Journal of Catalysis **198,** 136–141 (2001)
doi:10.1006/jcat.2000.3135, available online at http://www.idealibrary.com on IDEAL®

Continuous Production of H_2 at Low Temperature from Methane Decomposition over Ni-Containing Catalyst Followed by Gasification by Steam of the Carbon on the Catalyst in Two Parallel Reactors Operated in Cyclic Manner

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Received September 21, 2000; revised November 24, 2000; accepted November 27, 2000; published online February 1, 2001

CO-free H_2 in close to stoichiometric amounts was produced continuously at a constant H_2 production rate by the stepwise steam reforming of methane at low temperature (500°C) in two parallel catalytic reactors operated in cyclic manner. The process involved two simultaneous reactions: first, catalytic decomposition of methane to H_2 and carbon (deposited on the catalyst), and second, gasification of the carbon deposited on the catalyst by steam to H_2 and CO_2. The two reactions were carried out separately in two parallel reactors (both containing the same Ni-containing catalyst), operated in cyclic manner by switching a methane-containing feed and a steam-containing feed between the two reactors at a predecided interval of time. The process shows best performance at an optimum value of the feed switchover time. Among the different Ni-containing metal oxide (ZrO_2, MgO, ThO_2, CeO_2, UO_3, B_2O_3 or MoO_3) and zeolite [HZSM-5, Hβ, HM, NaY, Ce(72)NaY, or Si-MCM-41] catalysts, the Ni/ZrO_2 and Ni/Ce(72)NaY showed promising results for the cyclic process. © 2001 Academic Press

Key Words: **low-temperature CO-free hydrogen production; catalytic methane decomposition; gasification of carbon on catalyst by steam; Ni-containing catalysts; parallel catalytic reactors operated in cyclic manner; feed switchover between two reactors.**

INTRODUCTION

The demand for hydrogen is ever increasing due to its use in various hydrotreating processes in petroleum industries and also for hydrogen fuel cells. Hydrogen is a nonpolluting fuel and its use as fuel in fuel cells used in automobiles is increasing day by day. However, the hydrogen fuel cells require CO-free hydrogen to avoid deactivation of its costly noble metal catalyst. Apart from water, methane is a preferred source of hydrogen due to its high hydrogen-to-carbon ratio. The conventional steam reforming and autothermal reforming processes for the production of H_2 from methane are high-temperature processes (>800°C) and produce CO (which is converted by a water–gas shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, in a downstream processing step) as one of the major byproducts. Hence, efforts are being made for producing CO-free hydrogen from low-temperature catalytic stepwise steam reforming of methane (1–3), involving the following reactions in consecutive steps:

$$CH_4 \rightarrow C\ (\text{on catalyst}) + 2H_2 \quad [1]$$

$$C\ (\text{on catalyst}) + 2H_2O \rightarrow CO_2 + 2H_2. \quad [2]$$

Zhang and Amiridis (1) have carried out the above two reactions alternatively (one after another) over Ni/SiO_2. Choudhary and Goodman (2) have passed alternative pulses of methane (5% CH_4 in He) and water (2 μl) over Ni/ZrO_2 at 375°C to obtain CO-free hydrogen from the above reactions. Very recently, Choudhary and Goodman (3) have studied the two steps of the process by carrying out the two reactions above alternatively as a function of temperature and surface coverage of carbon. They observed that the removal of surface carbon in reaction [2] becomes increasingly difficult at higher temperatures and surface coverage of carbon. In all of the above investigations, the two reactions were carried out one after another in cyclic manner in the same reactor and there was no continuous decomposition of methane and/or gasification of carbon from the catalyst.

