

# Steam reforming of a clean model biogas over Ni/Al<sub>2</sub>O<sub>3</sub> in fluidized- and fixed-bed reactors

A. Effendi<sup>a,\*</sup>, Z.-G. Zhang<sup>a</sup>, K. Hellgardt<sup>b</sup>, K. Honda<sup>a</sup>, T. Yoshida<sup>a</sup>

<sup>a</sup> Hokkaido National Institute of Advanced Industrial Science and Technology (AIST),  
2-17-2-1 Tsukisamu-Higashi, Toyohira-ku, Sapporo 062-8517, Japan

<sup>b</sup> Department of Chemical Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

## Abstract

Simultaneous steam, carbon dioxide reforming of methane was conducted over 11.5 wt.% Ni/Al<sub>2</sub>O<sub>3</sub>, at 1 atm in micro-fluidized- and fixed-bed reactors using a constant molar ratio of CH<sub>4</sub>/CO<sub>2</sub>  $\approx$  1.5 as a model biogas. The performance of a fluidized reactor was compared to that of a fixed-bed reactor under similar conditions (feed gas to steam ratios of 1.5 and 0.75 at a reactor temperature of 750 °C, GHSV of 300 min<sup>-1</sup>). Conversions of CH<sub>4</sub> and CO<sub>2</sub> were 75 and 67%, respectively, in a fixed-bed reactor under the ratio of 1.5. Overall higher conversions (7–15%) were observed in the fluidized-reforming reactor. The initial activity of the fixed-bed reformer decreased rapidly and massive carbon deposition caused reactor blockage at the low steam concentration. Decreased the feed gas to steam ratio to 0.75 reduced carbon deposition and the nature of the carbon was suggested not to be the cause of the catalytic enhancement of the fluidized reforming.

A study of the fluidized-bed reformer under decreasing feed gas to steam ratios from 3.0 to 0.3 showed an almost complete CH<sub>4</sub> conversion (98% for feed gas to steam ratios below 1.0). With decreasing feed gas to steam ratio the H<sub>2</sub>/CO ratios increased as expected from 1.5 to 2.7. At the highest feed gas to steam ratio, a poor catalyst fluidization was observed due to massive carbon deposition, which was reduced dramatically when steam was provided in excess. Increasing temperatures from 650 to 850 °C enhanced both conversions and lowered H<sub>2</sub>/CO ratios.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Steam; CO<sub>2</sub>; Reforming; CH<sub>4</sub>; Biogas; Syngas; Fluidized-bed reactor; Carbon

## 1. Introduction

Global climate changes caused by CO<sub>2</sub> emissions are currently debated around the world; greener sources of energy are being sought as alternatives to replace fossil fuels. Hence, research activities on solar energy, wind and wave power, geothermal energy, fuel cell technology and renewable energy sources

are gaining more and more importance. Biomass is of particular interest as a sustainable energy source as it does not contribute to net CO<sub>2</sub> emissions if integrated over an annual growth cycle. Thus, attempts have been made to harness biogas, produced from anaerobic digestion processes of biomass for combined heat and power generation [1,2]. Biogas is composed of approximately 50–60% CH<sub>4</sub>, 40% CO<sub>2</sub>, 1% H<sub>2</sub>O and traces of NH<sub>3</sub> (80–100 ppm) and H<sub>2</sub>S (1000–3000 ppm) [2].

Biogas can be used as potential feed in CH<sub>4</sub> reforming with CO<sub>2</sub> for the production of H<sub>2</sub>; hydrogen being considered to be a clean fuel. Alternatively,

\* Corresponding author. Present address: School of Chemical Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK. Fax: +44-121-414-5330.

E-mail address: a.effendi@bham.ac.uk (A. Effendi).

co-generation of  $H_2$  and CO (syngas) may be employed to produce simple petrochemical feedstock. However, the reforming of biogas with  $CH_4/CO_2$  ratios of 1.5 would cause significant carbon deposition, resulting in a fast deactivation of the usual Ni-based catalysts and rapid reactor blockage [3–11]. Options to reduce carbon formation include coupling the biogas conversion with steam reforming. With steam addition, the C/H ratio in the feed decreases and the C/O ratio decreases as well resulting in controlled and limited carbon formation. Moreover, syngas could be produced whereby the desired hydrogen to carbon monoxide ratio could be adjusted easily [3–5].

Carbon formation can be minimized during dry reforming with  $CH_4/CO_2 \approx 1$  using a fluidized-bed reactor. A relatively slow catalyst deactivation is observed due to the relatively small amounts of carbonaceous species deposited onto the catalyst surface. An almost isothermal bed temperature for the highly endothermic reaction can be achieved [6–11]. However, the loss of catalyst material due to attrition should not be underestimated.

The present work compares the catalytic activity of 11.5 wt.% Ni/ $Al_2O_3$  in the steam reforming of a clean model biogas at 1 atm in a fluidized- and a fixed-bed reactor. The carbonaceous species formed on the surface of the catalyst during the reforming are characterized. The effects of feed gas to steam ratio (from 0.3 to 3.0) and temperature (650–850 °C) on  $CH_4$ ,  $CO_2$  conversions and  $H_2/CO$  ratio as well as carbon deposition are studied employing a fluidized-bed reactor.

