Short communication

Hydrogen production by coupled catalytic partial oxidation and steam methane reforming at elevated pressure and temperature

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Abstract

Hydrogen production by coupled catalytic partial oxidation (CPO) and steam methane reforming of methane (OSMR) at industrial conditions (high temperatures and pressures) have been studied over supported 1 wt.% NiB catalysts. Mixture of air/CH_4/H_2O was applied as the feed. The effects of O_2:CH_4 ratio, H_2O:CH_4 ratio and the gas hourly space velocity (GHSV) on oxy-steam reforming (OSRM) were also studied. Results indicate that CH_4 conversion increases significantly with increasing O_2:CH_4 or H_2O:CH_4 ratio. However, the hydrogen mole fraction goes through a maximum, depending on reaction conditions, e.g., pressure, temperature and the feed gases ratios. Carbon deposition on the catalysts has been greatly decreased after steam addition. The supported 1 wt.% NiB catalysts exhibit high stability with 85% methane conversion at 15 bar and 800 °C during 70 h time-on-stream reaction (CH_4:O_2:H_2O:N_2 = 1:0.5:1:1.887). The thermal efficiency was increased from 35.8% by CPO (without steam) to 55.6%. The presented data would be useful references for further design of enlarged scale hydrogen production system.
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Keywords: Hydrogen production; Catalytic partial oxidation; Steam reforming; Methane; Ni catalyst

1. Introduction

During the past 20 years, hydrogen has been widely used in oil refineries for hydrogenation reactions [1]. Recently, there has arisen a strong interest in using H_2-based fuel cells as future source of energy due to the high conversion efficiency of hydrogen energy to electricity as well as no emissions of pollutant gases [1,2]. Currently, steam methane reforming (SMR) (1) is the most commonly utilized process for hydrogen production [1,3,4], i.e.,

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H^{\circ}_{298} = +206 \, \text{kJ mol}^{-1} \quad (1)$$

This is a mature technology, but there is certainly room for improvement. High consumption of energy is inevitable due to the high endothermic nature of the reaction and the need to use excess steam to reduce carbon formation. The catalytic partial oxidation of methane (CPO) given by reaction (2) is a mild exothermic process with fast reaction rate. A few drawbacks,

such as catalyst deactivation due to carbon formation, the danger of explosion during feed-gas premixing and hot spots in catalyst bed, limit its commercial application [3–5].

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad \Delta H^{\circ}_{298} = -36 \, \text{kJ mol}^{-1} \quad (2)$$

Recently, oxy-steam reforming (OSRM), a combination of reactions (1) and (2), has been considered as an alternative route to hydrogen [4,6–9]. The use of steam as a co-reactant is beneficial for a number of reasons. It converts some of the carbon monoxide to carbon dioxide and additional hydrogen via the water–gas-shift (WGS), as represented by reaction (3), and hot spots in the catalyst bed may be extinguished. It can also avoid the explosion range, and mitigate carbon formation on the catalyst.

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H^{\circ}_{298} = +41 \, \text{kJ mol}^{-1} \quad (3)$$

Methane conversion via OSRM is higher than that of SRM or CPO under the same reaction temperature and pressure. A thermodynamic analysis by computer simulation [6] shows that simultaneous CPO and SMR processes require no extra heat from external sources. That is, the required thermal energy for

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endothermic SMR is obtained from the exothermic CPO, and the equilibrium product composition and the equilibrium temperature are both dependent on the oxygen:fuel ratio and water:fuel ratio. A very high methane conversion, 99.1%, has been reported for OSRM over a Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ catalyst [7] or a Ni/Ce-ZrO$_2$ catalyst [8] at 750 °C and 1 bar. The performance was maintained for at least 100 h. A much higher yield of hydrogen was observed for the catalytic partial oxidation of *n*-hexane over a Rh-containing monolith catalyst with steam as compared with that without steam [4]. It is noted that all the above examples were operated at atmospheric pressure. An industrial process under moderate pressures is preferred, however, since natural gas is usually supplied at pressure and the subsequent processes, including the water–gas-shift reaction, are all operated at high pressures, and pressure can impact carbon deposition profoundly [5]. For industrial applications, the OSRM catalysts are recommended to be studied at high pressures, i.e., >10 bar [1,5].