For commercial application, both reactions need to be carried out continuously without disturbing feed for reactions [1] and [2] for the continuous production of H_2 from methane and water. In this paper, we report a continuous production of H_2 from methane and water in two steps, reaction [1] followed by reaction [2], by carrying out the two reactions simultaneously and continuously in cyclic manner over a Ni-containing catalyst in two parallel fixed bed reactors at a low temperature (500°C) by switching two feeds—first, a methane–N_2 mixture, and second, a steam–N_2 mixture—between the two reactors at a fixed interval of

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0021-9517/01 $35.00

TABLE 1

Results of the Cyclic Stepwise Steam Reforming of Methane over Different Ni-Containing Metal Oxide (Ni/M = 1.0) Catalysts (Prereduced by H_2 at 500°C for 4 h)

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	No. of feed switchovers	TOF ($mmol \cdot g^{-1} \cdot h^{-1}$)	H_2 produced per mole of CH_4 converted (mol)	Pressure drop (atm)	
					Initial[a]	Final[b]
Ni/ZrO_2	62.8	36	11.3	3.8	0.02	0.02
Ni/MgO	33.0	12	7.9	3.6	0.02	0.02
Ni/ThO_2	59.0	10	9.5	2.9	0.02	0.21
Ni/UO_3	6.0	12	8.7	3.1	0.02	0.16
Ni/CeO_2	43.0	10	8.8	3.0	0.02	0.18
Ni/B_2O_3	37.4	12	7.7	3.2	0.02	0.08
Ni/MoO_3	11.4	12	6.4	3.5	0.02	0.04
Ni–Co/ZrO_2[c]	31.1	14	8.0	3.7	0.02	0.03

Note. Reaction conditions: Feed A = 18.2 mol% CH_4 in N_2, GHSV of Feed A = 7100 $cm^3\ g^{-1}\ h^{-1}$; Feed B = 20.5 mol% steam in N_2, GHSV of Feed B = 7290 $cm^3\ g^{-1}\ h^{-1}$; temperature = 500°C and feed switchover time = 10 min.

[a,b] Pressure drop across the catalyst bed for the methane decomposition step at the start of the first cycle and at the end of the last cycle, respectively.

[c] Ni : Co : Zr = 1 : 1 : 2.

time. A number of Ni-containing catalysts were evaluated for their performance in the process.

EXPERIMENTAL

Ni/ZrO_2, Ni/ThO_2, and Ni-Co/ZrO_2 catalysts (Table 1) were prepared by coprecipitating the corresponding metal hydroxides from their aqueous solution containing respective metal nitrates using sodium hydroxide at pH 9.0 at room temperature. The precipitate was thoroughly washed, dried, and then calcined at 600°C for 2 h under static air. Ni/MgO (Table 1) catalyst was also prepared by the similar coprecipitation method except that the precipitating agent used was sodium carbonate. Ni/CeO_2, Ni/UO_3, Ni/MoO_3, and Ni/B_2O_3 catalysts (Table 1) were prepared by thoroughly mixing nickel nitrate with ammonium cerium (IV) nitrate, uranyl acetate, ammonium molybdate, or boric acid while grinding the mixed salts in the presence of water just enough to form a thick paste, which was then dried and calcined as above. Ni/HZSM-5, Ni/Si-MCM-41, Ni/H-Mordenite, Ni/Hβ, Ni/NaY, and Ni/Ce(72)NaY catalysts (Table 2) were prepared by impregnating nickel nitrate on HZSM-5 (Si/Al = 40), Si-MCM-41, H-Mordenite (Z-900 H, Norton Co., USA), Hβ, NaY, or CeNaY (degree of Ce^{+3} exchange = 72%), using the incipient wetness technique, followed by drying and calcining in air at 500°C for 4 h. All the above catalysts were powdered, pressed, and crushed to particles of 30–52 mesh size.

The methane decomposition and carbon gasification reactions over the catalysts were carried out in two parallel stainless steel fixed bed reactors, each containing a 0.4-g catalyst. The two had different feeds but a common outlet.