## 2. Experimental

### 2.1. Activity measurement

Nickel on  $Al_2O_3$ , a commercial catalyst, for the steam reforming of  $CH_4$  was used throughout the experiments (supplied by Toyo CC Inc. coded as FCR-4-02). Approximately 300 mg catalyst ( $S_{BET}$  of  $2.0\text{ m}^2\text{ g}^{-1}$  with a particle size of 70–140  $\mu\text{m}$ ) was applied in all reforming experiments. Fresh oxidic catalyst was employed without prior pre-reduction. Nickel in its reduced oxidation states is suggested to be the active component for the reforming and it is suggested that an auto-reduction occurs: methane is readily cracked at 650 °C producing  $H_2$ , which

in turn reduces and activates the catalyst [3,4]. The presence of reduced nickel is evident from the thermo-gravimetric (TG) profiles obtained during the carbon determination (discussed further below). Experiments were performed in a quartz micro-reactor (i.d. of 8 mm) at various furnace temperatures and steam concentrations. The  $CH_4/CO_2$  ratio was kept constant at 1.5. Both, fluidized- and fixed-bed reforming was carried out in a gold-coated quartz reactor. A thermocouple within a thermo-well was used to measure the catalyst-bed temperature, whereas reactor surface temperature was controlled by another thermocouple placed on the outside of the wall of the reactor. An RF power supply (Chino SU KP3000) coupled to the gold-coated furnace facilitated a constant and uniform temperature profile along the reactor all. Gases ( $CH_4$ ,  $CO_2$ , and Ar) were purified by passage through appropriate adsorbents, and delivered to the reactor through mass flow controllers (Tokyo Keiso Co. Ltd.). Steam was generated by supplying the correct amount of water (Hitachi pump L-7110) to a heated line ( $\approx 300^\circ\text{C}$ ). The total flow rate was  $100\text{ ml min}^{-1}$ , STP, consisting of a mixture of  $CH_4/CO_2$  and steam (feed gas to steam ratios from 0.3 to 3.0,  $80\text{ ml min}^{-1}$ ) in Ar ( $20\text{ ml min}^{-1}$ ). This flow rate achieved fluidization with  $U/U_{mf} \approx 2$ , similar to a GHSV of  $\approx 300\text{ min}^{-1}$  ( $18,000\text{ h}^{-1}$ ). In the case of the fluidized-bed experiments, the feed was supplied up-flow through a porous quartz disc. A down-flow gas stream was employed for the fixed-bed experiments. Initially, the catalyst was purged with Ar ( $40\text{ ml min}^{-1}$ , STP) until the desired temperature was reached. Then the feed mixture was introduced to the reactor upon which Ar was reduced to  $20\text{ ml min}^{-1}$ , STP. Reactants and products ( $CO$ ,  $H_2O$  and  $H_2$ ) from the reactor effluent were passed through a condenser and anhydrous  $Mg(ClO_4)_2$  sorbent to trap the water. The amount of condensed water as well as the total flow rate of effluent-gas was monitored and quantified. Product gas separation was achieved using a GC (Yanaco G3800 GC) with a  $2\text{ m} \times 3\text{ mm}$  i.d. activated carbon column. The GC was operated isothermally at  $110^\circ\text{C}$  and  $50\text{ N ml min}^{-1}$  Ar carrier flow.

### 2.2. Catalyst and carbon characterization

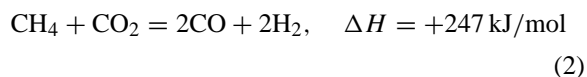
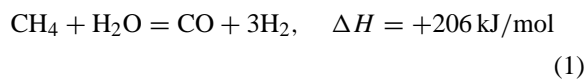
The bulk composition of the catalyst was determined using ICP-AES (Shimadzu GV-1000P). The

surface composition was analyzed by XPS analysis (VG ESCALAB 220i-XL). C 1s spectra were collected to examine the nature of the deposited carbonaceous species. Al K $\alpha$  radiation was used as an energy source (1486.6 eV) operating at 10 kV, 8 mA. The analyzer pass energy was set at 25 eV. The carbon binding energy (BE) was referenced to the Au 4f<sub>7/2</sub> transition with a BE of 84.0 eV (samples were gold coated prior to analysis). The amount of carbon deposited onto spent catalysts was determined using a TG analyzer (Seiko Instrument Inc.). Approximately 14 mg of sample was pre-dried at 110 °C in 10% O<sub>2</sub>/Ar (30 ml min<sup>-1</sup>) for 30 min. A weight-loss profile was then recorded from 110 to 825 °C at a ramp rate of 10 °C min<sup>-1</sup>. Temperature programmed oxidation (TPO) profiles of spent catalysts were collected to determine the amount of carbon deposited as well as to elucidate on the nature of the carbonaceous species. As an oxidizing agent, 1% O<sub>2</sub>/He (100 ml min<sup>-1</sup>) was introduced to 50 mg sample and the temperature was increased with a heating rate of 10 °C min<sup>-1</sup>. CO<sub>2</sub> and CO signals were recorded between 100 and 850 °C.

