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CO_2–CH_4 reforming over NiO/γ-Al_2O_3 in fixed-bed/fluidized-bed switching mode

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Abstract

CO_2 reforming of methane was conducted over 13 wt.%NiO/γ-Al_2O_3 in a micro quartz reactor in fixed-bed/fluidized-bed switching modes under the condition of 1 atm, a fixed furnace temperature of 800 °C and a fixed CO_2/CH_4 molar ratio of 1.5. In the fluidized-bed mode, CH_4 conversion at steady state was always as high as about 92%, while in the fixed-bed reforming, it depended strongly on the starting mode. As the reforming was started directly from the fixed-bed, CH_4 conversion was only 48%, while it increased to about 75% as the catalyst was first applied to fluidized-bed reforming and then the fixed-bed operation. To understand the causes of such better catalytic performance of the catalyst in the fluidized-bed reforming, TPO and H_2-TPR techniques were then applied to the spent samples recovered from the mode-switching reforming tests ended at the different times of different modes. The results showed that fluidized-bed operation could not only suppress carbon accumulation over the catalyst but also remove some of the carbon deposited on it in the preceding fixed-bed reforming already, thus leading to recovery of the catalyst activity. It was also found that the extent of reduction of the catalyst after the fluidized-bed mode reforming was larger than that of the sample experiencing the fixed-bed operation only. Possible reasons for all these observations were also explored and discussed in the paper.

Keywords: CO_2–CH_4 reforming; Ni-based catalyst; Fluidized-bed; Switching-mode

1. Introduction

Catalytic CO_2–CH_4 reforming combines two of the most problematic greenhouse gases to generate synthesis gas and therefore is an appealing reaction for control of global warming. Ni, due to its availability and low cost [1–3], is most often chosen as the active component of catalysts for the reaction. Simultaneously it has been shown that Ni-based catalysts are always faced with the deactivation problem caused by carbon deposition [4,5]. Thus, how to suppress or minimize the carbon formation has been the main concern of studies on the reforming reactions. Most of the studies to date mainly focused on developing coking-resistant catalysts [2,5,6–11], but a few approached the issue from the aspect of optimizing the conditions of catalyst bed [12–16]. Considering the highly endothermic characteristic of the reforming, unifying the catalyst bed temperature might be effective for suppression of carbon formation in the reaction. Mleczko and co-workers [13,16] have reported that a Ni-based catalyst deactivated in the CO_2 reforming of methane more rapidly in a fixed-bed reactor than in a fluidized-bed reactor in which bed temperature is much uniform. Further, by comparing the catalytic reforming performances of some similar Ni-based catalysts in an identical size of micro-quartz reactor but between different runs, Effendi et al. have also shown that fluidized-bed operation leads to significant enhancements in CH_4 conversion [17,18] and less carbon deposition [19]. In this study, through varying operation mode in the reaction a direct comparison of both fixed-bed and fluidized-bed CO_2–CH_4 reforming was realized over an identical Ni-based catalyst sample in one single run, and thus the direct evidence was obtained for verifying that fluidized-bed reforming was surely superior to fixed-bed operation in conversion and reduction of carbon deposition. Then, TPO and H_2-TPR experiments of the spent catalyst samples were conducted to explore reasons why the fluidized-bed reforming led to the better catalytic performance.

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2. Experimental

2.1. Catalyst

13 wt.%NiO/γ-Al_2O_3 (S_{BET} = 130 $m^2\,g^{-1}$) was prepared by impregnation of γ-Al_2O_3 (175–350 μm) using an aqueous solution of nickel nitrate, the sample was then calcined in air at 550 °C for 4 h. The nickel loading in the catalyst was determined by measurement of bulk compositions using ICP-AES (Shimadzu GV-1000P). Two commercial Ni-based catalysts for steam reforming of methane, FCR-4-02 ($S_{BET} = 2\,m^2\,g^{-1}$, wt.% composition: NiO:Al_2O_3:CaO = 12:78:10, Toyo CC Inc.) and N139 ($S_{BET} = 30\,m^2\,g^{-1}$, NiO:$Al_2O_3$:CaO:other = 18:36:27:19, Nikki Chemical Co.) were also employed for the reforming for comparison.

