CHEMICAL ENGINEERING TRANSACTIONS, Volume 11, 2007
Edited by Sauro Pierucci
Copyright © 2007, AIDIC Servizi S.r.l., ISBN 978-88-95608-00-6

Two stage operation for hydrogen production from methane in fluidized bed reactors

P. Ammendola[1], R. Chirone[1], G. Ruoppolo[1], G. Russo[1,2]
[1]Istituto di Ricerche sulla Combustione - CNR – P.le Tecchio 80, 80125 Napoli - Italy
[2]Dip. Ing. Chim., Università Federico II – P.le Tecchio 80, 80125 Napoli – Italy

Fluidized bed reactors have been recently proposed as an useful solution for the thermo-catalytic decomposition (TCD) of CH_4 into H_2. Present paper addresses on the possibility of carrying out a two stage operation for H_2 production from methane TCD, consisting into firstly operating a bubbling fluidized bed reactor for CH_4 decomposition until a limit deactivation degree of catalyst is achieved and then operating the fluidized bed as a combustor for catalyst regeneration by carbon removal. Typical behaviors of fluidized bed combustion contribute to the opportunity of adopting such regeneration strategy on the basis of an efficient carbon removal from the catalyst and the recovery of the performances of regenerated catalyst.

1. Introduction

The thermo-catalytic decomposition (TCD) of CH_4 is an attractive process towards the production of H_2 with reduced CO_2 emissions. The use of a catalyst is extremely advantageous since the non-catalytic thermal decomposition would require elevated process temperatures (above 1200°C), even if it deactivates due to deposition of produced carbon on its surface (Muradov and Veziroğlu, 2005).

Catalytic systems containing Ni (Takenaka et al., 2003) and Fe (Takenaka et al., 2004) have been largely tested in the past. The Ni based catalysts have a maximum operative temperature of 600°C, limiting the hydrogen concentration in the produced stream. On the contrary, Fe based catalysts are more stable at higher temperatures (700-1000°C), but deactivation occurs upon repeated cycles, resulting in a short lifetime (Ogihara et al., 2006). In addition, whatever the catalyst, deposited carbon has generally a filamentous form (nanofibres or nanotubes) with metal particles on their tips. This is an undesirable feature to the reference to applications where comminution phenomena can result into removal of the active metal phase away from the support, involving a decrease of hydrogen production and an increase of consumption of metals (Muradov and Veziroğlu, 2005).

Consequently, new criteria have to be taken into account for catalyst design. In particular, a suitable catalyst should be characterized by a low propensity to attrition in addition to the requirements of high thermal stability and conversion efficiency (Ogihara et al., 2006) when used in fluidized bed reactors, that have been indicated in the last years as a very attractive solution for TCD process (Muradov and Veziroğlu, 2005).

Muradov and Veziroğlu (2005) have investigated the feasibility of using carbon (activated carbon and carbon black) as a catalyst in fluidized beds. In spite of their advantages (low cost, high temperature resistance, tolerance to potentially harmful compounds), they are less active than metal catalyst and also deactivate because the carbon produced has a lower activity than that of initial catalyst.

Ammendola et al. (2007) have proposed a copper based catalyst. Advantages of this catalytic system are: i) relatively high catalytic activity (between that reported for carbon and nickel based catalysts); ii) high operative temperature (up to 1000°C); iii) relatively high mechanical resistance to attrition; iv) carbon deposition without formation of fibres with metal particles on their tips. The experimental activities (Ammendola et al., 2006) have shown that, under the operative conditions tested, attrition is not able to prevent catalyst deactivation due to carbon deposition and a regeneration strategy of the catalyst is required.

Both carbon combustion (Monnerat et al., 2001) or carbon gasification (Choudhary et al., 2001) can be considered attractive procedures even if both have advantages and drawbacks. In the first case CO_x are in principle only formed during the carbon removal from the catalyst in the regeneration phase and as a consequence they are separated in time from H_2. An additional advantage due to the coupling of the endothermic hydrocarbon cracking and the exothermic carbon oxidation is that the heat released during the carbon oxidation can be used in situ to sustain the decomposition reaction. In the second case the use of steam as regeneration agent results in an additional H_2 production also during the catalyst regeneration and in the prevention of catalyst re-oxidation.

