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Carbon dioxide reforming of methane under periodic operation

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Abstract−The carbon dioxide reforming of methane under periodic operation over a commercial $Ni/SiO_2 \cdot MgO$ catalyst was investigated at two different temperatures, 923 and 1,023 K. According to this operation, pure methane and carbon dioxide were alternately fed to the catalyst bed where methane cracking and the reverse Boudouard reaction took place, respectively. Therefore, hydrogen and carbon monoxide products appeared separately in different product streams. The performance of this operation was compared to that of the steady state operation with simultaneous feed of both carbon dioxide and methane. At 1,023 K, the methane conversion and hydrogen yield from the periodic operation initially decreased with time on stream and eventually leveled off at values about half of those obtained in the steady state operation with co-feed of both reactants. The decreased catalytic activity was due to the accumulation of carbonaceous deposit and loss of metal active sites. However, a different trend was observed at 923 K. The methane conversion and hydrogen yield were almost constant over the time on stream, although more carbonaceous deposit was progressively accumulated on the catalyst bed during the reaction course. At this temperature, the periodic operation offered the equivalent hydrogen yield to the steady state operation. The observed behavior could be due to the different mechanisms of carbon formation over the catalyst. Finally, it was found that cycle period and cycle split did not influence the reaction performance within the ranges of this study.

Key words: Periodic Operation, Dry Reforming, Methane, Nickel Catalyst, Hydrogen

INTRODUCTION

Carbon dioxide reforming of methane is an effective way to produce synthesis gas and to utilize green house gases simultaneously. The reaction produces synthesis gas with low H_2/CO ratio, which is suitable for producing valuable chemicals such as alcohol, aldehyde and isobutene. Several supported transition metal catalysts (Ni, Ru, Rh, Pd, etc.) have been used for the carbon dioxide reforming of methane [Gadalla et al., 1988; Rostrup-Nielsen et al., 1993; Inui et al., 1997]. Nickel is well-known as an active catalyst for this highly endothermic reaction and mainly used in industry due to its low cost. A typical problem found for this reaction is catalyst deactivation due to the carbonaceous deposition, which is mainly generated from the following catalytic cracking of methane [Kim et al., 2003].

$$CH_4 \rightarrow C+2\,H_2 \tag{1}$$

However, the presence of carbon dioxide theoretically helps the removal of deposited carbon according to the following reverse Boudouard reaction [Takano et al., 1996].

$$C+CO_2 \rightarrow 2CO \tag{2}$$

According to the above reactions, the carbon dioxide reforming of methane [Eq. (3)] can be operated periodically by feeding methane and carbon dioxide alternately.

$$CH_4+CO_2 \rightarrow 2CO+2\,H_2 \tag{3}$$

Under periodic operation, hydrogen and carbon monoxide are generated at different time, and therefore, these products can be directly separated without additional significant effort. This operation is attractive particularly in the case when carbon monoxide-free hydrogen is required for some applications as in a proton-exchange membrane (PEM) fuel cell. The periodic operation for this reaction is conceptually attractive; however, there is still no effort to demonstrate experimentally the benefit of the operation.

Although researches focusing on the use of carbon dioxide for removing deposited coke on catalysts are not widely performed, the uses of oxygen and/or steam are more common. It was reported that both oxidation with oxygen, and steam gasification could restore the catalytic activity of Ni-based catalyst after deactivation due to carbon formation [Zhang, and Amiridis, 1998]. In previous studies, Ni/SiO_2 catalyst could be fully regenerated at 923 K with steam for up to 10 successive cracking/regeneration cycles without any significant loss of catalytic activity [Aiello et al., 2000]. While the hydrogen production from cracking of methane over Ni guaze catalyst [Monnerat et al., 2001] could be optimized by operating reaction periodically with the catalyst regeneration in oxygen atmosphere under suitable period and cycle split. Moreover, the Ni/Al_2O_3 showed more activity with low carbonaceous deposition, by repeating many cracking/regeneration cycle (D-R treatment) [Ito et al., 1999] with carbon dioxide before using in reforming reaction.

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In this work, the periodic operation for the carbon dioxide reforming of methane was investigated. The operation involved two steps of 1) methane decomposition reaction and 2) catalyst regeneration via oxidation in carbon dioxide mixture of the deposited coke. The effects of operating variables of periodic operation such as operating temperature, cycle period (τ) and cycle split (s) on conversions of methane and carbon dioxide, and yield of hydrogen are investigated and compared to the results from steady state operation with simultaneous feed of both carbon dioxide and methane.