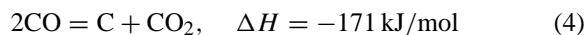
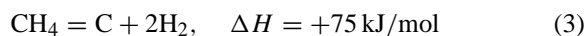
### 3. Results and discussion

#### 3.1. Steam reforming of biogas in fluidized- and fixed-bed reactors

The overall stoichiometries for simultaneous CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/steam reforming are

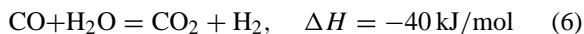


Carbon deposition on catalysts is a major concern during steam reforming of hydrocarbons. The reforming reactions as given by Eqs. (1) and (2), are highly endothermic and only favored at high temperatures where carbon formation via Eqs. (3) and (4) is thermodynamically feasible:



Thus, Eq. (1) can be seen as consisting of Eq. (3) and the reverse of Eq. (4). As the formation of carbon is governed by the H/C ratio of the feed, a low H/C as present in the simulated biogas, would lead to extensive carbon formation [3–5]. Ideally, carbon formed via Eq. (3) should be rapidly consumed by the reverse of Eq. (4), and/or by Eq. (5). So, if the carbon removal rate(s) are faster than the formation rate(s) (Eq. (3)), then there will be no build-up of carbon. Potential carbon formation through CO disproportionation (Eq. (4)) and the reverse of Eq. (5) is favored only at low temperatures [3–5]. It is also suggested that the use of a fluidized-bed reactor during dry reforming would minimize the risks of carbon formation compared to fixed-bed reactors [6–11].

If steam is also present in the feed, then the water gas shift reaction (WGSR) (Eq. (6)) will have a significant influence on the overall product distribution:



In order to determine the catalytic activity during the steam reforming of biogas, extended run time experiments were conducted in fluidized- and fixed-bed reactors under similar conditions. Tests were performed in the presence of feed gas (a constant CH<sub>4</sub>/CO<sub>2</sub>  $\approx$  1.5) to steam ratios of 1.5 and 0.75, which ensured H<sub>2</sub>/CO ratios of  $\approx$  1.6 and 2.0. Fig. 1 and Table 1 show the results of the steam reforming of a model biogas using both fluidized- and fixed-bed reactors for both feed gas to steam ratios. For all feeds, overall conversions of CH<sub>4</sub> and CO<sub>2</sub> in the fluidized-bed reformer were higher (by 7–15%) than those obtained in the fixed-bed reactor. Consequently, less CH<sub>4</sub> and CO<sub>2</sub> remained in the effluent. In the case of the fixed-bed reformer, less H<sub>2</sub> and a higher CO selectivity was observed, thus a relatively higher CH<sub>4</sub> concentration remained in the product stream. In general, reducing the steam in the feed increased the selectivity to CO and enhanced CO<sub>2</sub> conversions in both types of reactors in accordance with Eq. (6). The initial activity during fixed-bed reforming decreased rapidly, allowing operation for only 360 min due to fast carbon formation. When the feed gas to steam ratio was decreased to 0.75, the catalytic activity decreased and reached a steady conversion after 500 min. The CH<sub>4</sub> conversion was close to that expected from equilibrium calculations. This was not the case for the CO<sub>2</sub> conversion. It may be speculated that CH<sub>4</sub> decomposition and/or

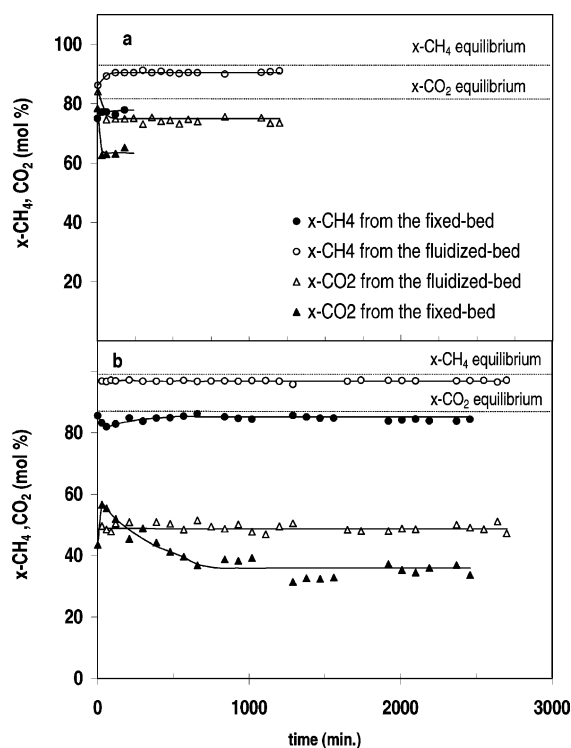


Fig. 1. CH<sub>4</sub> and CO<sub>2</sub> conversions in fluidized- and fixed-bed reactors at 750 °C and feed gas to steam ratios of (a) 1.5 and (b) 0.75, respectively.

dissociation occurred earlier, before the reforming reaction, and did not take place simultaneously with CO<sub>2</sub> and steam in the mixture as with CO<sub>2</sub> alone or steam alone [12].

Generally higher conversions were observed from the fluidized-bed reforming compared to those from the fixed-bed reactor, and relatively minor amounts

of carbon were deposited under the low feed gas to steam ratio. To explain this activity difference, particular parameters such as carbon deposition in relation to pressure drop and catalyst-bed temperatures need to be discussed further.