We have recently found a low Ni loading (<1 wt.%), Ca-decorated-Al$_2$O$_3$ supported NiB catalyst for CPO, on which low coke formation as well as high activity/selectivity were measured even at 15 bar pressure [10]. In this paper, the above NiB catalysts are studied for OSRM at furnace temperatures from 750 to 950 °C and pressures from 1 to 15 bar. Methane conversion of 85% can be obtained under 800 °C and 15 bar, which are conditions very near to those encountered in industrial operation. The effect of H$_2$O:CH$_4$ ratio (and O$_2$:CH$_4$ ratio) on the methane conversion and H$_2$ yield, as well as carbon formation, are also investigated.

2. Experimental

The catalysts applied in this paper were prepared via the same procedures as previously reported [10]. In short, commercial γ-Al$_2$O$_3$ was modified by impregnating with aqueous Ca(NO$_3$)$_2$ with 7 wt.% of Ca, dried at 100 °C overnight, and then calcined at 800 °C for 5 h. This Ca-modified γ-Al$_2$O$_3$ support is denoted as Ca-AlO. The 1 wt.% NiB/Ca-AlO catalyst was prepared in two steps: first, the 1 wt.% Ni/Ca-AlO was prepared by wet impregnation. The prepared catalyst was dried at 100 °C overnight, then calcined at 300 °C for 2.0 h. Second, 1 wt.% NiB/Ca-AlO was obtained by chemical reduction with KBH$_4$.

OSRM was carried out in the stainless-steel jacketed, quartz, tubular reactor [10]. The outlet temperature of the gas phase was measured by sliding a Cr–Al thermocouple from the bottom of the reactor. The water flow rate was controlled by a liquid delivery unit (Shimadzu LC-10AT) and the feed lines were heat traced to insure complete vaporization. Oxygen was pre-mixed with steam before it mixed with methane. The flow rate of feed gas was controlled by Brooks 5850E thermal mass flow controllers. The outlet gas was cooled by a cold trap to condense the high boiling point components before analysis by gas chromatography (GC 8000 Top, CE Instruments). Analysis by MS shows that O$_2$ was converted completely in our study. Methane conversion and selectivity of carbon-containing products were calculated on a C-atom basis using a normalized method.
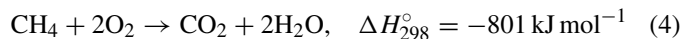
In the study of the steam:CH$_4$ ratio effect, 150 mg of 1 wt.% NiB/Ca-AlO catalyst was charged to the reactor, the H$_2$O:CH$_4$ ratio was varied from 0 to 3 while the CH$_4$:O$_2$ ratio was fixed at 2. The reaction was tested at a gas hourly space velocity (GHSV) of 3000 and 8000 CH$_4$ ml g$_{cat}$$^{-1}$ h^{-1}, pressure of 1 bar (or 15 bar, respectively), and furnace temperature of 850 °C. The GHSV is based on the flow rate of methane. The effect of the O$_2$:CH$_4$ ratio on methane conversion and H$_2$ yield (the H$_2$ mole number derived from one mole of methane) was studied at 15 bar and 850 °C with a constant CH$_4$ flow rate of 20 ml min^{-1}, and a H$_2$O:CH$_4$ ratio of 1.35 (or 2, respectively).

The thermodynamic equilibrium calculation was carried out using 'React!' software based on minimization of the Gibbs free energy. Carbon was not included in the calculation. Carbon contents on the used catalysts were measured by TGA/DTA (SETARAM, Labsys^{TM}). The morphology of used catalysts was investigated by means of a JEOL scanning electronic microscope (FEG SEM SM 6700 F).

3. Results and discussion

To understand the results obtained, it is useful to discuss the reactions involved during OSRM. As proposed by many researchers, such as Lunsford and co-workers [11] and Choudhary et al. [12], CPO reaction starts with the total oxidation of methane (Eq. (4)) and this is followed by the steam (Eq. (1)) and CO$_2$ (Eq. (5)) reforming reactions.