EXPERIMENTAL

1. Reaction Procedure

An industrial steam reforming catalyst, Ni/SiO$_2$·MgO, containing 55 wt% of nickel with surface area of 1.23×10^5 m^2/kg and nickel diameter of 44 nm was employed for the carbon dioxide reforming of methane in this research. A schematic diagram of the experimental setup, as shown in Fig. 1, consists of a gas feeding section, a fixed-bed reactor and an analytical section. High purity methane (99.999%) and carbon dioxide (99.999%) were used as the reactant gases. The feed was switched periodically between opening and closing by Solenoid valve (Flon industry, Japan), which was controlled by an on-off timer (Sibata BT-3). Argon was used for purging the system, and hydrogen was used for reducing catalyst before the experiment.

The reaction was carried out in a quartz tube fixed-bed reactor (internal diameter=0.011 m, length=0.5 m) heated by a temperature controlled electric oven. A thermocouple was placed in the furnace, at the level of the catalyst bed, to monitor temperature. A U-tube manometer, which was filled with silicone oil was positioned at the entrance of the reactor for indication of the pressure drop in the reactor, could be used as an emergency pressure relief valve. Experiments were performed using 0.3 g of Ni/SiO$_2$·MgO catalyst, diluted with silicon carbide (1.0 g). The catalyst was reduced in a hydrogen flow (5×10^{-7} m^3/s) at 923 K for 1 h before use. The reaction was conducted at atmospheric pressure. The reactor effluent from periodic operation experiments was collected by a sample bag at the exit of the reactor. The sample product gas was analyzed with a TCD gas chromatograph (Schimadzu GC-8A, Japan) equipped with a Porapak-Q and Molecular Sieve 5A column. Argon was used as the carrier gas in the gas chromatograph with the flow rate of 0.5×10^{-6} m^3/s.

2. Catalyst Characterization

Spent catalyst from the deactivation and regeneration experiments was studied with a JEOL JSM-35CF scanning electron microscopy (SEM) that was operated by using the back scattering electron (BSE) mode at 15 kV. The XRD spectra of fresh and spent catalysts were measured by a SIEMENS D5000 X-ray diffractometer using Cu Kα radiation with an Ni filter in the 10-80° 2-θ angular region.

RESULTS AND DISCUSSION

1. Characteristics of Carbon Dioxide Reforming of Methane Under Periodic Operation

The behavior of the carbon dioxide reforming of methane under periodic operation was first investigated. In the first step, the catalytic cracking of methane [Eq. (1)] was carried out by feeding pure methane (4.167×10^{-7} m^3/s) to the catalyst bed operated at 1,023 K to determine the catalyst activity along time on stream of methane for 225 min. The methane conversion of Ni/SiO$_2$·MgO was approximately 73% at the beginning and declined rapidly to about 50% within 25 min, Fig. 2. Then the conversion decreased to 15% after 50 min of reaction and fell slightly until the end of reaction. The U-tube pressure manometer indicated stable pressure drop in the first period of reaction. However, after 20 min, the pressure drop increased gradually until reaching a plateau in about 50 min of time on stream. It was revealed from the results that catalyst loses its activity due to carbonaceous deposition on the catalyst according to the methane cracking reaction, resulting in lowering conversion and increasing pressure drop within about 20 min.

After testing the catalytic activity of the methane cracking, we performed catalyst regeneration with carbon dioxide at the same operating temperature to investigate the time to restore spent catalyst. In this experiment, a spent catalyst after exposure in methane cracking for 25 min was used to prevent complete deactivation with coke formation. Significant amount of coke was accumulated in the catalyst bed after the methane cracking (not shown). The catalyst regeneration was performed by feeding pure carbon dioxide