### 3.2. Carbon deposits and pressure drops

TG, TPO and XPS analyses were carried out to determine the amount and nature of deposited carbon and to relate it to the catalytic activity. Table 1 gives the wt.% carbon formed during all experiments. Conducting the fixed-bed reforming with a feed gas to steam ratio of 1.5 resulted in significant carbon deposition of 16 wt.% causing in a complete reactor blockage after 360 min. Although a remarkable amount of carbon was deposited, this did not immediately deactivate the Ni particles on the catalyst. However, prolonged carbon formation would result in complete encapsulation Ni particles by polymorphic graphite. This would cause catalyst deactivation as the encapsulated Ni particles are isolated from the reacting mixture [13]. Along with amount of carbon deposited, Fig. 2 shows the exponential increase in pressure drop over the fixed bed as a function of time on stream. Concurrent TPO profiles (Fig. 3) taken at different sampling times demonstrated a rapid increase in the relative amount of CO<sub>2</sub> released, supporting the above observation. The peak maxima shift to higher temperatures and the concentration of carbon species present on the catalyst increases with longer exposure to the reaction mixture.

In the case of the fluidized-bed reformer, the spent catalyst indicates a limited amount of carbon being present, resulting in no change of pressure drop for 1200 min. As Fig. 4 illustrates, the TPO profile

Table 1

Results of steam reforming of a clean model biogas using fluidized- and fixed-bed reactors at atmospheric pressure

Reforming in	Feed gas/H <sub>2</sub> O	Catalyst-bed temperature (°C)	Reactor-wall temperature (°C)	Conversions (mol%)		Effluent distribution (mol%)				Carbon (wt.%)
				CH <sub>4</sub>	CO <sub>2</sub>	H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	
Fluidized bed after 1200 min	1.5	723	750	90.4	74.6	57.0	35.1	2.9	5.1	<0.1
Fixed bed after 360 min	1.5	684	750	74.8	67.3	51.4	33.0	8.4	7.3	>16
Fluidized bed after 2700 min	0.75	737	750	96.8	49.3	61.2	28.8	0.9	9.1	<0.1
Fixed bed after 2700 min	0.75	691	750	84.8	36.1	58.3	25.3	4.3	12.1	<0.1
Fixed bed after 1380 min	0.75	738	800	97.0	49.8	61.2	28.8	0.8	9.2	<0.1
Fluidized bed after 1920 min	0.75	690	700	89.1	36.2	59.6	25.7	3.0	11.7	<0.1
Equilibrium calculation	0.75	750	—	100.0	85.7	60.7	33.6	0.0	5.7	—

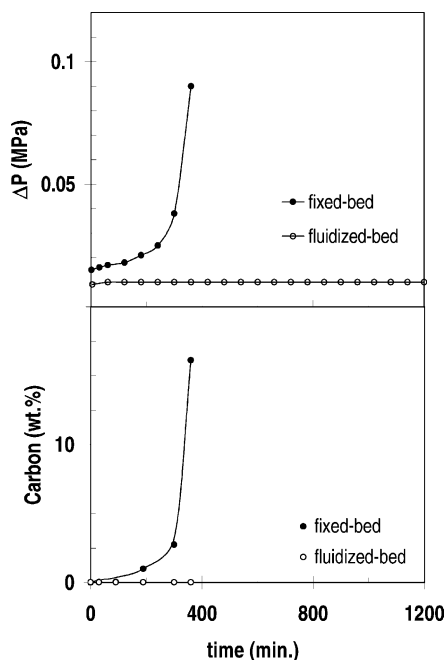


Fig. 2. Pressure-drop profile of the fluidized- and fixed-bed reforming at 750 °C with feed gas to steam ratio of 1.5 and the carbon formation.

after 1200 min shows carbon species exhibiting a peak maximum at 660 °C compared to the fixed-bed one after 360 min with a maximum at 690 °C. Based on the analysis of the carbon deposits, it can be concluded that the fluidized bed prevents carbon build-up and only causes relatively low amounts of low temperature carbon to form. By decreasing feed gas to steam ratio to 0.75, carbon deposition was reduced dramatically for all samples and no carbon was observed with increasing temperatures from the TPO profile.

Although very limited carbon deposition was observed for both cases, the catalytic activities for both reformers were not the same. Enhanced conversions during fluidized-bed reforming are probably due to the different nature of carbonaceous species deposited. Both TPO profiles are similar indicating only small peaks at low temperature. Surface XPS analysis of both catalysts (Fig. 5) shows similar C 1s transitions at  $\sim 285$  and  $\sim 288$  eV, assigned to crystallized ( $-\text{C}-\text{C}-$ ) and amorphous ( $-\text{C}-\text{CO}-$ ) structures [7]. The full width at half maximum (FWHM) of the peak at 285 eV for the fixed-bed reactor sample

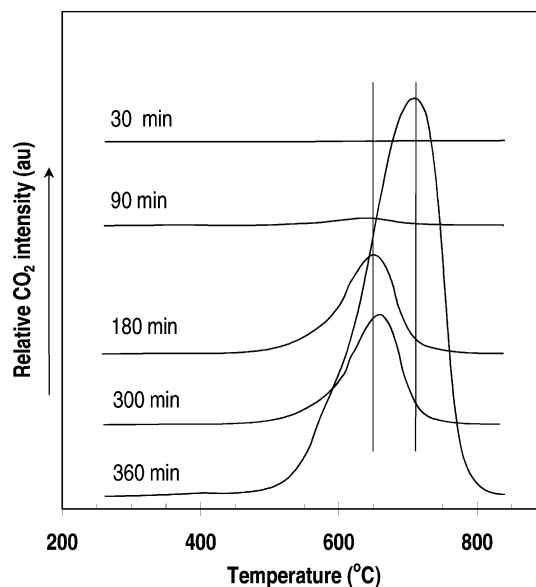


Fig. 3. TPO profiles resulted from the fixed-bed reforming under feed gas to steam ratio of 1.5 before plugging the reactor.