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \quad \Delta H^{\circ}_{298} = -801 \, kJ \, mol^{-1} \quad (4)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad \Delta H^{\circ}_{298} = +247 \, kJ \, mol^{-1} \quad (5)$$

As it is well known that CPO (Eq. (2)) is a very fast reaction that can proceed in the range of milliseconds while SMR (Eq. (1)) is a relative slow reaction. On the other hand, CPO is slightly exothermic and SMR is strongly endothermic. Therefore, in the integrated reaction of these two, contact time, steam:CH$_4$ ratio and O$_2$:CH$_4$ ratio affect the methane conversion and selectivity pronouncedly. High contact times and high temperatures favour the endothermic reforming reactions (1) and (5), while low contact times and low temperatures favour the oxidation reaction (4). The water–gas-shift reaction (Eq. (3)) is involved and is also favoured at low temperatures. In the following sections, the effects of H$_2$O:CH$_4$, O$_2$:CH$_4$ ratios and GHSV on OSRM are studied.

3.1. Effects of H$_2$O:CH$_4$ ratio and GHSV on OSRM

The influence of the steam:CH$_4$ ratio (fixed CH$_4$:O$_2$ ratio of 2) was studied at pressures of 1 bar (Figs. 1 and 2) and 15 bar (Fig. 3). The GHSV (based on the flow rate of methane) effect was investigated at 1 bar with GHSVs of 3000 ml g$_{cat}$$^{-1}$ h^{-1} (Fig. 1) and 8000 ml g$_{cat}$$^{-1}$ h^{-1} (Fig. 2).

Methane conversion and CO selectivity are shown in Fig. 1(a) and the H$_2$:CO ratio and H$_2$ yield (i.e., mole number of H$_2$ in product derived from 1 mol of methane) are presented in Fig. 1(b). The solid lines are experimental results under the operation conditions of 1 bar, a GHSV of 3000 ml g$_{cat}$$^{-1}$ h^{-1}, and a furnace temperature 850 °C. The dotted lines are calculated results at 1 bar and a reaction temperature 710 °C. Methane con-
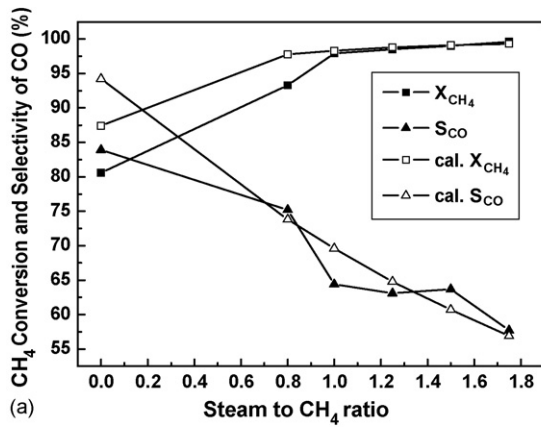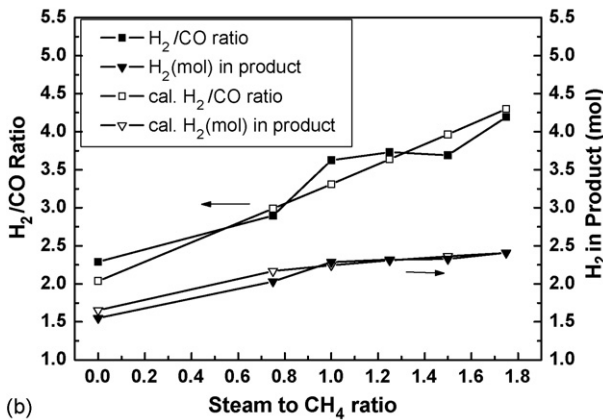
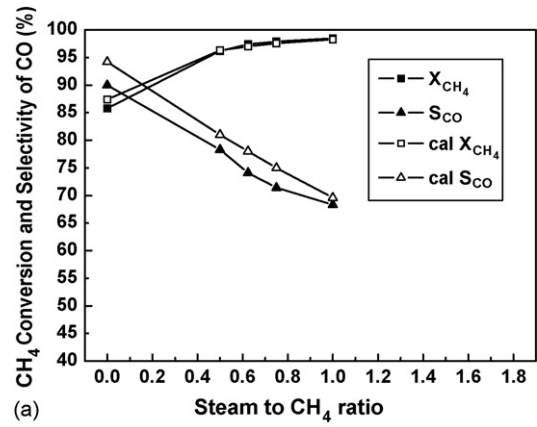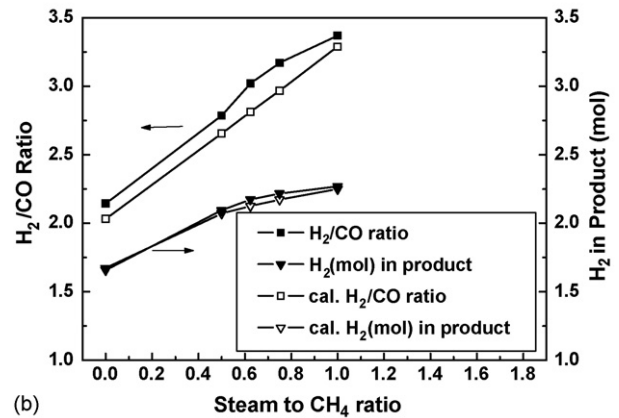Fig. 1. Effect of steam:CH$_4$ ratio on: (a) CH$_4$ conversion and CO selectivity and (b) H$_2$:CO ratio and H$_2$ yield (H$_2$ mole number derived from 1 mol of methane) for OSRM reaction over 1 wt.% NiB/Ca-AlO catalyst (furnace temperature $T_f = 850\,°C$, $P = 1$ bar, GHSV = 3000 ml g$_{cat}^{-1}$ h^{-1}, CH$_4$:O$_2$:N$_2$ = 1:0.5:1.887). For comparison, thermodynamic calculation results of OSRM reaction under $P = 1$ bar and reaction temperature $T = 710\,°C$ are included (dashed lines).