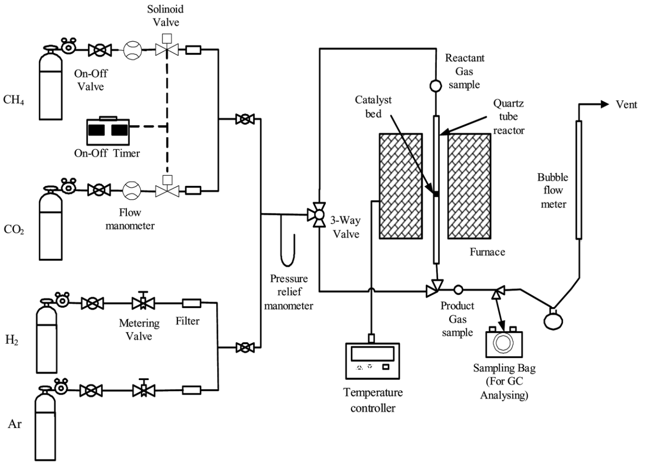


Fig. 1. Schematic diagram of the experimental setup for carbon dioxide reforming of methane under periodic operation.

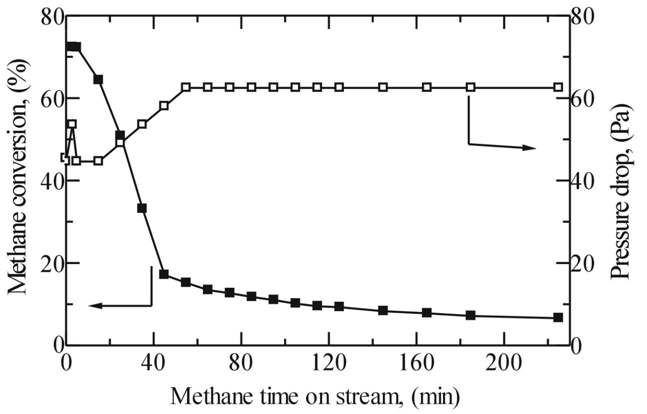


Fig. 2. Changes in catalytic activity and pressure drop of the catalytic cracking of methane over Ni/SiO$_2$·MgO (T=1,023 K and methane flow rate=4.167×10^{-7} m^3/s).

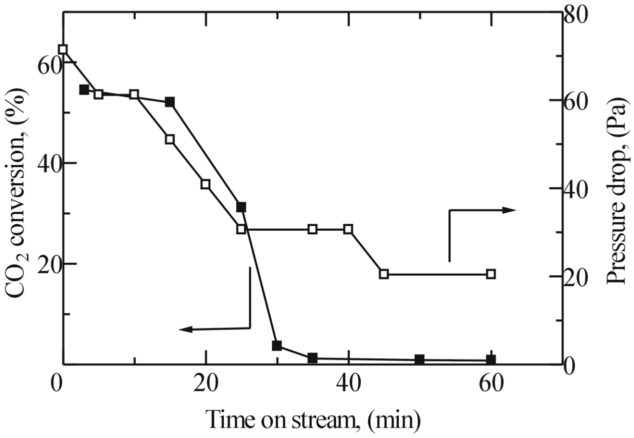


Fig. 3. Changes in CO_2 conversion and pressure drop over spent $Ni/SiO_2 \cdot MgO$ catalyst after 25 min of methane cracking (T= 1,023 K and CO_2 flow rate=4.167×10^{-7} m^3/s).

(4.167×10^{-7} m^3/s) to the catalyst bed. Only carbon monoxide was detected as a main product according to the reverse Boudouard reaction [Eq. (2)].

Fig. 3 shows that the conversion of carbon dioxide was stable at about 54% for 20 min and then decreased steeply to about 3% after 30 min of time on stream of CO_2. Pressure drop decreased gradually from 60 Pa to 30 Pa in about 25 min, and declined slightly until the feed was stopped. It is expected that most of deposited coke could be removed from the spent catalyst within about 20 min of the regeneration step by reacting with carbon dioxide. From the above results, further studies were performed using a cracking period not to exceed 20 min for preventing complete deactivation of catalyst. Moreover, the regeneration period with carbon dioxide was not kept longer than 20 min to allow efficient utilization of carbon dioxide.