2.2. Activity measurement

CO_2–CH_4 reforming was performed in a quartz micro-reactor (8 mm of i.d.) that can be operated in either fixed-bed or fluidized-bed mode. Flowing the reactant mixture down-flow or up-flow determined circumstances of the catalyst bed in fixed- or fluidized-bed mode, while mode-switching in the reaction was realized by a four-way valve on the feed line before the reactor. A gold-coated furnace (40 mm (Φ) × 410 mm (L)) was used as heater. A thermocouple within a thermo-well inside the catalyst bed was used to measure its temperature, whereas the furnace temperature was controlled by another thermocouple placed on a fixed position of the outside wall of the reactor. Fresh (or prepared) oxidative catalyst was used without further pre-treatment. In all cases, the amount of catalyst and the flow rate of a feed mixture of CO_2 and CH_4 (CO_2/CH_4 = 1.5) were fixed to be 160 mg and 250 ml/min (STP, GHSV = 93750 h^{-1}), respectively. Initially, the catalyst was heated in an argon flow up to 800 °C of the furnace temperature, and then the feed mixture was supplied to the reactor. Reactants and products were analyzed on-line by a TCD-GC (Yanaco GC3800) using an active carbon column after passing through an ice-water cooled condenser and then an anhydrous $Mg(ClO_4)_2$ packed water-adsorption tube.

2.3. Evaluation of deposited carbon on spent catalyst and its Ni reduction extent

Evaluation of the carbon deposited over a spent catalyst by using temperature-programmed oxidation (TPO) technique, followed by a measurement of its Ni reduction with a temperature programmed reduction (TPR) procedure, was carried out in a flow type of temperature-programmed desorption (TPD) apparatus with a quadrupole mass spectrometer as detector (TPD-1-A, Bel Japan, Inc.). About 50 mg of the spent catalyst was used for these measurements. The sample was heated first in 100 ml/min of 1%O_2/He up to 820 °C at a rate of 10 °C/min to burn all the deposited carbon off, and then secondly in a flow of 1%H_2/He flow (100 ml/min) to obtain its H_2-TPR pattern. Additionally, thermogravimetric analysis (TG, Shimadzu DT40) was also applied for characterizing the deposited carbon and X-ray diffraction measurement (XRD, Rigaku Ltd. Using Cu Kα radiation 35 kV, 20 mA) was used to determine phase compositions of the prepared and spent catalysts.

3. Results and discussion

3.1. Reforming with a single mode-switching from fixed-bed to fluidized-bed

To confirm that fluidized-bed reforming surely provides a higher CH_4 conversion than fixed-bed one, a single mode-switching reforming was first conducted with self-prepared 13 wt.%NiO/γ-Al_2O_3 catalyst. The experiment was started in the fixed-bed mode and continued for about 2 h to confirm that the catalyst activity was to indeed become stable in the period. Then, the mode-switching to fluidized bed operation was conducted and another 3 h reforming followed. As shown in Fig. 1, this switching operation led to instantly large increases of CH_4 and CO_2 conversions while the subsequent fluidized-bed operation maintained the conversions and H_2/CO ratio stable at the high levels till the run was stopped. Different from previous studies [13,16–18], in which the fluidized-bed and fixed-bed reforming experiments for comparison were conducted separately in different reactors or in different runs, the present fixed-bed and fluidized-bed reforming was subsequently performed over the identical catalyst sample in one single run, and therefore the results in the two operation modes were more comparative and provided a direct evidence for the effectiveness of fluidized-bed operation on improving catalytic reforming performance of the catalyst. Further to make sure that such improving effect of fluidization of catalyst particles was non-specific phenomenon, similar