version increases greatly from 80.8 to 98.6% when the H$_2$O:CH$_4$ ratio increases from 0 to 1.25. It then increases slightly to 99.6% when the ratio increases further to 1.75. Note that the measured methane conversions are lower than the calculated values when the steam-to-CH$_4$ ratio is less than 1, but the two results fit very well when the ratio is between 1 and 1.8. The large discrepancy between the experimental and calculated data for H$_2$O:CH$_4$ < 1 may be due to the too small water flow rate that is difficult to measure accurately. The H$_2$ yield follows the same trend as that of CH$_4$ conversion, and agrees well with the calculated data; it reaches 2.4 mol when the steam-to-CH$_4$ ratio is 1.75. The selectivity of CO decreases linearly with increasing H$_2$O:CH$_4$ ratio, whereas the H$_2$:CO ratio increases from around 2 to 4.25. The increment of H$_2$ yield and H$_2$:CO ratio is the result of the

Fig. 2. Effect of steam:CH$_4$ ratio on: (a) CH$_4$ conversion and H$_2$ yield and (b) H$_2$:CO ratio and CO selectivity for the OSRM reaction over 1 wt.% NiB/Ca-AlO catalyst ($T_f = 750\,°C$, $P = 1$ bar, GHSV = 8000 ml g$_{cat}^{-1}$ h^{-1}, CH$_4$:O$_2$:N$_2$ = 1:0.5:1.887). Calculations are based on conditions: $P = 1$ bar and $T = 715\,°C$).

SRM and WGS reactions, which favour the formation of H$_2$ and CO$_2$. Because both these reactions are endothermic, the energy consumption is so intense that the actual reaction temperature (thermodynamic equilibrium temperature) is much lower than that of the furnace (i.e., 710 °C versus 850 °C). By contrast, with a higher GHSV of 8000 ml g$_{cat}^{-1}$ h^{-1} (Fig. 2), the methane conversion reaches 98.4% at a steam:CH$_4$ ratio of only 0.75 and a lower furnace temperature of 750 °C. The experimental results are close to the thermodynamic equilibrium values at 715 °C.