TABLE 2

Results of the Stepwise Steam Reforming of Methane over Different Nickel (10 wt%) Impregnated Zeolite Catalysts (Prereduced at 500°C for 4 h)

Catalyst	Surface area ($m^2 \cdot g^{-1}$)	No. of feed switchovers	TOF ($mmol \cdot g^{-1} \cdot h^{-1}$)	H_2 produced per mole of CH_4 converted (mol)	Pressure drop (atm)	
					Initial[a]	Final[b]
Ni/H-ZSM-5	266.0	12	9.6	3.7	0.03	0.04
Ni/Si-MCM-41	786.0	12	8.7	3.7	0.03	0.04
Ni/H-Mordenite	319.7	18	6.9	3.6	0.03	0.04
Ni/H-beta zeolite	408.0	10	10.8	3.4	0.03	0.15
Ni/NaY	450.0	12	9.6	3.3	0.03	0.20
Ni/Ce(72)NaY	341.8	12	10.7	3.6	0.03	0.05

Note. Reaction conditions: same as those given in Table 1.

[a,b] Pressure drop across the catalyst bed for the methane decomposition step at the start of the first cycle and at the end of the last cycle, respectively.

A flow switchover valve was connected to inlets of the two reactors to switch the two different gaseous feeds between the two reactors. One feed (called Feed A) was a mixture of methane and nitrogen, and the other (called Feed-B) was a mixture of steam and nitrogen. The two feeds were switched between the two reactors at a fixed interval of time (called feed switchover time). The experimental arrangement is shown schematically in Fig. 1. Before carrying out the reactions, the catalyst in both reactors was reduced in a flow of H_2–N_2 mixture (50 mol% hydrogen) at 500°C for 4 h. The reaction temperature in both reactors was controlled by a Cr–Al thermocouple located in the catalyst bed. The reactor effluent gases were cooled to about 2°C using a coiled condenser immersed in the ice-water slurry to remove the water from the product gases. The product gases were collected in a collapsible plastic bag for a reaction period of 2 h and then analyzed by a gas chromatograph with TCD detector, using Porapak Q and Spherocarb columns. Also in the separate experiments, the product gases at a constant flow rate (35 $cm^3 \cdot min^{-1}$) were passed through the TCD and FID detectors connected in series (without any gas chromatographic column) using nitrogen as a carrier gas, for continuously measuring the concentrations of hydrogen (by TCD) and methane (by FID) present in the product gases as a function of reaction time (time-on-stream).

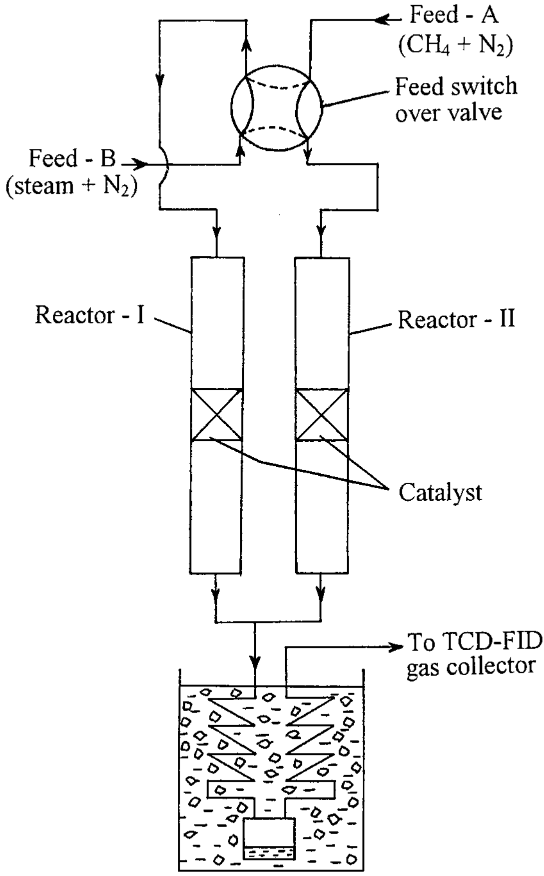

FIG. 1. Schematic experimental arrangement for carrying out catalytic methane decomposition and carbon gasification reactions simultaneously in two separate parallel catalytic reactors in cyclic manner by switching two different feeds (Feed A and Feed B) between the two reactors after an interval of time in order to produce H_2 continuously at a constant rate by the cyclic stepwise steam reforming of methane.