The present study addresses on the possibility of a periodic operation strategy for the thermo-catalytic decomposition of methane and for the removal of the deposited carbon from the catalyst surface with different oxygen mixtures. In particular, the possibility to carry out a two stage operation for hydrogen production from methane TCD in a bubbling fluidized bed reactor has been investigated. The objective of the activity has been: i) the definition of a suitable catalyst deactivation degree before regeneration; ii) the possibility of using air as regeneration agent; iii) the time of the regeneration phase. The regeneration strategy has been analyzed on the basis of the efficiency of carbon removal and the performances of regenerated catalyst with respect to the operation in the TCD process. The practical applicability of such regeneration strategy is strictly related to the use of a fluidized bed combustion process as expected on the basis of peculiar aspects of such process and as confirmed by a comparative analysis carried out in the framework of this activity on the performances obtained with fixed and fluidized bed reactors during catalyst regeneration.

2. Experimental

A home-made Cu based catalyst (300-400μm particle size) (Ammendola et al., 2007), resistant to attrition, has been used. The material belongs to the group B of Geldart's classification of powders (Geldart, 1973). The catalytic fluidized bed apparatus used for catalytic tests is described in Ammendola et al. (2006).

Methane decomposition experiments were carried out at 800°C and with an inlet gas made of methane (5%vol.) in nitrogen flow. A 2.5%vol. oxygen in N_2 stream or air have been used for the regeneration step at 800°C. Decomposition and regeneration tests were carried out using 25g of catalyst at a superficial gas velocities of 8.7cm/s, corresponding to 3 times the value of the minimum fluidization velocity (2.9cm/s experimentally determined at bed temperature). During each test the time resolved profiles of pressure drops, bed temperature and concentrations of different species analyzed have been recorded.

The regeneration strategy has been analyzed on the basis of the efficiency of carbon removal and the performances of regenerated catalyst with respect to the operation in the TCD process. The reactor has been operated under repeated cycles of decomposition and regeneration tests using the same batch of catalyst, in order to verify the catalyst stability. In addition, methane decomposition test in the bubbling fluidized bed has been carried out until a limit deactivation degree of catalyst is achieved and then as a combustor for catalyst regeneration by carbon removal. N_2 is fluxed for two minutes to wash the reactor between the two phases. Different combustion times and oxygen concentrations in the inlet gas have been used. A comparison between the performances obtained with fixed and fluidized bed configuration during the catalyst regeneration step has been also carried out under the same experimental conditions.

3. Results and discussion

Typical curves of CH_4 conversion and of H_2 production obtained during a TCD test carried out in the fluidized bed reactor are reported in fig.1. At time t=0 an inlet gas made of CH_4 (5% vol.) and N_2 is fed to the reactor. Analysis of the curves shows that there are three stages. Firstly, all the methane reacts with the oxygen of the oxidized catalyst (linked to the copper) according to the total oxidation reaction ($4\ O_s + CH_4 \rightarrow CO_2 + 2\ H_2O$). This reaction is faster than those of decomposition and partial oxidation. After this initial step, CH_4 still reacts with the residual oxygen O_s of the catalyst according to CH_4 partial oxidation reaction ($O_s + CH_4 \rightarrow CO + 2\ H_2$), probably due to the reduced O_s availability, and CO and not CO_2 is produced. Accordingly, CO monotonically decreases corresponding to the consumption of the O_s present in the catalyst. At the same time the decomposition reaction ($CH_4 \rightarrow 2\ H_2 + C$) also occurs and H_2 is produced according to both methane partial oxidation and decomposition reactions, justifying the initial hydrogen peak. The curves show that it is not possible to achieve a stationary regime due to catalyst deactivation as a result of carbon deposition. However, CH_4 conversion does not drop to zero and a relatively low residual conversion is observed, probably related to a catalytic activity played by the deposited carbon (Muradov, 1998).

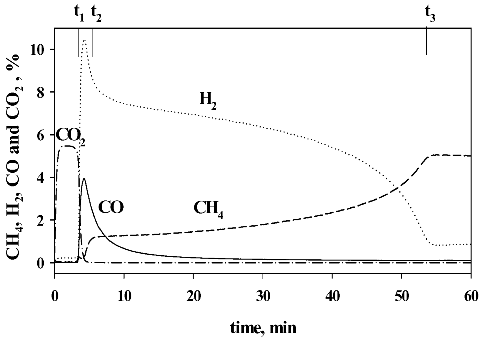

Figure 1: Typical catalytic activity test in the fluidized bed reactor. Feed composition: CH_4 (5%vol.) in N_2; T=800°C; m_{cat}=25g; U=8.7cm/s.

After the decomposition test, a regeneration treatment of catalyst has been carried out using poor (2.5vol%) or concentrated (21%vol.) oxygen mixture at 800°C.

In fig.2 the concentration curves of products obtained during a regeneration treatment carried out after a first methane decomposition step with poor oxygen mixture in both fixed and fluidized bed reactor configurations are reported. The same amount of carbon deposited on the catalyst was initially present.

