increased tendency to coke formation when hydrogen was removed from the reactor. The hypothesis that this deactivation could be recovered by stopping the hydrogen extraction was checked. It was found that the membrane activity was not recovered. An example of this behavior is shown in Fig. 7 (exp 1). In this experiment hydrogen was extracted from the beginning, and stopped after 150 min of time-on-stream.

In a second experiment the extraction of hydrogen through the membranes was started after a period without hydrogen removal (experiment 2 in Fig. 7). The hydrogen extraction was started in this experiment after 150 min of time-on-stream. As can be clearly seen in Fig. 5, an increase in conversion was observed in the second experiment when the hydrogen removal started, as would be expected because of the equilibrium shift caused by hydrogen removal. From these experiments, we concluded that it is preferable to start the process without hydrogen extraction, following the normal operation (i.e. without hydrogen permeation) for some time

before using the membranes. A possible explanation could be that removing hydrogen when the reaction starts causes the catalyst to interact with a more oxidant atmosphere. In these conditions the metal is oxidized and consequently decay in activity is produced.

Experiments in TZFBR + MB

Experiments combining the TZFBR with the use of selective membranes are now described. A larger amount of catalyst than in the previous experiments was used, this amount being 30 g in order to achieve a higher fluidized bed and to create two zones (reaction and regeneration). The gas velocity was also modified in these experiments: the relative gas velocity (u$_r$) was three times the minimum fluidizing velocity (u$_{mf}$) in the upper zone (the reaction zone) and 1.2 u$_{mf}$ in the lower zone (the regeneration zone). The amount of synthetic biogas was 60% of the total feed (CH$_4$:CO$_2$ ratio 1:1).

Each experiment included 4 stages: a) operation as a conventional fluidized bed reactor- FBR-, b) operation as a TZFBR with CO$_2$ as the regeneration gas, c) the same as the previous stage, but including hydrogen extraction through the membrane, thus in the configuration TZFBR + MB, and d) the same as the previous stage (i.e. TZFBR + MB) but using O$_2$ instead of CO$_2$ as the regenerating gas.

As an example of the results, Fig. 8 shows the methane conversion for two experiments carried out at 500 °C and 525 °C with the 5%Ni—10%Ce/Al$_2$O$_3$ catalyst. In the first stage, after an initial period of transient operation, the conversion obtained in the FBR configuration slowly decreased with the time-on-stream. In the second stage, operating as a TZFBR with CO$_2$, a small increase in conversion and a more stable operation along time-on-stream was achieved, because the CO$_2$ counteracted the catalyst deactivation. In the third stage (TZFBR + MB), a clear increase in the methane conversion was achieved, because of the selective removal of hydrogen
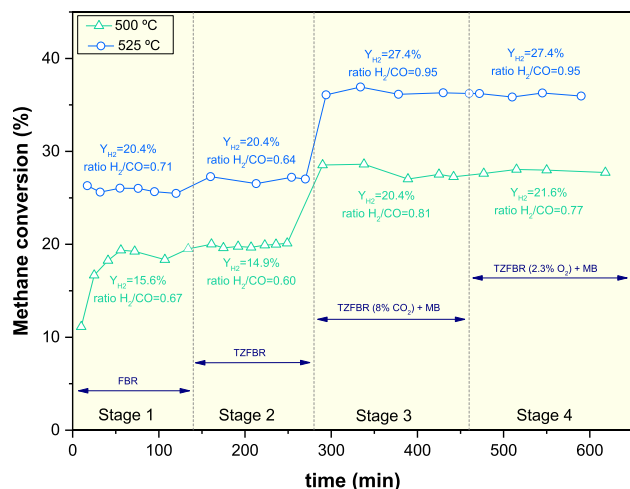
Fig. 8 – Methane conversion in two experiments at 500 and 525 °C (each including four stages) for DRM in TZFBR + MB. Operating conditions: Catalyst: 5%Ni–10%Ce/Al$_2$O$_3$; W_{cat} = 30 g; WHSV = 1.3 h^{-1}; T = 500 and 525 °C and CH$_4$/CO$_2$ = 1.

Fig. 9 – Evolution of the methane conversion in experiments with O$_2$ or CO$_2$ as regenerating gas, in TZFBR and TZFBR + MB. Operating conditions: (Catalyst: 10%Ni/Al$_2$O$_3$, W_{cat} = 30 g, WHSV = 1.3 h^{-1}, T = 500 °C and CH$_4$/CO$_2$ = 1).

through the membranes. In the fourth stage, where O$_2$ was introduced as the regenerating gas in the TZFBR + MB configuration, the methane conversion had a similar value to that in previous stage. These results suggest that CO$_2$ and O$_2$ are both effective as regenerating gases. With both regenerating gases the methane conversion was much higher in the TZFBR + MB than in the conventional FBR reactor, and was highly stable during the time-on-stream. In all cases, an increase in methane conversion was observed when the temperature was increased, as may be expected since DRM is an endothermic reaction.