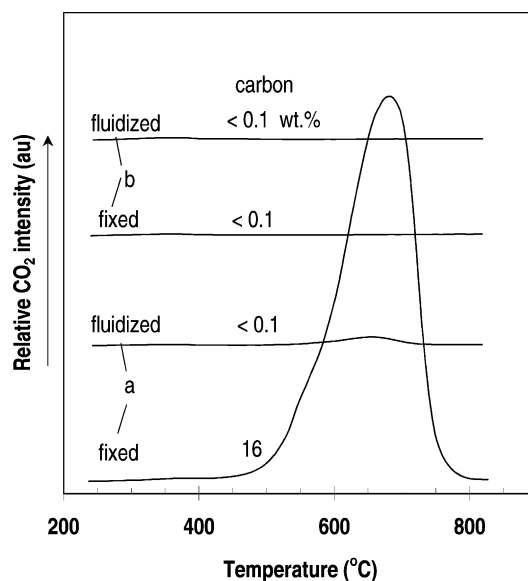


Fig. 4. TPO profiles of spent catalysts after the reforming with a feed gas to steam ratio of 1.5 in (a) fluidized- and fixed-bed reactors for 1200 and 360 min, respectively, and (b) both reactors for 1200 min.

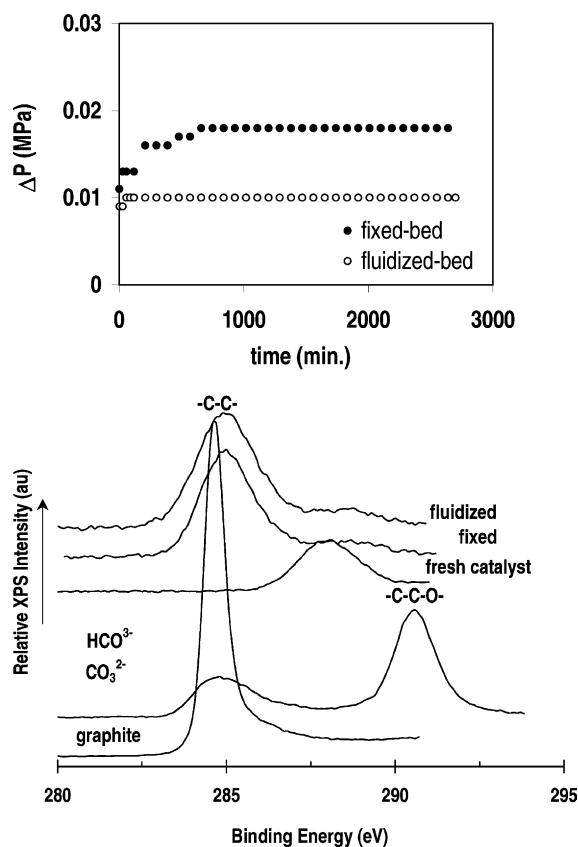


Fig. 5. C 1s spectra of the fluidized- and fixed-bed spent catalysts and pressure drops over the beds during the reforming with feed gas to steam ratio of 0.75.

indicates a smaller value, namely 1.79, compared to 2.0 determined for the fluidized-bed sample. XPS and TPO results suggest that carbon of identical nature is present although a remarkable catalytic difference was observed between the two reforming reactors. Insignificant changes to the pressure drops over the reactors during 2700 min of operation were recorded, reflecting limited carbon deposition. Overall pressure drop over the fixed-bed reactor was substantially larger than that over the fluidized-bed one, which was consistent with the relatively high space velocity applied.

### 3.3. Catalyst-bed temperature

As the highly endothermic reforming reaction may cause a significant temperature gradient and hence affect the catalytic activity a great deal, temperature

uniformity was addressed. Under Ar flow and a reactor-wall temperature of 750 °C, no temperature difference was observed between the catalyst bed and the wall. When a mixture of the feed gas to steam of 1.5 was introduced, the catalyst-bed temperature gradually decreased to 723 °C in the case of fluidized reforming and to 684 °C in the case of fixed-bed operation. When the feed gas to steam ratio was decreased to 0.75 the catalyst-bed temperature in the case of fixed-bed operation decreased only to 691 °C, conversely the fluidized-bed temperature decreased to 737 °C (see Table 1). It appears that as the feed gas/steam ratio is increased the overall heat of reaction increases. This can only be due to the WGS, since all other reactions are endothermic or do not involve H<sub>2</sub>O [14]. It is also clear that fluidized-bed operation is beneficial in order to avoid the development of a significant temperature profile in the catalyst bed. It is well known that the heat transfer rates that can be achieved in fluidized-bed reactors are significantly higher than those in fixed-bed reactors.