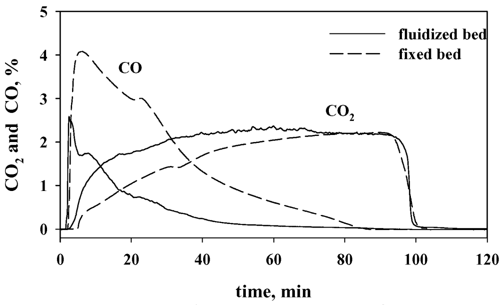

Figure 2: CO and CO_2 concentration curves as function of time obtained during the regeneration treatment in fixed (– – –) and fluidized (—–) bed configuration . Feed composition: O_2 (2.5%vol.) in N_2; T=800°C, m_{cat}=25g; U=8.7cm/s.

In both cases CO_2 and CO are produced even if the product distributions are different: the CO_2/CO ratio is 5 and 1.2 in the fluidized and fixed bed respectively; about 100 minutes are required to complete the regeneration.

In both cases, the total amount of carbon removed (25mg_C/g_{cat}), evaluated from the amounts of CO_x produced, is in agreement with the carbon deposited on the catalyst during the previous decomposition step (23mg_C/g_{cat}). The catalyst regeneration with O_2 2.5%vol. mixture is able to remove all the carbon deposited. A surplus of oxygen consume (26-28mmmol), in addition to this related to the CO_x formation, has been observed, due to the re-oxidation of the catalyst, already reduced by methane during the decomposition test.

The reactor temperature doesn't increase during the regeneration carried out in the fluidized bed, confirming its high efficiency of heat transfer, while a temperature increase of about 13°C has been observed in the fixed bed.

In both reactor configurations after the regeneration treatment the activity of catalyst in the decomposition phase is completely restored, even after more than one cycle (10 cycles).

As regards the use of air as regeneration agent, the complete regeneration of catalyst required a lower (about ten times) time of treatment than that performed with a 2.5% oxygen containing mixture. Also in this case, the total amounts of CO_x produced are in agreement with the carbon deposited on the catalyst during the respective decomposition step. The CO_2/CO ratio obtained during the regeneration with undiluted air is 6.7 and 0.7 in the fluidized and fixed bed, respectively.

A temperature increase higher than 70°C has been observed in the case of fixed bed, while the use of fluidized bed prevent the overeating of the catalyst.

Decomposition tests carried out after the regeneration treatment with undiluted air in the fluidized configuration show that also in this case the activity of catalyst is completely restored and the catalyst is stable under repeated decomposition-regeneration cycles. On the contrary, a decomposition test carried out after the regeneration treatment with air in the fixed bed configuration shows a lost of catalyst activity of about 30%. The catalyst deactivation, occurring in the fixed bed, is probably due to the local overheating of the catalyst surface, which reaches very high temperatures.

On the basis of these results it is possible to conclude that the catalyst is stable under repeated decomposition-regeneration cycles, also using air, provided that the process is carried out in fluidized beds.

In first analysis, the cyclic process has been simulated in fluidized conditions switching between two different feeds, the first containing CH_4 (5%vol.) in N_2 and the second containing O_2 (2.5%vol.) in N_2 or undiluted air. The decomposition time (about 25 min) has been chosen as that corresponding to the change in the slope of the methane conversion curve of the test reported in fig.1. A symmetric period (time of decomposition = time of regeneration), as reported by Monnerat et al. (2001), has been chosen for poor oxygen mixture, while the regeneration time has been fixed at different values (4min, 3min, 2min, 90s, 60s and 30s), lower than the decomposition one, for undiluted air. The periodic variation of the product concentrations is presented in fig.3a (2.5%vol. O_2) and fig.3b (air with a regeneration time of 2min), where D and R stay for the decomposition and the regeneration step, respectively.