2. Performance Comparison of Carbon Dioxide Reforming of Methane Under Periodic and Steady State Operations

Performance comparison was considered for two cases of interest: steady state operation and periodic operation. All experiments were conducted at 1,023 K, atmospheric pressure and total reaction time of 200 min. For the steady state operation, a mixture of methane (2.083×10^{-7} m^3/s) and carbon dioxide (2.083×10^{-7} m^3/s) was allowed to flow through the catalyst bed in the reactor, whereas the periodic operation experiments were performed using a constant cycle split (s) of 0.5 and the flow rate of each reactant was kept at (4.167×10^{-7} m^3/s). The cycle split is defined as the duration of the cracking period divided by the duration of the cycle period (τ). In this study the cycle period (τ) was varied from 40 min (5 cycles) to 20 min (10 cycles), and 10 min (20 cycles). It should be noted that the time-average feed flow rates were equivalent in all experiments; therefore, the performance comparison was based on the same average feed rate or time on stream. Fig. 4 shows the profiles of methane conversion with time on stream for both steady state and periodic operations. It should be noted that the methane conversion of the periodic operation was time-average conversion calculated from average composition of gas product collected after the end of each cracking/regeneration cycle. It was found that the steady state operation offered a stable methane conversion at 90%, indicating no significant deactivation at least within 200 min of time on stream. In contrast, the periodic operation showed an initial conversion of about 80% which was around 10% lower than that of the steady state operation. The conversion further decreased and became stable after approximately 160 min of time on stream. It is obvious that the methane conversion from the periodic operation was inferior to that of the steady state operation over all ranges of reaction time.

The profiles of carbon dioxide conversion with time on stream are shown in Fig. 5. Similar to the previous results, the carbon dioxide conversion from the steady state operation (85%) did not change with time on stream, whereas the carbon dioxide conversion from the periodic operation decreased with increasing repeating cracking/regeneration cycles and then leveled off at high reaction cycles. However, after 160 min of time on stream the rates of coke formation and the coke removal seemed to be equivalent as the conversions of methane and carbon dioxide became nearly the same at around 40%; consequently, the conversions for both reactants no longer changed with reaction time. The profiles of hydrogen yield are shown in Fig. 6.

Clearly, periodic operation offered much lower hydrogen yield

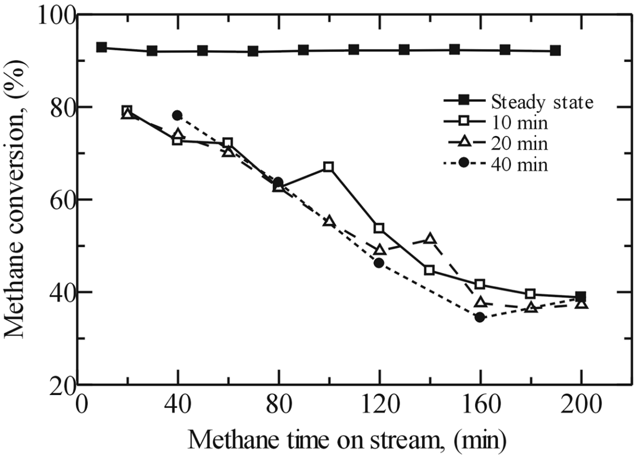


Fig. 4. Comparison of methane conversion between steady state operation and periodic operation at different cycle periods over $Ni/SiO_2 \cdot MgO$ catalyst (T=1,023 K).

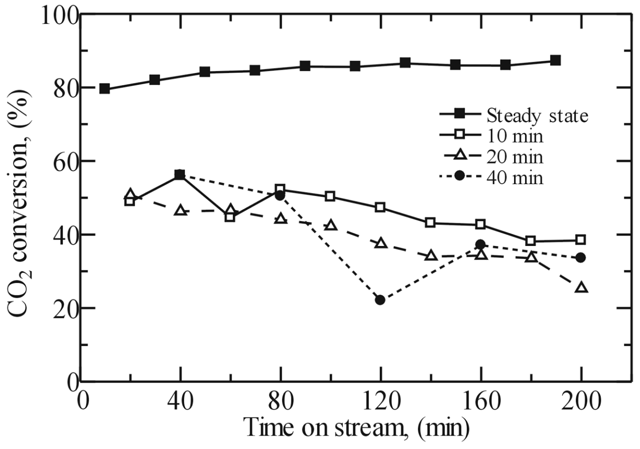


Fig. 5. Comparison of CO_2 conversion between steady state operation and periodic operation at different cycle periods over $Ni/SiO_2 \cdot MgO$ catalyst (T=1,023 K).