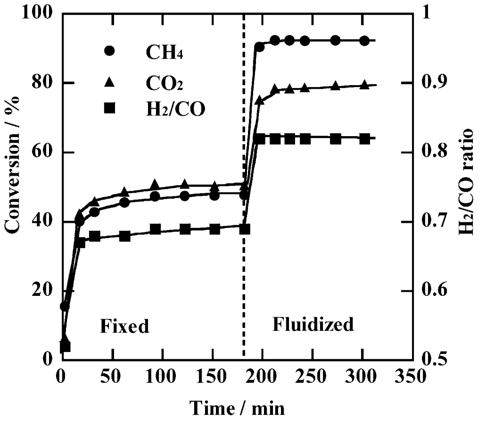

Fig. 1. Dynamic jump of NiO/γ-Al_2O_3 activity in the fixed-bed/fluidized-bed mode-switching reforming.

mode-switching experiments were also performed with the two commercial Ni-based catalysts, FCR-4-02 and N139. The results are summarized in Table 1. Again, the mode switching from fixed-bed to fluidized-bed to make particles of the catalysts circulated in the bed during the reforming significantly improved the catalytic performances of the catalysts. As listed in the table, CH_4 and CO_2 conversions recorded at steady state in the fixed-bed mode were 77 and 65% for FCR-4-02 and 59 and 52% for N139, while under the fluidized-bed operation they increased, respectively, to 89 and 76% for the former and 70 and 64% for the latter. All these increased conversions in the fluidized-bed mode, plus our previous observations with other catalysts [17,18], strongly suggest that it might be a universal phenomenon that fluidization of the particles of catalyst in a bed in the CO_2–CH_4 reforming led to a significant improvement in its catalytic performance. Simultaneously, slightly higher H_2/CO ratios were also observed for all three catalysts in the fluidized-bed reforming presently, and it might be attributed to relatively less selectivity toward the reverse water-gas shift reaction (RWGS) under the circumstances of fluidized-bed reforming [17,18].

For the highly endothermic CO_2–CH_4 reforming reaction favored by high temperature, fluidized-bed might be favorable than fixed bed since its excellent heat and mass transfer characteristic usually makes its bed temperature higher and uniform. Thus, the effect of higher bed-temperatures being possibly established in the fluidized-bed reforming period on increasing the corresponding conversions must be primarily considered and evaluated. For this, the bed-temperature was continuously monitored and recorded in the reforming. However in all the cases, as shown in Table 1, the temperatures in the fluidized-bed mode were unexpectedly slightly lower than those in the period of fixed-bed reforming. This finding is contrary to observations by Effendi et al. with a large mass of catalyst sample for their catalyst beds [17]. Actually, we confirmed that the difference in the temperature of a catalyst bed between fluidized- and fixed-bed operation modes was influenced by many factors including furnace temperature, gas flow rate, the height of catalyst bed and conversion. As the reforming was operated under non-equilibrium condition with high GHSV, it was observed that fluidized-bed operation always provided much higher conversion than fixed-bed as well as lower bed-temperatures as shown presently. Considering that a high CH_4 conversion means a large amount of reaction heat on the one hand, and the temperature of furnace used to supply the reaction heat needed was fixed in the present work on the other hand, the lower bed temperatures recorded in the higher-conversion fluidized-bed modes were theoretically possible. If these observed numbers in Table 1 reflected the true bed-temperatures, the temperature difference observed in each run between the two operation modes completely rules out the possibility of the higher conversions of fluidized-bed reforming being caused by its higher bed temperatures. Thus the evaluation on carbon deposition on the spent catalysts and then their Ni reduction extents were followed to clarify what is really responsible for the above better catalytic performance of the catalysts in the fluidized-bed reforming mode.