For comparison, Table 1 lists the H$_2$ yield and H$_2$:CO ratio that correspond to the same methane conversion of 98% but under different reaction conditions in Figs. 1 and 2, respectively. It is clear that the two different reaction conditions, either low furnace temperature, low steam-to-CH$_4$ ratio and high GHSV or high furnace temperature, high steam-to-CH$_4$ ratio and low GHSV, can both achieve the same CH$_4$ conversion and hydrogen

Table 1
Catalytic performance of OSRM on 1 wt.% NiB/Ca-AlO catalyst under different reaction conditions

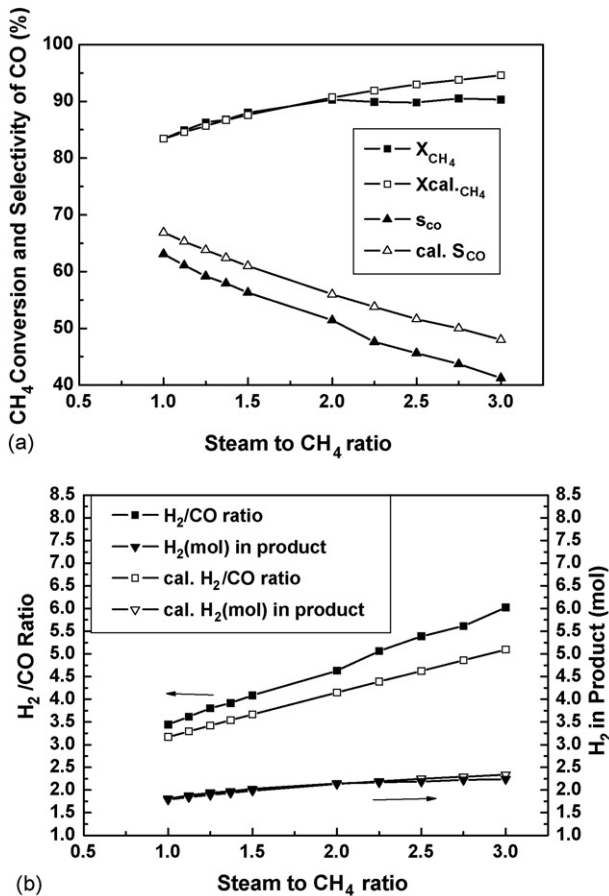| Reaction conditions			Reaction results		
Furnace temperature (°C)	GHSV (ml g$_{cat}^{-1}$ h^{-1})	Steam:CH$_4$ ratio	CH$_4$ conversion (%)	H$_2$ yield (mol)	H$_2$:CO ratio
850	3000	1.25	98.4	2.3	3.65
750	8000	0.75	97.6	2.2	3.05

Fig. 3. Effect of steam:CH_4 ratio on: (a) CH_4 conversion and H_2 yield and (b) CO selectivity and H_2:CO ratio for OSRM over 1 wt.% NiB/Ca-AlO catalyst under conditions: $T_f = 850\,°C$, $P = 15\,bar$, GHSV = 8000 ml $g_{cat}^{-1}\,h^{-1}$, CH_4:O_2:N_2 = 1:0.5:1.887.

Fig. 4. Effect of O_2:CH_4 ratio on: (a) CH_4 conversion and CO selectivity and (b) H_2 yield and H_2:CO ratio for OSRM over 1 wt.% NiB/Ca-AlO catalyst. ($T_f = 850\,°C$, $P = 15\,bar$, GHSV = 8000 ml $g_{cat}^{-1}\,h^{-1}$, CH_4:H_2O:N_2 = 1:2:1.887.) For comparison, thermodynamic calculation results of OSRM reaction under $P = 15\,bar$ and reaction temperature $T = 810\,°C$ are included (dashed lines).

yield. This is understandable since more heat is generated with a higher GHSV due to the exothermic property of the CPO reaction and the increase in furnace temperature will in turn facilitate CH_4 conversion through the CPO and SRM reactions. The difference in the H_2:CO ratio reflects the effect of the steam-to-CH_4 ratio.