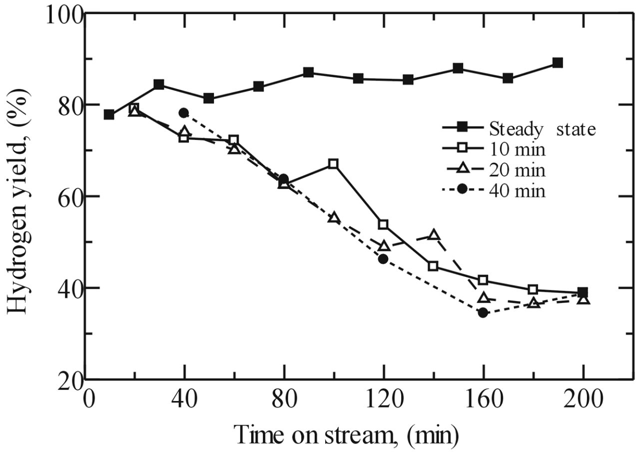


Fig. 6. Comparison of hydrogen yield between steady state operation and periodic operation at different cycle periods over Ni/SiO_2·MgO catalyst (T=1,023 K).

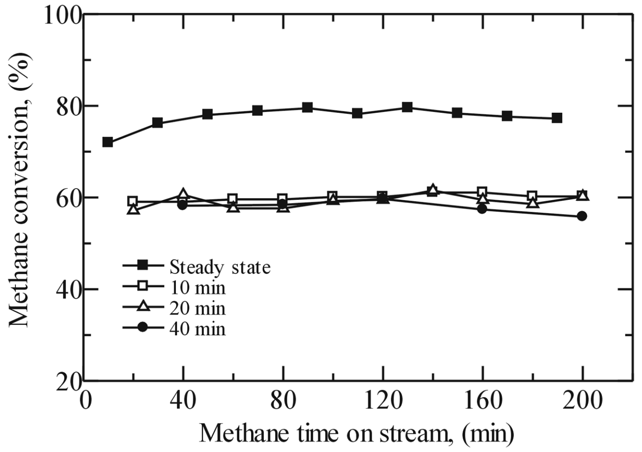


Fig. 7. Comparison of methane conversion between steady state operation and periodic operation at different cycle periods over Ni/SiO_2·MgO catalyst (T=923 K).

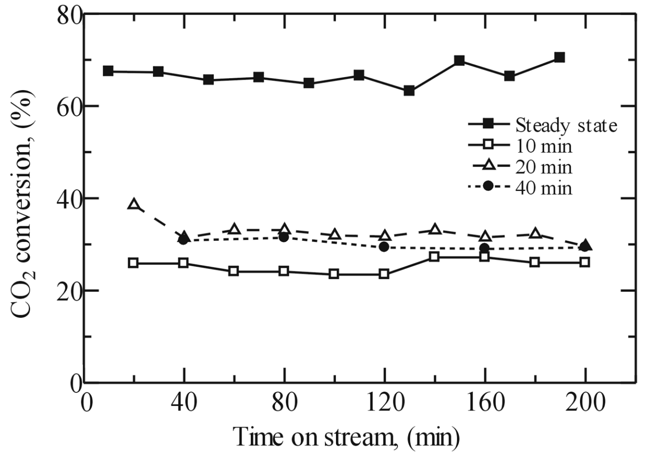


Fig. 8. Comparison of CO_2 conversion between steady state operation and periodic operation at different cycle periods over Ni/SiO_2·MgO catalyst (T=923 K).

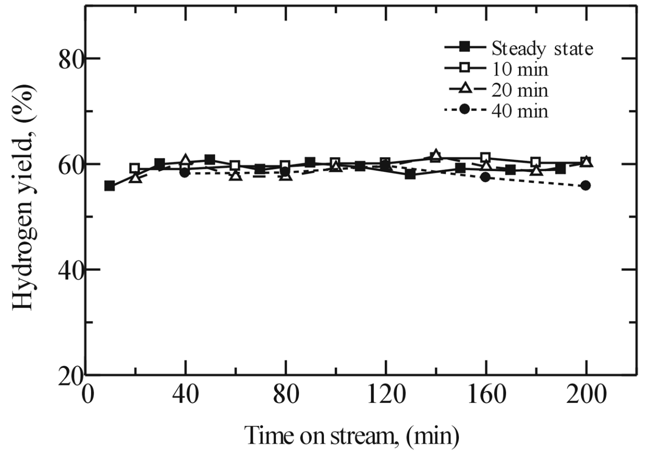


Fig. 9. Comparison of hydrogen yield between steady state operation and periodic operation at different periods over Ni/SiO_2·MgO catalyst (T=923 K).