3.2. Carbon deposition on the spent catalyst

Carbon deposited over the catalyst in the reforming was first evaluated by TG analysis for the spent samples from 3 h fixed-bed reforming runs with different catalysts. As listed in Table 1, the amount of carbon accumulated in the reaction varies significantly with kinds of catalysts. For the two commercial catalysts used, this amount was surprisingly large, being 8 and 21 wt.%, respectively. In general, such much of carbon deposition must cause a serious catalyst deactivation. But in fact, the corresponding time-courses of CH_4 conversions (similar to the cases of the fixed-bed reforming region in Fig. 1) showed no apparent activity loss in all the cases, suggesting that not all carbon formed on the catalysts in the 3 h fixed-bed reforming was related to their activities or deactivation. Thus, characterizing the carbon deposited at the very initial stage of the reforming or evaluating it only when its amount is very little might become valuable. Presently, we mainly focused on the small amount of carbon formed on the self-prepared NiO/γ-Al_2O_3 catalyst and employed TPO technique to determine its amount as well as nature.

Fig. 2 shows the TPO-profiles of the spent NiO/γ-Al_2O_3 catalysts recovered from the single fixed-bed/fluidized-bed mode switching experiments ended at the different times

Table 1
Results of CO_2–CH_4 reforming over Ni-based catalysts in fixed-bed/fluidized-bed switching mode[a]

Catalyst	Mode[b]	Bed temperature (°C)	CH_4 conversion (%)	CO_2 conversion (%)	H_2/CO	Deposited C[c] (wt.%)
NiO/γ-Al_2O_3	Fixed	742	48	51	0.70	0.9
	Fixed-fluidized	736	92	80	0.82	0.6
FCR-4-02	Fixed	749	77	65	0.76	8.3
	Fixed-fluidized	738	89	76	0.79	4.5
N139	Fixed	748	59	52	0.69	20.9
	Fixed-fluidized	741	70	64	0.71	13.1

[a] All recorded at steady state.
[b] Fixed/3 h; Fixed-fluidized/3 h–2 h.
[c] Determined by TG.

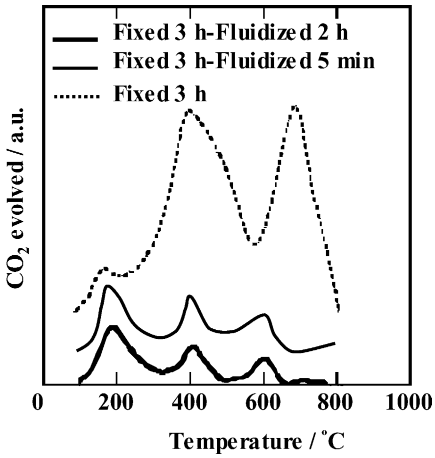

Fig. 2. CO_2 evolution in TPO of the spent NiO/γ-Al_2O_3 catalyst recovered from mode-switching reforming ended at different times of the different modes.

of different modes. For all the samples, three CO_2 peaks centering respectively at the temperatures of 200, 400 and 600–700 °C were observed. This indicates that there were three types of carbon species existing on the samples after the reforming, and according to [20,21], they can be assigned to α-, β- and γ-C, respectively. Comparing the relative intensities of the CO_2 evolution peaks of the profiles in the figure clearly shows that the amount of carbon on the catalyst after the 3 h fixed-bed reforming is large while that on the sample after the fixed- and then fluidized-bed operations little. This implies that the fluidized-bed operation removed some of the surface carbon, not only the most reactive α-C but also less reactive β- and γ-C, formed in the first 3 h reforming in the fixed-bed mode, and the concrete amount of the carbon removed was listed in Table 1. Prolonging the period of fluidized-bed operation from 5 min to 2 h caused no much further reduction in the relative intensity of all the CO_2 evolution peaks, on the other hand, indicating that the carbon removing process during the fluidized-bed reforming proceeded vary fast and could complete in the first 5 min after the mode-switching. Noting that the catalyst activity in the mode-switching experiment showed a rapid increase with the switching and then maintained constantly in the subsequent fluidized-bed reforming period (Fig. 1), there must be a cause–effect relationship between the carbon removing and activity increase observed in Fig. 1 after the mode was switched to fluidized bed operation. That is to say, significant improvement of the catalyst activity after the mode-switching (Fig. 1), even not all but at least partially, could be attributed to such partial removing of the deposited carbon from the catalyst surface under fluidization of the catalyst bed.