Methane conversion and H_2 yield as a function of steam:CH_4 ratio under the reaction conditions of 15 bar, a furnace temperature $850\,°C$ and a GHSV of 8000 ml $g_{cat}^{-1}\,h^{-1}$ are displayed in Fig. 3. With an increasing ratio from 1.0 to 2.0, methane conversion increases linearly up to 90%, and the values fit well to the thermodynamic equilibrium data at $800\,°C$. As the ratio increases from 2.0 to 3.0, the calculated values increase slightly while the experimental methane conversion remains constant. This may be explained by the fact that as the amount of steam in the feed gas increases, the contribution of the steam reforming reaction increases in the overall reaction. Since steam reforming is highly endothermic, the external heat supplied by the furnace may not be sufficient to maintain the reaction. In other words, at high steam:CH_4 ratios the thermodynamic equilibrium is not established. The steam that does not react limits the reaction temperature by taking up some of the heat released by the oxidation reactions. This is also reflected in a lower CO selectivity
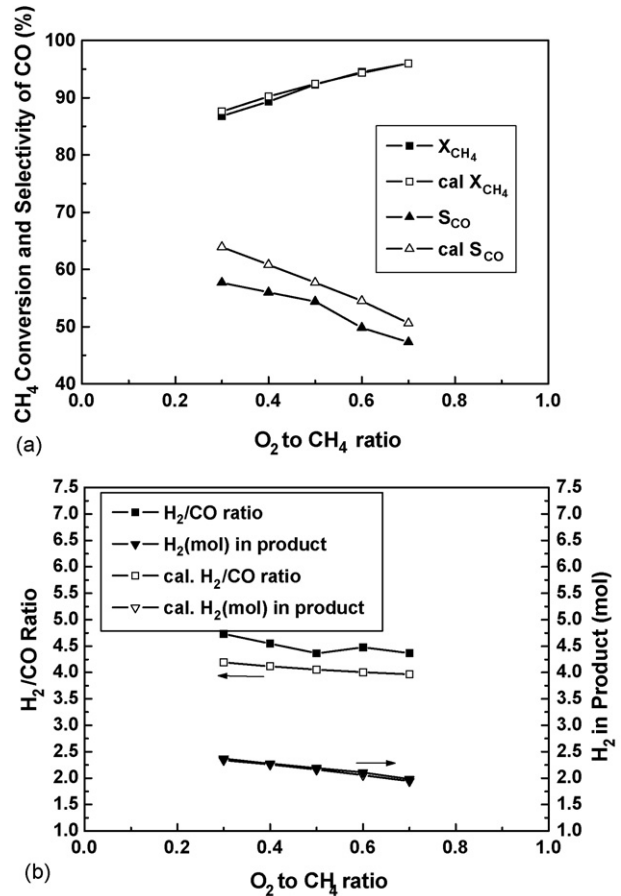
and a higher H_2:CO ratio, since the ratio is 3 for SRM but 2 for CPO. These competing effects ultimately give rise to an optimum amount of steam that properly balances the extent of WGS, steam reforming with the resulting reaction temperature [2]. From the data in Fig. 3, it may be concluded that a moderate H_2O:CH_4 ratio (e.g., 2.0 at 15 bar) is suitable for achieving a thermodynamic high methane conversion and a high H_2 yield at high pressures, though both of these are lower than those at lower pressures (i.e., 90% versus 98% methane conversion and 1.3 versus 2.3 H_2 yield).