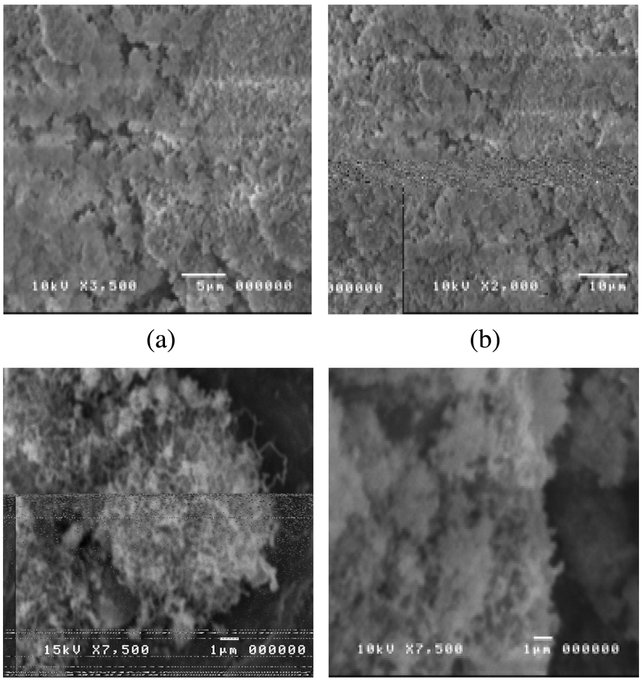
than steady state operation. The experimental results at different cycle periods (τ=40, 20 and 10 min) indicate that the cycle period does not pronouncedly affect the reaction performance, Figs. 4-6. At higher cycle period, although the catalyst highly deactivated due to the formation of coke during the methane cracking step, more coke can be removed during the regeneration step. Therefore, the average reaction performance does not change significantly.

Another set of experiments was performed using operating conditions similar to the previous study, except that the temperature was changed from 1,023 K to 923 K. Figs. 7, 8 and 9 show the profiles of methane conversion, carbon dioxide conversion and hydrogen yield with time on stream at 923 K, respectively. The result indicates that for the steady state operation, the methane conversion at 923 K was also stable but the activity is about 10% lower than that at 1,023 K. This should be due to the lower reaction rate and less thermodynamic feasibility at lower temperature. For the periodic operation it was found that the methane conversion at 923 K was also stable at approximately 60% and independent of the cycle period. However, unlike the operation at 1,023 K, no indication of activity loss was detected at this operating temperature.

The profiles of carbon dioxide conversion with time on stream for both steady state and periodic operation at 923 K (Fig. 8) also show stable conversions at approximately 70% and 25-30%, respectively. Considering the obtained hydrogen yield (Fig. 9), it was found that the periodic operation provided hydrogen yield as high as that of the steady state operation, indicating equivalent performance of periodic operation at 923 K. Based on these results, the periodic operation seemed to become an attractive operation mode at 923 K regarding the equivalent hydrogen yield and stable performance as well as the capability to separate product streams of hydrogen and carbon monoxide.

According to the measurement of carbon deposition on the catalyst surface after exposure in the periodic operation at 923 K by comparing the conversions of methane and carbon dioxide, the results surprisingly indicate that more coke was further accumulated in the catalyst bed after each cracking/regeneration cycle. The unusual stable reaction activity throughout the reaction course at 923 K, which was in contrast to the behavior at 1,023 K reported earlier, was then further investigated. Scanning electron microscopy (SEM) technique was used to observe the differences between catalyst samples that were subjected to 10 cracking/regeneration cycles (τ=20 min) with reaction temperature 923 K and 1,023 K, as well as a fresh catalyst sample. Both micrographs of the spent catalysts at 923 K (Fig. 10d) and 1,023 K (Fig. 10c) show the surface to be covered with filamentous carbon, in contrast to the clean surfaces of fresh catalyst (Figs. 10a and 10b).