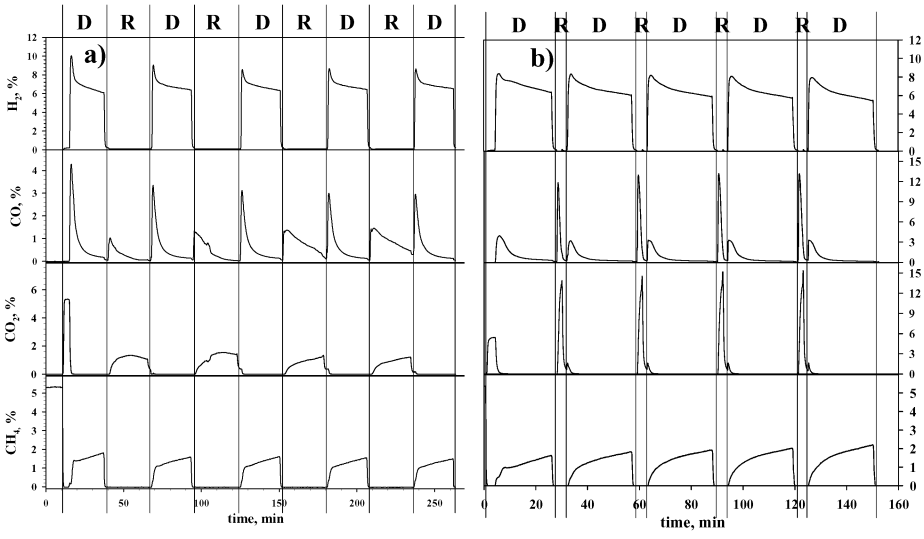

Figure 3: Concentrations profiles during the cyclic process in fluidized bed. D=decomposition, R=regeneration. Decomposition feed: CH_4 (5%vol.) in N_2; T=800°C, m_{cat}=25g; U=8.7cm/s. Decomposition time=25min; N_2 washing time=2min. a) Regeneration feed: O_2 (2.5%vol.) in N_2 and regeneration time=25min. b) Regeneration feed: O_2 (21%vol.) in N_2 and regeneration time=2min.

Analysis of fig.3a shows that: i) the methane conversion, i.e. the hydrogen production, is stable during the different cycles; ii) after the first cycle the total amount of CO_x produced during the decomposition phase is reduced with respect to that obtained during the first one; iii) from the second cycle the only oxygenate species produced during the decomposition phase is CO and the production of CO_2 is totally suppressed. The last behaviour could be explained by a non complete re-oxidation of the catalyst. In fact, as before evidenced, in order to completely regenerate and to completely re-oxidize the catalyst, a period of 100 min is required under the same operative conditions.

The suppression of the production of CO_2 in the first cycle could be easily obtained pre-reducing the catalyst as shown in a previous work (Ammendola et al., 2007).

As concerns the cycles with air the production of CO_2 is not totally suppressed during the decomposition phase (traces are present at the outlet) suggesting that the time of regeneration treatment of only two minutes is enough not only to restore the catalyst activity but also to re-oxidized the catalyst itself too much.

Comparison of performances obtained during cyclic processes carried out with air at different regeneration times highlighted that the regeneration time influences not only the catalyst re-oxidation, i.e. the CO_x production during the decomposition phase but also the amount of carbon removed, i.e. the regenerated catalyst activity. In particular, in order to obtain a stable H_2 production regeneration time larger than 2min are required; while to suppress the CO_2 production regeneration times shorter than 90s are required. In any case, the CO production can not be avoided. The optimal regeneration time should take into account these two opposite effects.

4. Conclusions

The possibility of carry out a two stage operation for hydrogen production from methane TCD has been investigated. Results shows that the catalyst is stable under decomposition and regeneration in oxidative atmosphere, even using undiluted air provided that the process is carried out in a fluidized bed reactor. A stable and continuous production of CO_2 free hydrogen could be obtained by cycling process using low oxygen concentration mixture during the regeneration phase. The use of undiluted air allow to strongly reduce the regeneration time, even if a stable hydrogen production is always associated to a not negligible CO_2 formation.

5. References

Ammendola, P., Chirone, R., Lisi, L.,Ruoppolo, G., Russo, G., 2007, J. Mol. Catal. A-Chem., 266, 31 in press.

Ammendola, P., Ruoppolo, G., Chirone, R., Russo, G., 2006, in F. Winter (Ed.), Proceedings of 19th International Conference on Fluidized Bed Combustion, Vienna, Austria.

Choudhary, V. R., Banerjee, S., Rajput, A. M., 2001, J. Catal. ,198, 136.

Geldart, D., 1973, Powder Technol., 7 285.

Monnerat, B., Kiwi-Minsker, L., Renken, A., 2001, Chem. Eng. Sci., 56, 633

Muradov, N. Z., 1998, Energ. Fuel., 12, 41.

Muradov, N. Z. and Veziroğlu, T. N., 2005, Int. J. Hydrogen Energ., 30, 225.

Ogihara, H., Takenaka, S., Yamanaka, I., Tanabe, E., Genseki, A., Otsuka, K., 2006, J. Catal., 238, 353.

Takenaka, S., Kobayashi, S., Ogihara, H., Otsuka, K., 2003, J. Catal., 217, 79.

Takenaka, S., Serizawa, M., Otsuka, K., 2004, J. Catal., 222, 520.