3.2. Effect of O_2:CH_4 ratio on OSRM

Since a methane conversion above 90% is preferred by industry, the effect of O_2:CH_4 ratio on methane conversion and H_2 yield is studied at a fixed H_2O:CH_4 ratio of 2.0 or 1.35 to obtain high methane conversion. As shown in Fig. 4 (for H_2O:CH_4 = 2.0) and Fig. 5 (for H_2O:CH_4 = 1.35), methane conversion increases with increasing O_2:CH_4 ratio in the feed, while the H_2 yield, CO selectivity and H_2:CO ratio decreases. This is due to the fact that the increment of O_2 concentration enhances the total oxidation reaction so that CH_4 conversion is increased
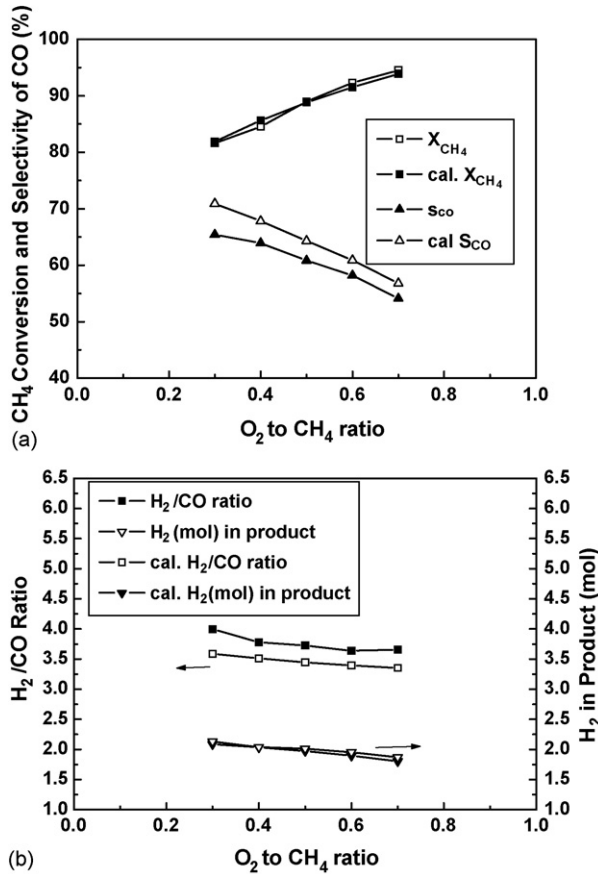
Fig. 5. Effect of O_2:CH_4 ratio on: (a) CH_4 conversion and CO selectivity and (b) H_2 yield and H_2:CO ratio for OSRM over 1 wt.% NiB/Ca-AlO catalyst ($T_f = 850\,^\circ C$, $P = 15$ bar, GHSV = 8000 ml $g_{cat}^{-1}\,h^{-1}$, CH_4:H_2O:N_2 = 1:1.35:1.887). For comparison, thermodynamic calculation results of OSRM reaction under $P = 15$ bar and reaction temperature $T = 810\,^\circ C$ are included (dashed lines).
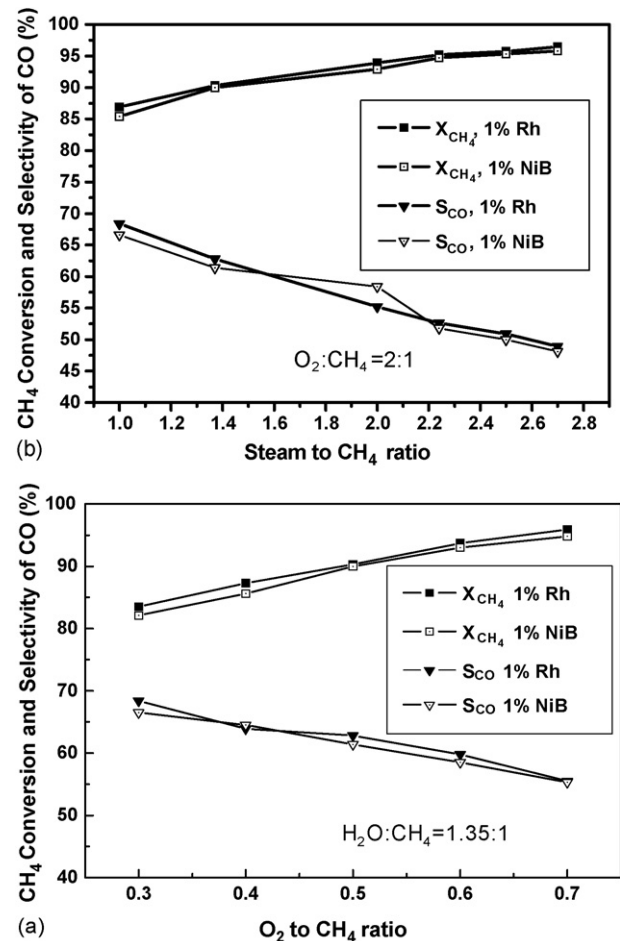

Fig. 6. Comparison of methane conversion and carbon monoxide selectivity over 1 wt.% Rh/Ca-AlO and 1 wt.% NiB/Ca-AlO catalysts as function of: (a) H_2O:CH_4 ratio and (b) O_2:CH_4 ratio.

while H_2 and CO selectivity decrease. Methane conversion of 90% and 2.25 mol of H_2 yield are obtained with a O_2:CH_4 ratio of 0.4 and a H_2O:CH_4 ratio of 2.0 at 15 bar and 810 $^\circ C$. Though a lower H_2O:CH_4 ratio (1.35) and higher O_2:CH_4 ratio (>0.5) can give >90% methane conversion (see Fig. 5(a)), the H_2 yield decreases to 2.0. Hence, in order to produce more hydrogen while maintaining high methane conversion, a moderate O_2:CH_4 ratio of 0.4 and a high H_2O:CH_4 ratio of 2.0 are preferred.