In order to directly compare the catalytic activity in the fixed-bed reformer with that of the fluidized-bed reactor, a catalyst-bed temperature of 738 °C was set by increasing the reactor wall to 800 °C. The results in Table 1 show that enhancing the fixed-bed temperature to that of the fluidized bed did increase the catalytic activity to the same value (based on CH<sub>4</sub> and CO<sub>2</sub> conversions). To confirm this observation, the wall temperature of the fluidized reactor was also lowered to approximately 700 °C (catalyst-bed temperature of 690 °C). This again gave the same conversion as observed in the fixed-bed reactor with the same bed temperature. Isothermal behavior of the catalyst bed in a fluidized reformer provides better control of reaction temperatures eliminating cold spots and minimizing a temperature gradients.

### 3.4. Surface composition of (spent) catalysts

Despite of the above advantages of a fluidized-bed reformer, mechanical loss due to catalyst attrition may take place caused by the solid circulation. Catalyst surface atomic compositions are listed in Table 2 for samples run at feed gas to steam ratios of 1.5 and 0.75 after 2700 min. In the case of the low feed gas to steam ratio (0.75), the only difference observed between the surface composition of the fixed-bed catalyst



Table 2

Results of XPS analysis of the spent catalysts obtained after the fluidized- and fixed-bed reforming

Catalysts (spent)	Feed gas/H <sub>2</sub> O	Relative XPS elemental surface compositions (at.%)			
		Ni	Al	O	C
Fresh		5.7	20.2	58.4	15.7
Fluidized bed after 1200 min	1.5	2.9	22.3	56.2	18.6
Fluidized bed after 2700 min	0.75	2.1	54.0	32.5	11.4
Fixed bed after 2700 min	0.75	1.2	54.6	33.6	10.4

and that of the fluidized-bed catalyst is the loss of surface nickel. It is not clear what might have caused this apparent loss. When the feed gas to steam ratio was decreased from 1.5 to 0.75, a significant enrichment of the surface with aluminum occurs. Even under reducing conditions, the Al will be present in the form of the oxide. We believe that the Al<sub>2</sub>O<sub>3</sub> interacts with the H<sub>2</sub>O present in the gas phase and causes the Al<sub>2</sub>O<sub>3</sub> to migrate to the surface. The surface concentration of carbon does not depend on the mode of operation and was found to be relatively low supporting the evidence from the TPO experiments. The Ni 2p spectra for the fixed- and the fluidized-bed catalysts are compared to that of the fresh catalyst in Fig. 6. There is clear evidence that the used catalyst in both cases has been reduced (BE reduction from 855.9 eV to approximately 852.7 eV).

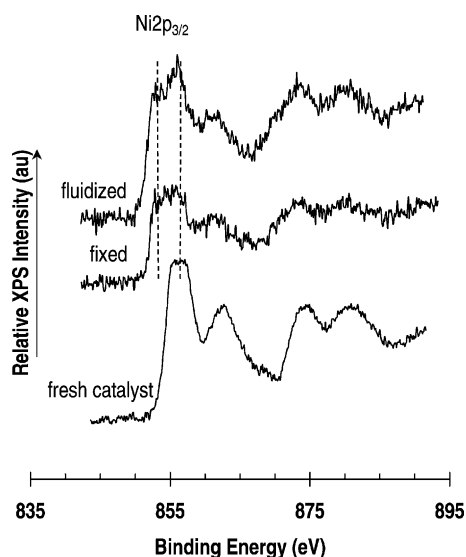


Fig. 6. Ni 2p spectra of fresh and spent catalysts after the reforming with a feed gas to steam ratio of 0.75.

### 3.5. Steam reforming of biogas in a micro-fluidized-bed reactor

#### 3.5.1. Effect of steam

Results of the fluidized-bed reforming with various feed gas to steam ratios for 300 min at a furnace temperature of 750 °C are presented in Fig. 7. At the given temperature, the catalytic activity of Ni/Al<sub>2</sub>O<sub>3</sub> with respect to CH<sub>4</sub> conversion increased with decreasing feed gas to steam ratio from 1.5 to 0.3. An almost

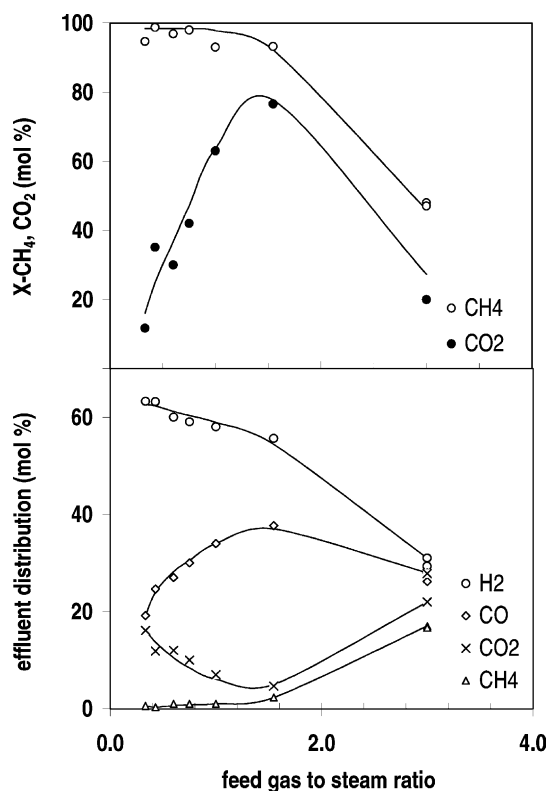


Fig. 7. Effect of steam on the conversions and effluent distribution in the fluidized reformer at 750 °C.