Now the question to ask is why the fluidized-bed operation (circulation of the catalyst particles inside the bed) could remove the carbon deposited on the catalyst in the fixed-bed reforming period and suppress carbon's newly accumulating in the subsequent reforming. If we simply assume that the CO_2–CH_4 reforming reaction (Eq. (1)) involves two steps: the decomposition of CH_4 to form carbon and hydrogen (Eq. (2)) and gasification of the deposited carbon with CO_2 (Eq. (3)), we can see that whether carbon will deposit or be removed in the reforming depends on the rate difference of the two steps. When the rate of CH_4 decomposition is greater than that of the carbon gasification, carbon accumulation must take place, while in the reverse case the removing of the deposited carbon will proceed. If both the rates balance, there would be no occurrence of carbon accumulation.

$$CO_2 + CH_4 = 2CO + 2H_2 \quad \Delta H = +247\,\text{kJ/mol} \tag{1}$$

$$CH_4 = C + 2H_2 \quad \Delta H = +75\,\text{kJ/mol} \tag{2}$$

$$CO_2 + C = 2CO \quad \Delta H = +171\,\text{kJ/mol} \tag{3}$$

Considering that such step reactions might take place everywhere of the catalyst bed, the present assumptions should be applicable not only to the whole bed but also to its any local regions or individual particles. Serious carbon accumulation occurred in the first 3 h reforming in the fixed-bed mode (Table 1) for all the catalysts tested indicate that the total (or average) environment of catalyst bed under the employed reaction conditions (temperature, flow rate and CO_2/CH_4 ratio) might be favorable to carbon formation, that is, to the CH_4 decomposition rather than the carbon gasification. But, according to the previous finding that the amount of carbon deposited in fixed catalyst beds in the reforming was non-uniform and varied significantly with the bed axis [19], it was highly possible existence of some local zones or regions in the bed rich in CO_2 and favorable to the carbon gasification. If this was also applicable to the present fluidized bed operation, in some specific local regions of the bed carbon might form just as occurred in the fixed-bed mode, but at the following moment when the particles of catalyst in the regions circulated to pass through the CO_2-rich regions it might be quickly gasified and removed. Additionally, very short average residence times of the particles of the catalyst in the carbon-depositing regions that prevent transformation of newly formed carbon to stable non-reactive forms might be also the reason for such rapid gasification of the deposited carbon occurring under the fluidized-bed operation. Consequently, not only carbon accumulation was suppressed but also partial removing of the deposited carbon could be possible under the fluidized-bed operation.

Then, a coming question is whether or not such carbon removing occurred in the fluidized-bed was fully responsible for the activity jump with the mode-switching from fixed- to fluidized-bed operation in Fig. 1. If it was so, the identical degree of activity drop should be observed in the reverse mode-switching case from fluidized-bed to fixed-bed operation with carbon formation taking place. Thus, a mode-switching reforming starting in the fluidized-bed mode was performed. Fig. 3 shows the time courses of the recorded CH_4 and CO_2 conversions. As expected this time, a stable high activity as shown by the two conversions was observed in the fluidized-bed reforming period first, and

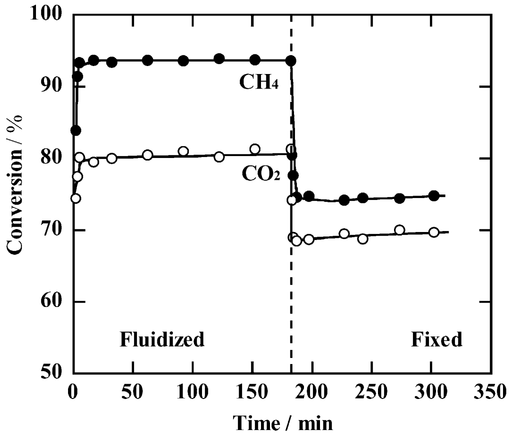

Fig. 3. Dynamic drop of NiO/γ-Al_2O_3 activity in the fluidized-bed/fixed-bed mode-switching reforming.