In order to understand this dissimilar behavior, an X-ray diffraction technique was chosen to identify the crystal structure of Ni metallic and other metal forms on the catalysts. The characterizations were performed for the spent catalysts obtained after the periodic operation experiments at 923 K (τ=10 and 20 min) and 1,023 K (τ=10 min) with the cycle split (s) of 0.5. Measurements of the fresh catalyst and the spent catalyst after the steady-state operation at 923 and 1,023 K were also carried out for comparison. The XRD patterns, shown in Fig. 11, indicate that nickel contained in the fresh catalyst has crystal structure of NiO (peaks at 2θ=37.1, 43.1 and 62.7), which would be reduced with hydrogen to convert nickel oxide into the metallic nickel before the reaction is started. It also shows that the presence of carbon of graphitic nature, evident from the strong peak at 2θ=26, was accumulated in the fresh catalyst sample as well as carbon accumulated in the spent catalysts. Considering the spent catalyst from the periodic experiment with a cycle period (τ) of 20 min at 1,023 K, the strong peaks of Ni metallic crystallites at 2θ=44.5, 51.8, and 76.4 were observed with only small intensity of NiO peaks. It was presumed that NiO in the fresh catalyst could be completely reduced to metallic form after pre-reduction step. For the spent catalysts at lower temperature (923 K), the XRD patterns of the spent catalysts with τ=10 and 20 min indicated the existence of NiO peaks with lower Ni metallic intensity. It was suggested that NiO could be formed during the cracking/regeneration period and considered to be the active components for cracking period at 923 K. The XRD patterns of the spent catalysts from the steady-state operation for both temperature levels also indicate results similar to those of the periodic operation. Therefore, it is evident that the metal active sites involved in the reaction are in different form depending on the operating temperature.



(a) (b)

(c) (d)

Fig. 10. SEM Micrograph of (a) and (b) fresh catalyst, (c) spent catalyst at 1,023 K, and (d) spent catalyst at 923 K after 10 successive cracking/regeneration cycles.

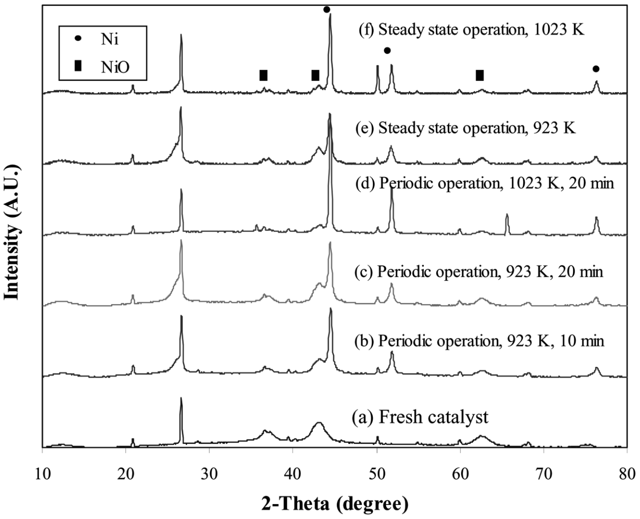


Fig. 11. XRD spectra of fresh catalyst and spent catalysts.

It can be concluded that, according to the different operating temperature and form of metal active site, the mechanisms of coke formation are different. Many researchers have suggested that the main type of carbon species which would be formed during the cracking period at high temperature was carbon whisker [Kuijpers et al., 1981; Poirier et al., 1997]. In the early stages of the deposition step, deposited carbon filaments could detach small nickel cores from bulk nickel on support. Then, the detached nickel cores which act as a growing core of whisker carbon could still accelerate the rate of carbonaceous deposition and increase their length with time on stream. After switching to the regeneration step, the carbon filaments are burned out with carbon dioxide and the nickel particles fall on the surface. The small nickel particles removed by regeneration may become inactive after the next cracking steps. Based on this suggestion, at a reaction temperature of 1,023 K, it may be stated that the growth of new carbon filaments could be terminated as a result of losing nickel active sites and no accumulation of carbon whisker on catalyst surface would occur during repeating cracking/regeneration. Consequently, the methane conversion decreased with time on stream as clearly shown in Fig. 4.

Considering the experimental results at 923 K, the formation of carbon filament was expected to be hindered by the low solubility of carbon in metal particle at low temperature. Moreover, the strong interaction between surface oxygen and metallic Ni, which results in formation of NiO in periodic operation at 923 K, was suggested to terminate the diffusivity of carbon into the nickel. These should be the cause of the different type of carbon formation at 923 K. In addition, the coke formed on the metal active sites may further move to the catalyst support, according to the drain-off phenomena that has been reported in some reaction systems. Therefore, the accumulation of coke on the catalyst could not hinder the catalyst activity, at least within a reaction time of 200 min in this study. It should be noted that more detailed study on the Ni forms and coke formed is required to understand the behavior of the reaction system under periodic operation. It is suggested that the characterizations should be carried out separately at each reaction step of periodic operation and that operation with inert purge gas fed between each reaction step would provide additional useful data for understanding the behaviour of periodic operation.