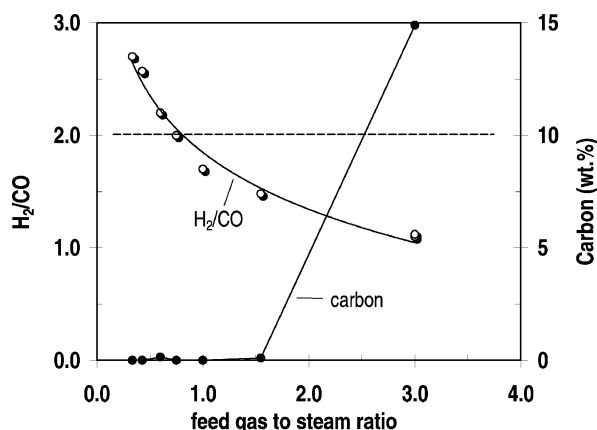


Fig. 8. Effect of steam addition on syngas ( $H_2/CO$ ) ratios and carbon amount in the fluidized reformer at 750 °C.

complete  $CH_4$  conversion was achieved for the ratios  $<1.5$ . On the other hand, the  $CO_2$  conversion exhibited a maximum at a feed gas to steam ratio of 1.5, and then was followed by a rapid decrease. The reforming reaction is favored with  $CH_4$  over that with  $CO_2$  and the product spectrum demonstrated a higher selectivity for  $H_2$  and suppression of  $CO$ . This phenomenon is consistent with the simultaneous occurrence of the WGSR (Eq. (6)).

As shown in Fig. 8, the  $H_2/CO$  ratios depend strongly on the steam concentration and increase from 1.4 to 2.7 for decreasing feed gas to steam ratios from 3.0 to 0.3. These results are in good agreement with previous estimations that desired ratios can be estimated from thermodynamic calculations, knowing the atomic ratio of  $O/C$  and  $H/C$  [3–5]. Similarly, reforming with  $CH_4:(CO_2+H_2O)=0.86:1$  consisting of a constant ratio of mixed steam and  $CO_2$  did alter  $H_2/CO$ , however, the  $CH_4$  conversion remained unchanged [5]. Steam concentrations not only altered  $H_2/CO$  ratios but also changed the carbon deposition rate onto the catalyst. The carbon deposited on spent catalysts was dramatically reduced with the addition of steam in the ratio  $<1.5$ . For ratios of  $>1.5$ , the reaction indicated critical conditions for carbon formation due to a low  $H/C$  ratio. Furthermore, it was observed that the catalyst fluidization was very poor due to the massive carbon deposits causing agglomeration of particles. Thus, steam plays an important role in the effective removal of carbon (Eq. (5)).

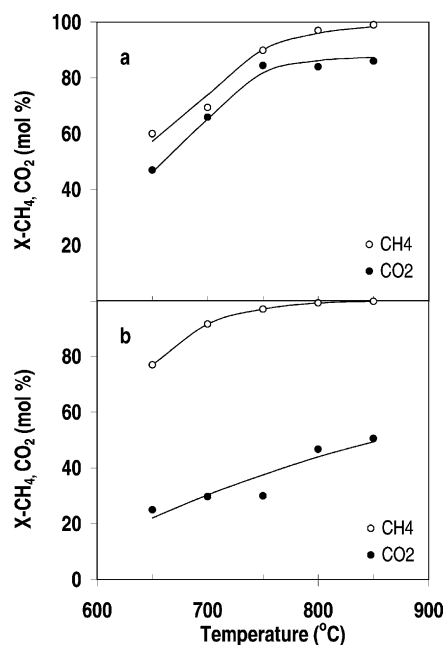


Fig. 9. Effect of temperature on the conversions under feed gas to steam ratios of (a) 1.5 and (b) 0.60, respectively.

### 3.5.2. Effect of temperature

Results of conversions as a function of wall temperature for feeds with feed gas to steam ratios of 1.5 and 0.6 are presented in Fig. 9. In general, all conversions increased with the increase of temperatures and overall  $CH_4$  conversions were consistently higher than the  $CO_2$  conversions. For all cases, increasing the temperatures enhanced the selectivity towards  $H_2$  and  $CO$ , suggesting that the results were consistent with the fact that Eq. (6) is not favored thermodynamically at higher temperatures [5]. Under low feed gas to steam ratios, an almost complete conversion ( $\approx 100\%$ ) of  $CH_4$  was achieved at 850 °C and  $CO_2$  conversion was also highest. When the steam concentration was reduced, the overall  $CH_4$  conversions were reduced. Lowering the steam concentration decreased the  $H_2$  selectivity and increased the  $CO$  selectivity. As shown in Fig. 10, with increasing temperatures,  $H_2/CO$  ratios decreased for both feeds and varied between 1.4 and 2.7. Eq. (6) is favored at lower temperature and in the presence of high steam concentrations, promoting  $H_2$  selectivity and consuming  $CO$ . Hence, decreasing  $H_2/CO$  ratios with increasing temperature were observed.