The gas hourly space velocity (GHSV) of both the feeds was measured at 0°C and 1 atm pressure. Under the reaction conditions employed in the present investigation, no formation of carbon monoxide in the cyclic process over all the catalysts was observed.

RESULTS AND DISCUSSION

Results of a representative experiment for the cyclic stepwise steam reforming of methane (at 500°C) over the Ni/ZrO_2 catalyst in the two parallel reactors operated in cyclic manner with a feed switchover time of 10 min are presented in Fig. 2. In this case, the combined feed streams (without steam) and the combined gaseous product streams (after the removal of water from them) are directly passed through the TCD and FID detectors connected in series. The frontal chromatograms obtained by the FID (Figs. 2a, 2b) show the relative concentration of methane in the combined feed streams and in the combined product streams. The chromatogram (Fig. 2b) indicates a steady conversion of methane (19.6%, after correcting for a change in the gas flow rate due to the reaction) in the process. The observed downward spikes, which are due to a momentary change in flow rate, correspond to the switchover of Feed A and Feed B between the two reactors (Figs. 1 and 2). The frontal chromatograms obtained by the TCD (Figs. 2c, 2d) indicate the formation of hydrogen in the process; the detector response for the product stream is higher because of the higher thermal conductivity of H_2 present in the products, as compared to the components in the feed. Because of the detector's high sensitivity toward a small change in the gas flow rate, which results from the feed switchover between the two reactors, upward spikes and up-and-down steps in the chromatogram (Fig. 2d) are observed. Nevertheless, the results (Fig. 2) clearly show that H_2 can be produced continuously almost at the same rate and also without affecting the feed flow rates by carrying out the methane decomposition (reaction [1]) and the carbon gasification by steam (reaction [2]) simultaneously in two separate reactors operated in parallel, while switching the methane-containing feed (Feed A) and the steam-containing feed (Feed B) between the two reactors at a predecided interval of time. Under the experimental conditions, the conversion of methane at thermodynamic equilibrium is estimated to be 59.4%. However the observed methane conversion is less than the equilibrium one.

The amount of carbon formed in the methane decomposition for the total reaction period of 6 h (36 cycles) is