In practical operation, it is desired, for periodic operation, that coke formation be kept as low as possible to avoid catalyst deactivation. Therefore, another set of experiments was carried out at 923 K with various values of cycle split (s). The cycle period was fixed at 20 min and the time-average flow rates of the reactant gases were kept at the same values as described earlier. It is expected that due to the slow rate of catalyst regeneration by carbon dioxide, the increase of regeneration period by lowering the feed flow rate of carbon dioxide (in order to keep the same average carbon dioxide flow rate) should help to increase the removal of coke arising from the methane cracking step and the corresponding reaction performance may be improved. The results for the cycle split (s) of 0.25, 0.4 and 0.5 are shown in Figs. 12 and 13. It was found that the decrease of the cycle split did not improve the reaction performance as expected. On the other hand, it slightly lowered both the methane and carbon dioxide conversions. This might be due to the shorter residence time during the methane cracking which caused the lower methane conversion. The decrease of carbon dioxide conversion should be due to the higher effect of mass transfer resistance at low reactant flow rate.

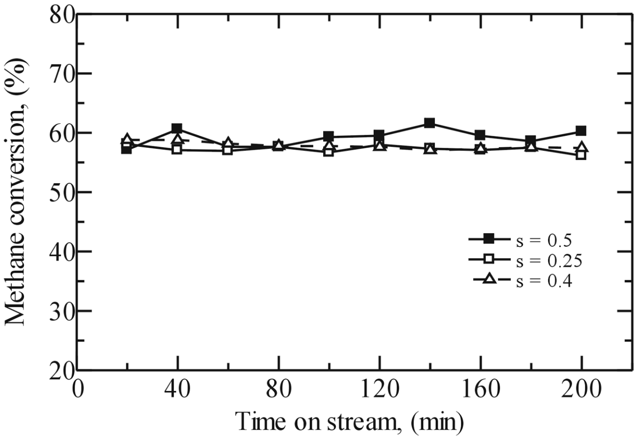


Fig. 12. Comparison of methane conversion between periodic operation at different cycle splits over Ni/SiO_2·MgO catalyst (T=923 K).

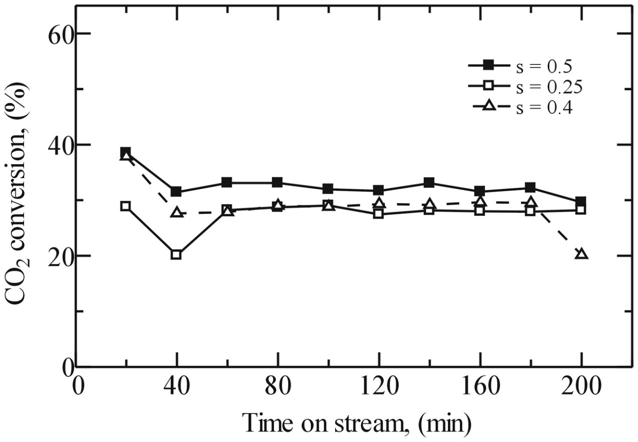


Fig. 13. Comparison of CO_2 conversion between periodic operation at different cycle split over Ni/SiO_2·MgO catalyst (T=923 K).

CONCLUSIONS

Periodic operation was applied for the carbon dioxide reforming of methane. The effects of key parameters such as reaction temperature, cycle period and cycle split on the methane and carbon dioxide conversions and the hydrogen yield were investigated. By operating at the same time-average flow rates of the reactants, the results of the periodic operation were compared among different operating conditions and those of steady state operation. It was found that periodic operation was inferior to steady state operation at 1,023 K. However, at 923 K, the periodic operation offered the equivalent hydrogen yield of the steady state operation with an additional benefit on the separated hydrogen and carbon monoxide products in the different product streams. It was observed that the carbonaceous deposit was progressively accumulated in the catalyst bed during the course of reaction. Further studies are required to investigate the observed results in more detail.

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