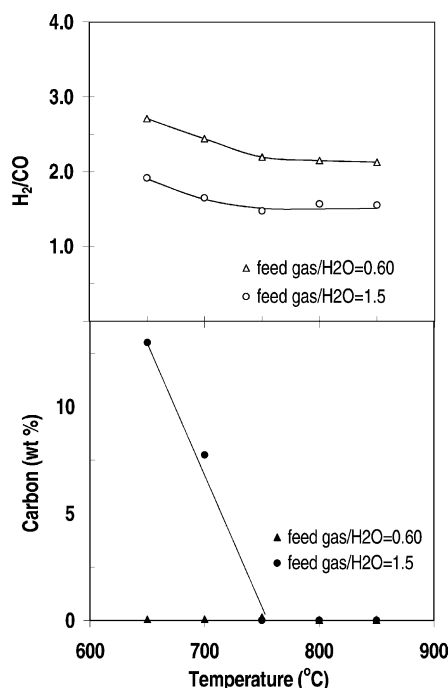


Fig. 10. Effect of temperature on syngas ( $H_2/CO$ ) ratios and carbon amount under feed gas to steam ratios of 1.5 and 0.60, respectively.

#### 4. Conclusions

Steam reforming of a clean model biogas over a  $Ni/Al_2O_3$  catalyst in fluidized- and fixed-bed reactors was performed. Conducting the reforming in a fluidized-bed reactor increased the performance of the catalyst compared to that in the fixed-bed one. Conversions increased between 7 and 15%. Fast carbon formation was observed in the fixed bed with a feed gas to steam ratio of 1.5 causing complete reactor blockage. A feed gas to steam ratio of 0.75 reduced carbon deposition and only limited amounts were deposited, moreover, the nature of the carbon might not affect the catalytic activity. The inferior heat distribution in the fixed-bed reactor created cold spots in the catalyst bed yielding much lower conversions than the fluidized-bed reactor. Studies on the fluidized reformer alone showed increasing steam concentrations leading to higher  $H_2$  and lower  $CO$  selectivities. Carbon deposition reduced significantly when steam concen-

trations were increased. Increasing temperatures increased overall conversions.

For further reading see [15–18].

#### Acknowledgements

We acknowledge financial support by the Japan International Science and Technology Exchange Corporation under the STA Fellowship Program.

#### References

- [1] R. Burch, B.W.L. Soutward, *J. Catal.* 195 (2000) 217–226.
- [2] United States Environment Protection Agency/White House Initiative on Global Climate Change <http://www.whitehouse.gov/Initiatives/Climate/main.html> and related sites.
- [3] J.R. Rostrup-Nelson, in: J.R. Anderson, M. Boudart (Eds.), *Catalytic Steam Reforming, Catalysis Science and Technology*, vol. 5, Springer, New York, 1984 (Chapter 1).
- [4] J.R. Rostrup-Nelson, *Stud. Surf. Sci. Catal.* 36 (1987) 73–78.
- [5] V.R. Choudhary, A.M. Rajput, *Ind. Eng. Chem. Res.* 35 (1996) 3934–3939.
- [6] A. Effendi, Z.-G. Zhang, M. Sahibzada, T. Yoshida, *Am. Chem. Soc. Div. Petrol. Chem. Prepr.* 45 (2000) 135–137.
- [7] A. Effendi, Z.-G. Zhang, T. Yoshida, *Proceedings of the ACS Symposium Series*, vol. 809, American Chemical Society, Washington, DC, 2002, Chapter 18.
- [8] A. Effendi, O. Nishimura, Z.-G. Zhang, T. Yoshida, *Proceedings of the 89th CAJT*, vol. 42, no. 6, 2000, p. 3104.
- [9] T. Wurzel, S. Malcus, L. Mleczko, *Chem. Eng. Sci.* 55 (2000) 3955–3966.
- [10] L. Mleczko, S. Malcus, T. Wurzel, *Ind. Eng. Chem. Res.* 35 (1997) 4459–4465.
- [11] O. Olbye, L. Mlecko, T. Wurzel, *Ind. Eng. Chem. Res.* 36 (1997) 5180–5188.
- [12] D. Qin, J. Lapszewicz, X. Jiang, *J. Catal.* 159 (1996) 140–149.
- [13] V.C.H. Kroll, *Fuel Energy Abstr.* 38 (1997) 89.
- [14] A.M. Gadalla, B. Bower, *Chem. Eng. Sci.* 44 (12) (1989) 2825–2829.
- [15] V.R. Choudhary, B.S. Uphade, A.S. Mamman, *Appl. Catal.* 168 (1998) 33–46.
- [16] J.R. Rostrup-Nielsen, *Natural gas conversion II*, *Stud. Surf. Sci. Catal.* 81 (1994) 25–41.
- [17] D. Kunii, O. Levenspiel, *Fluidization Engineering*, 2nd ed., Butterworths/Heinemann, London, 1991.
- [18] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of XPS*, Perkin Elmer Corporation, Physical Electronics Division, MN, 1992.