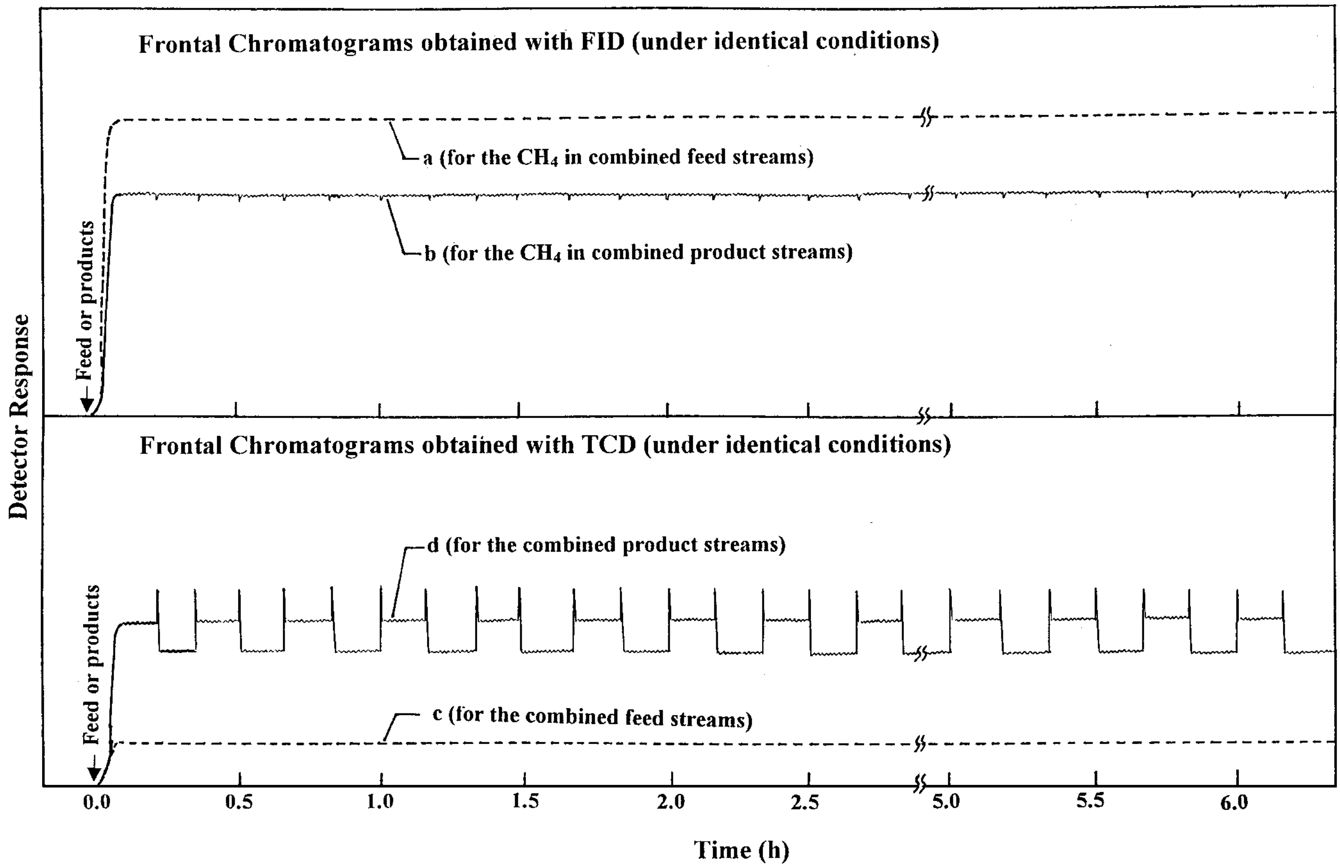

FIG. 2. Representative frontal chromatograms obtained with FID and TCD for the combined feed streams and the combined product streams of the stepwise steam reforming of methane carried out in two parallel reactors, each containing the same catalyst (Ni/ZrO_2), at 500°C and with a feed switchover time of 10 min. Feed A = 18.2 mol% CH_4 in N_2; Feed B = 20.5 mol% steam in N_2; GHSV of Feed A = 7100 $cm^3 g^{-1} h^{-1}$; GHSV of Feed B = 7290 $cm^3 g^{-1} h^{-1}$.

estimated as 0.82 g per gram of catalyst, whereas the carbon leftover on the catalyst after the reaction (at the end of 36th cycle) was 0.044 g per gram catalyst. This shows that almost 95% of the carbon formed in the process was gasified in the steam treatment cycles and hence there was no increase in the pressure drop across the catalyst bed in both parallel reactors. However, when the carbon formed in the methane decomposition was not removed intermittently by its gasification with steam, there was an appreciable and continuous increase in the pressure drop with an increase in the time-on-stream, particularly about the reaction period of 30 min.

It may also be noted that the catalyst did not show a sign of deactivation in the process for a sufficiently long period (Fig. 2). However, when we carried out the methane decomposition alone (without the cyclic operation) over the same catalyst under similar conditions continuously for a period of 2 h, we observed a steady conversion of methane (19.6 ± 0.2%), even though there was a continuous built up of carbon (estimated as 0.27 g per gram at the end of the run) on the catalyst. The pressure drop across the catalyst bed was increased continuously from its initial value of 0.02 to 0.12 atm. A steady methane conversion in the decomposition of methane for a long period was also observed earlier for the Ni/SiO_2 catalyst (1) and Ni (or Co)/Al_2O_3 (4) catalyst. However, a need for the intermittent removal of carbon from the catalyst by its gasification by steam is necessary to avoid the undesirable large pressure drop across the catalyst due to formation of excessive carbon between the catalyst particles. Moreover, the removal of carbon from the catalyst is more and more difficult at higher and higher surface coverage of carbon (3). The aging of carbon during the methane decomposition process is also expected to cause a change in the nature and/or form of the carbon deposited on the catalyst, making removal of the carbon increasingly difficult. Moreover, the aging may lead to a permanent deactivation of the catalyst or reduce drastically the catalyst regenerability.