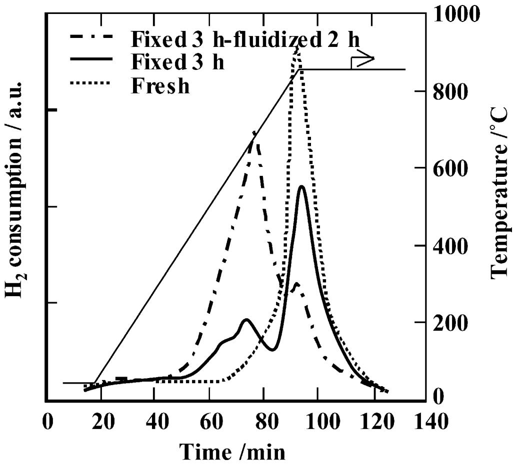

Fig. 4. H_2-consumption in the TPR experiments subsequent to the TPO described in Fig. 2.

then a low one in the subsequent fixed-bed reforming. A rapid activity drop was observed in a short transition period after the mode switching, but the magnitude of the activity drop finally achieved was not large as expected. If defined in terms of CH_4 conversion, it was only about 19%, much smaller that 44% of the activity jump observed in Fig. 1. Since no bed-temperature decrease was observed after the mode switching in the present case, this 19% activity drop must be caused by carbon deposition over some of the active Ni sites of the catalyst. In fact, we confirmed that the amount of the carbon deposited in the transition period indeed showed a rapid increase. If this number of 19% was true and also applicable to the carbon-removing case with the mode-switching reversely from the fixed-bed to fluidized-bed operation, that is, the case of Fig. 1, about 25% of the difference occurs to the activity jump. Thus, it is concluded that there must be also some other causes responsible for the activity jump shown in Fig. 1.

Additionally, it is also worthy to note here that both CH_4 and CO_2 conversions in the first 3 h fluidized-bed reforming almost completely duplicated the numbers observed in the 2 h fluidized-bed reforming after the 3 h fixed-bed operation in Fig. 1. This clearly indicates that the numbers or catalytic characteristics of active Ni sites in the catalyst might be identical after a period of fluidized-bed operation no matter how the catalyst was applied to the fluidized-bed reforming, directly or after experiencing the fixed-bed reforming first. That is, the present comparison between the activity drop in Fig. 3 and that jump in Fig. 1 was on the same high activity base and thus meaningful.

3.3. Catalyst reduction in the reforming

To fully understand the activity jump observed in Fig. 1, H_2-TPR technique was applied to the TPO-experienced spent NiO/γ-Al_2O_3 catalysts to evaluate their reduction extents after the reforming. Fig. 4 compares the observed H_2 consumption profiles of the two samples that were recovered, respectively, from a 3 h fixed-bed reforming and a 3 h fixed-bed/2 h fluidized-bed mode switching experiment and then TPO-treated. The TPR profile of the fresh catalyst is also shown in the figure for comparison. For the fresh catalyst, only one single H_2-consumption peak was observed with a maximum at 820 °C, while the TPO-experienced spent samples essentially exhibited two peaks, one centering at the same temperature of 820 °C and the second at a low temperature of around 660 °C. With the XRD measurement and also Refs. [22–24], the high temperature peak was attributed to the reduction of a $NiAl_2O_3$-likely Ni-Al oxide, while that low temperature one to the reduction of NiO weakly bound to the support. By comparing the reduction temperatures with the recorded bed temperatures (Table 1), it is reasonably presumed that only the Ni reducible in the low temperature range was reduced to the metallic state in the reforming and thus active. Since no nickel specie but metallic Ni and $NiAl_2O_3$-likely Ni-Al oxide was identified by XRD analysis in the spent catalysts, the NiO ascribed here by the low temperature H_2-consumptions in the TPO-experienced spent samples must be formed via the oxidation of reductive Ni through the TPO. That is, the low-temperature H_2-consumption in the TPR profiles actually reflects the amount of reduced metallic Ni in the sample. Thus, comparison of the TPR profiles between the fresh and spent samples clearly indicates that reduction of the catalyst from $NiAl_2O_3$-likely Ni-Al oxide to metallic Ni surely took place in the reforming, while the difference of the H_2-consumption patterns in the low temperature region between the two spent samples shows that there was more metallic Ni in the fixed-bed/fluidized-bed mode switching reforming-experienced sample than in that fixed-bed reforming-experienced sample only. This implies that more active Ni sites might be formed under the fluidized-bed operation, and thus, the better catalytic reforming performance achieved.