A series of experiments was made to check the effect of using O$_2$ or CO$_2$ as the regenerating gas, and the effect of the amount of regenerating gas used. To this end the catalyst with the highest tendency to coke formation was chosen (10%Ni/Al$_2$O$_3$). These two-stage experiments were conducted with the reactor acting as a TZFBR in the first stage and as a TZFBR + MB (i.e. extracting hydrogen through the membrane) in the second stage. Fig. 7 shows the results for experiments with two different percentages of oxygen in the feed and with a given percentage of CO$_2$. The methane conversion is given for the three experiments. By comparing the results using oxygen as the regenerating gas, it may be seen that with a percentage of oxygen of 2.3% some deactivation was observed, which indicates that the amount of oxygen was not enough to remove in the bottom zone all the coke formed in the upper zone. When the percentage of oxygen in the feed was increased to 3.5% a steady performance was achieved, suggesting that there was enough oxygen to continuously burn the coke in the lower zone at the same rate as it was formed in the upper zone. The experiment using CO$_2$ was carried out with 7% of this gas in the feed because, according to the stoichiometry, the amount of CO$_2$ needed to gasify a given amount of coke is twice that of O$_2$. It was found, as may be seen in Fig. 9, that a steady operation was achieved both in the TZFBR and in the TZFBR + MB configurations. In all cases the increase in methane conversion
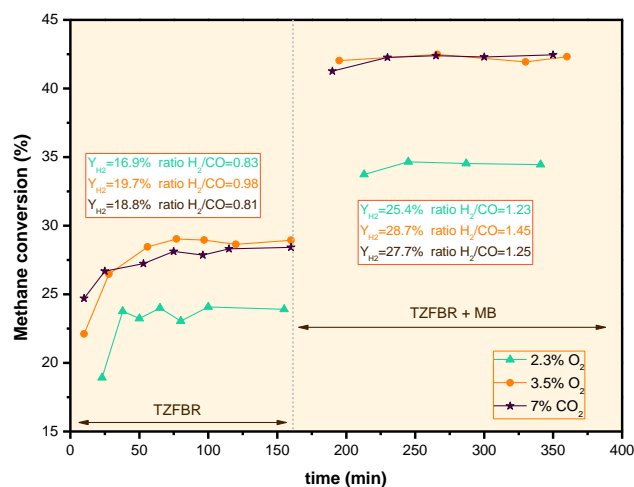
when hydrogen was removed through the membrane was clear. Therefore, it may be concluded that CO$_2$ can be employed as a regenerating gas in this system, including when there is high coke formation because hydrogen is removed from the reactor. The use of CO$_2$ has the advantage over O$_2$ that the risk of forming an explosive atmosphere inside the reactor is avoided. This could be a decisive advantage for the industrial implementation of a TZFBR.

Comparison with the literature

In addition to the improvement in activity and stability described above (e.g. as illustrated in Fig. 7), the use of a TZFBR + MB configuration also provided an interesting increase in the overall selectivity to hydrogen. An analysis of the
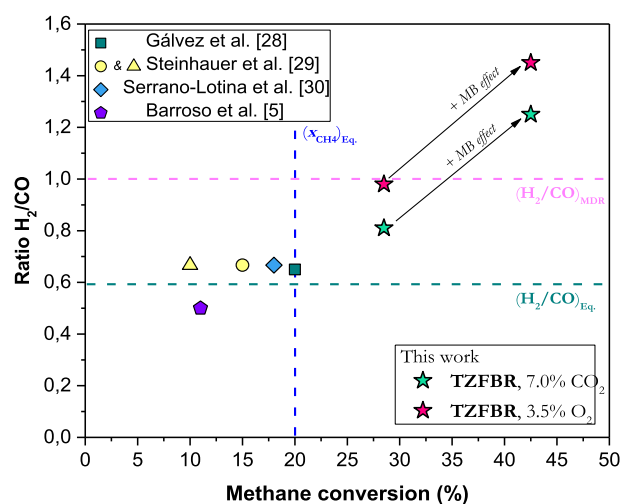
Fig. 10 – H$_2$/CO ratio in the global outlet gas stream. Comparison with previous studies using similar temperatures and feed ratios.

H_2/CO ratio in the products obtained clearly shows the improvement over previous results reported in the literature. Fig. 10 shows a comparison with other results using a $CH_4:CO_2$ molar ratio of 1:1, in all cases with similar catalysts. The use of a TZFBR provided small increases in methane conversion and the H_2/CO ratio compared with other published results, but the increases obtained with a TZFBR + MB configuration are substantially larger. In fact, the methane conversion and the H_2/CO are higher than the values that could be achieved according to the thermodynamic equilibrium in a conventional reactor.

An additional advantage is that part of the H_2 is obtained with a high degree of purity and can therefore be employed in cases where such purity is essential, for example in fuel cells.

All these advantages are a result of the process intensification derived from carrying out the desired reaction, the catalyst regeneration and the separation of the products simultaneously in the same reactor [28—30,5].

Conclusions

It is possible to carry out the dry reforming of methane in fluidized bed reactors, achieving methane conversion values close to the thermodynamic equilibrium and without observing loss of conversion with time-on-stream. The four catalysts prepared in this study, based on Ni, Ni—Ce and Ni—Co as the active phase, showed similar results with very close values of conversion, selectivity and yields. The catalyst containing Ce had the least coke formation while the catalyst containing only Ni, with 10%wt, gave the highest yield to hydrogen, although also the highest selectivity to coke. The four catalysts showed a negligible loss of active phase and surface area after reaction.

It was found that the TZFBR + MB needs an initial period of activation without the removal of hydrogen because otherwise the loss of catalyst activity at the start of the reaction is too quick. This could be related with deactivation caused by an excessively oxidizing atmosphere, because the amount of coke initially deposited on the catalyst was too small to consume all the oxygen in the lower zone of the reactor.

The use of the TZFBR + MB system provided much higher conversion than the same system without membranes, and the former system operated in a steady manner throughout the experiment. It was found that CO_2 can be employed as a regenerating gas with a similar effectiveness as O_2, providing similar trends and values of conversion, H_2/CO ratio and selectivity.

Although there is still room for a broader study analyzing the effect of every operation variable for a detailed optimization, the above conclusions point to the high potential of the TZFBR + MB for dry reforming of methane or other similar reactions, because of the high conversion and hydrogen yield achieved.

Acknowledgements

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