Results showing the influence of the feed switchover time on the process performance are presented in Fig. 3. Both the methane conversion and the H_2 productivity, and consequently the CO_2 produced in the process, are passed

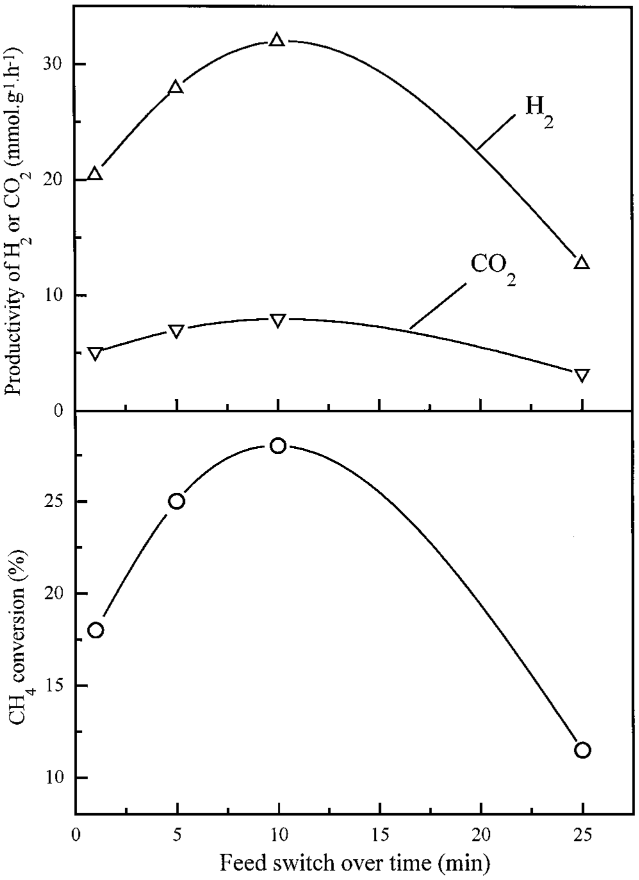

FIG. 3. Effect of feed switchover time on the process performance using Ni/ZrO_2 (Ni/Zr = 1.0) catalyst. Feed A = 20 mol% CH_4 in N_2; Feed B = 80.9 mol% steam in N_2; GHSV = 3225 (feed A) and 6770 (feed B) $cm^3 \cdot g^{-1} \cdot h^{-1}$; temperature in both reactors = 500°C.

through a maximum (at a feed switchover time of about 10 min) with increasing feed switchover time from 1.0 to 25.0 min. The amount of H_2 produced per mole of the methane converted was 3.9 ± 0.05, which is very close to the stoichiometric amount (4.0) expected to be formed in the cyclic process. The results clearly show that there is an optimum value for the feed switchover time; it is 10 min for the Ni/ZrO_2 catalyst under the specified reaction conditions. However, the optimum value may vary with the reaction conditions for the same catalyst and it may also differ from catalyst to catalyst. Further studies are required for knowing the carbon retained on the catalyst after each successive cycle (i.e., the methane decomposition followed by the carbon gasification) and its dependence on the different process conditions.

The observed lower methane conversion and consequently the lower H_2 productivity, at the high switchover time (25 min), is certainly due to a larger amount of carbon deposited on the catalyst. However, the observed lower methane conversion for the shorter feed switchover time (1 and 5 min) as compared to that at the optimum switchover time (10 min) is unusual. At the very short feed switchover time (1.0 min), the carbon deposited on the catalyst is expected to be much smaller and hence a higher methane conversion is expected. The observed higher methane conversion at the intermediate feed switchover time indicates a beneficial effect of the presence of carbon species at an optimum concentration on the surface of the catalyst for it to be more active in the methane decomposition. A further detailed investigation is required for understanding the observed optimum feed switchover time in the process of this investigation. Also longer duration tests (>100 h) are necessary to assess deactivation and to determine steady-state carbon deposition on the catalyst.