Why did the fluidized-bed operation after the fixed-bed reforming lead to such further reduction of the catalyst?

This, again, might involve the characteristic difference of the fluidized- and fixed-beds. A specific characteristic of fixed-bed is its concentration gradient in both radius and axis directions. This means that in the reforming there must be the regions in the bed are relatively rich in CO_2 and under oxidative atmospheres. Thus, the catalyst in these regions might be never reduced and remain in its original oxidative state. The catalyst particles in the fluidized-bed mode reforming, on the other hand, were circulated to pass through the different regions of the bed from time to time. As they were in the regions under the oxidative atmosphere, their oxidation might take place, while through the regions rich in H_2 and CO their reduction would surely process. That is to say, in the fluidized-bed mode, all the catalyst particles, due to the continuous circulation, always have opportunities to pass through the regions in the reductive atmosphere and to be reduced. As shown by the TPR profiles of the TPO-experienced spent samples, once the catalyst was reduced and its Ni was separated from Ni-Al oxides or the support, it would not, at least not fully, be re-oxidized back to its original non-reactive form such as $NiAl_2O_3$-likely Ni-Al oxide even in the presence of O_2. Consequently, a larger degree of reduction of the catalyst is achieved.

Now, it is clear that the fluidized-bed operation has an effect on promoting the reduction of the catalyst, in addition to its carbon-removing function. Since an increase in the reduction extent of a catalyst is not always equal to the increasing of its active sites, there still is a need to further confirm the effect of the catalyst reduction extent on its reforming performance. For this, an in situ H_2-reduction procedure (800 °C, 1 h) was taken prior to the reforming. The catalyst used was the $NiO/\gamma\text{-}Al_2O_3$, same as that in Figs. 1 and 3, while the reforming was conducted this time separately in a fluidized-bed or a fixed-bed mode. Fig. 5 shows the results obtained. Again, an apparent different in the stable activity of the catalyst appeared between the fluidized-bed reforming and fixed-bed operation, and it is high in the former operation mode while low in the latter. All these are in very good agreement with the above observations in Figs. 1 and 3, further verifying the superiority of the fluidized-bed operation in the reforming. Compared with the cases of fluidized-bed reforming in Figs. 1 and 3, a slightly lower rather than high stable activity (in terms of CH_4 conversion) was observed here over the pre-reduced sample in the same fluidized-bed mode, suggesting that the reduction extent of the catalyst that experienced a period of the fluidized-bed reforming might surely reach a considerably high level. In the fixed-bed mode, on the other hand, the activity of the pre-reduced catalyst behaved vary similar to that in Fig. 3 after the mode was switched from the fluidized-bed to fixed-bed, decreasing very rapidly at the very initial stage and then falling to a considerably stable level. The final stable activity did not fall to the level as low as that recorded in the fixed-bed reforming over the fresh catalyst in Fig. 1 but maintained high at the level close to that of the fluidized-bed operation-experienced fixed-bed mode reforming in Fig. 3, indicating that a large degree of reduction of the catalyst indeed leads to a high reforming activity. That is, the difference in the activity between the two fixed-bed modes reforming in Figs. 1 and 3 was surely caused by that of the reduction extent of the catalyst.