Results on a few more Ni-containing metal oxides and zeolite catalysts for the stepwise steam reforming of methane (at 500°C) operated in the cyclic manner in the two parallel reactors with a feed switchover time of 10 min for a time-on-stream of 2 h are presented in Tables 1 and 2. TOF was estimated as the amount of methane converted per unit mass of catalyst per unit time. The initial and final pressure drops across the catalyst bed were measured for the methane decomposition step in the cyclic process.

Among the Ni-containing metal oxide catalysts (Table 1), the Ni/ZrO_2 showed the best performance in the cyclic process, whereas among the Ni-containing zeolite catalysts (Table 2), the Ni/Ce(72)NaY showed the best performance. Although the Ni/Hβ showed methane conversion activity comparable to that of Ni/Ce(72)NaY, the former produced less H_2 per mole of methane converted and also a larger amount of carbon accumulated on the catalyst, resulting in an undesirable pressure drop across the catalyst bed. The Ni/UO_3, Ni/ThO_2, Ni/CeO_2, Ni/B_2O_3, and Ni/NaY catalysts also showed a high pressure drop across the catalyst bed; the pressure drop was found to increase exponentially with increasing reaction period (or number of cycles). The high pressure drop observed for these catalysts resulted mainly due to the formation of filamentous carbon blocking the interparticle voids in the catalyst bed. This was confirmed by observing a drastic reduction in the pressure drop, approaching its initial value, due to an air oxidation of the catalyst at 500°C. Because of the larger amount of carbon accumulated on these catalysts, the H_2 produced per mole of the methane converted was appreciably lower than the expected theoretical value (4.0). For the cyclic process, the Ni/ZrO_2 catalyst, however, showed the best performance—highest TOF (methane conversion activity), highest moles of H_2 (3.8) produced per mole of CH_4 converted, and almost no pressure drop across the catalyst bed, even when operated for a much larger number of cycles.

In their earlier cyclic pulse studies, Choudhary and Goodman (2, 3) obtained 1.0 to 1.3 mol H_2 per mole of methane consumed in the methane decomposition step over Ni/ZrO_2 catalyst at 375°C. However, in the present cyclic process the H_2 produced is almost close to the stoichiometric amounts. This is expected most probably because of the fact that, unlike the cyclic pulse process, the present process operates under or very close to a steady state and also involves the reforming by steam of partially hydrogenated carbon species (produced in the methane decomposition step) into CO_2 and H_2 in the steam treatment step.

Apart from its low-temperature operation, another important advantage of the present process is that the CO conversion by the water gas-shift reaction, which is an integral part of the H_2 production processes practiced at present, is not required, thus eliminating the low- and high-temperature water-gas shift reactors for the downstream processing of the product stream. The commercial feasibility of the process will be increased by achieving higher methane conversion close to that at equilibrium through optimizing process parameters and developing a better catalyst for the process.

CONCLUSIONS

The following important conclusions have been drawn from this investigation:

(i) It is possible to produce continuously hydrogen at a constant rate and also close to stoichiometric amounts by the cyclic stepwise steam reforming of methane at a low temperature (500°C), by carrying out catalytic methane decomposition and gasification of carbon deposited on the catalyst during the methane decomposition separately in two parallel catalytic reactors containing the same catalyst, operated in cyclic manner by switching the methane-containing feed and the steam-containing feed between the two reactors at a known interval of time.

(ii) The feed switchover time has an optimum value for achieving the best performance in the process.

(iii) Ni/ZrO_2 and Ni/Ce(72)NaY are promising catalysts for the cyclic stepwise steam reforming of methane to hydrogen and CO_2 at a low temperature (500°C).

ACKNOWLEDGMENT

S. Banerjee is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for awarding him a Senior Research Fellowship.

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