3.4. Reforming in multi-switching mode

Finally, a reforming test in a multi-switching mode was conducted over an identical $NiO/\gamma\text{-}Al_2O_3$ catalyst sample to confirm all the results in Figs. 1 and 3. The test was started in fixed-bed mode, followed in fluidized-bed, then fixed-bed again, and finally fluidized-bed mode again. Fig. 6 shows the result. The time-course of CH_4 conversion by the end of the second fixed-bed mode reforming basically reproduced those of the single mode-switching reforming tests in Figs. 1 and 3. CH_4 conversion showed a great jump after the first mode switching from fixed-bed to fluidized-bed operation and then a rapid decrease with the second mode-switching

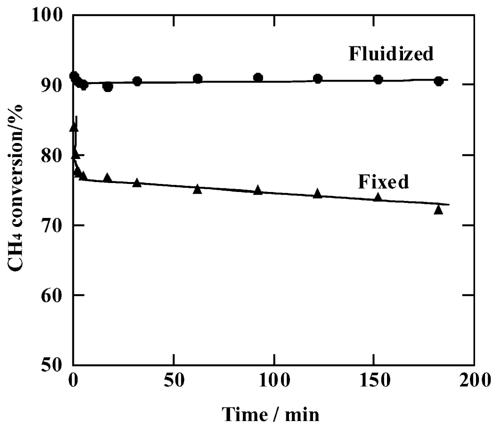

Fig. 5. CH_4 conversion in fixed- and fluidized-bed reforming over H_2 pre-reduced $NiO/\gamma\text{-}Al_2O_3$ catalyst.

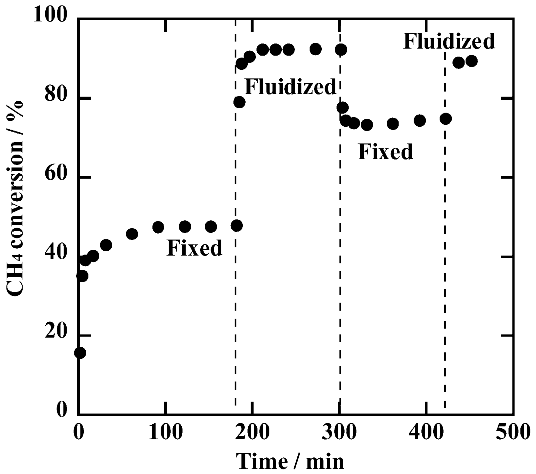

Fig. 6. Dynamic variation of catalytic activity in the reforming over $NiO/\gamma\text{-}Al_2O_3$ catalyst in the multi-switching mode.

reversely from fluidized-bed to fixed-bed mode. The extent of the jump in CH_4 conversion was larger than that of the decrease, confirming the conclusion reached from Figs. 1 and 3 that the fluidized-bed operation promoted the reduction of the catalyst. Additionally, the third mode switching from fixed-bed back to fluidized-bed reforming leads to recovery of CH_4 conversion essentially to the level recorded in the period of the first fluidized-bed mode reforming, further confirming the effect of fluidized-bed on removal of deposited carbon and suppression of carbon formation.

4. Conclusions

The present observations in the mode-switching CO_2–CH_4 reforming over NiO/γ-Al_2O_3 catalyst have shown that fluidized-bed operation could not only suppress the carbon accumulation over the catalyst but also remove some of the carbon deposited on it in the fixed-bed reforming already. As the catalyst was used without pre-reduction, the fluidized-bed operation was also functional to promote its reduction in comparison with that in the fixed-bed mode. All these contributed to the better catalytic reforming performance of the catalyst in the fluidized-bed mode.

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