3.3. Comparison of catalytic performance between Ni and Rh catalysts

Noble metal catalysts, especially Rh catalysts, are considered as the most active, selective and least carbon-formation catalysts for the SRM and CPO reactions. Therefore, a 1 wt.% Rh catalyst was prepared and evaluated in comparison with the catalytic performances of 1 wt.% NiB catalysts under identical reaction conditions. The effect of H_2O:CH_4 and O_2:CH_4 ratio on methane conversion and CO selectivity at 15 bar and a furnace temperature of 850 $^\circ C$ is shown in Fig. 6. The catalytic performance of the NiB catalyst is as good as that of the Rh catalyst.

3.4. Thermo-stability of catalysts and carbon deposition during a 70 h reaction

OSRM over 1 wt.% NiB/Ca-AlO catalyst was tested for 70 h at 15 bar, a feed gas mixture of CH_4:O_2:H_2O:N_2 = 1:0.5:1:1.887, and a GHSV of 3000 ml $g_{cat}^{-1}\,h^{-1}$ (and 8000 ml $g_{cat}^{-1}\,h^{-1}$), respectively. As shown in Fig. 7, the methane conversion increases from 67% initially to 79% at 15 h of time-on-stream. Methane conversion then becomes stable until the end of the experiment. Obviously, the induction time is long with such a low GHSV. With a higher GHSV of 8000 ml $g_{cat}^{-1}\,h^{-1}$, methane conversion reaches equilibrium very fast. No obvious deactivation of the catalyst can be found during the 70 h reaction. The thermal efficiency is 55.6%, whereas, under the same reaction temperature (800 $^\circ C$) and pressure (15 bar) the thermal efficiency of CPO (without steam) is only 35.8%. The thermal efficiency was calculated using Eq. (5), i.e.,

$$\eta = \frac{LHV_{H_2}}{LHV_{CH_4}} \times \frac{n_{H_2,out}}{n_{CH_4,in}} \tag{6}$$

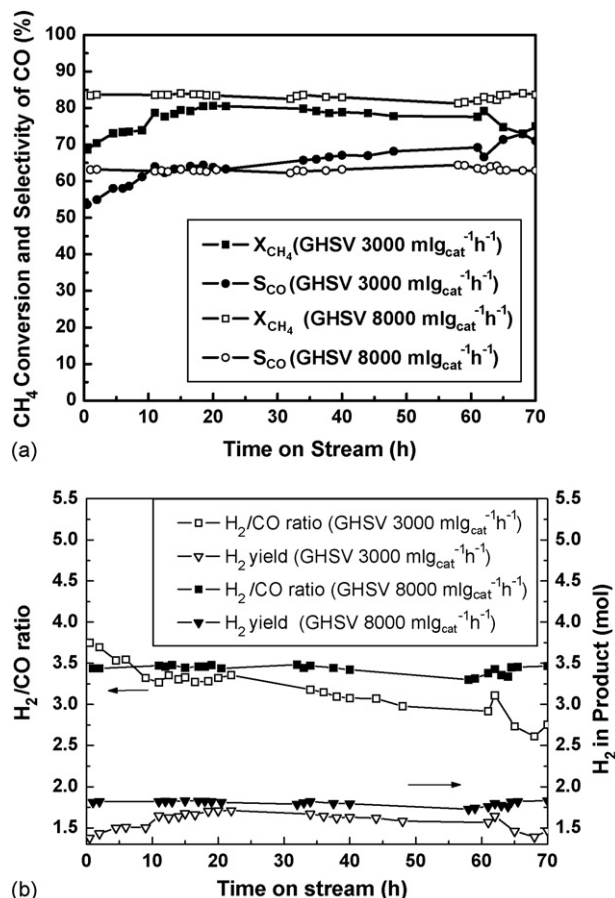where n_i is the moles of species i, and LHV_i is the lower heating value of species i.

Fig. 7. (a) CH_4 conversion and CO selectivity and (b) H_2:CO ratio and H_2 yield for OSRM reaction over 1 wt.% NiB/Ca-AlO catalyst with different GHSV as a function of time-on-stream under conditions: $T_f = 850\,°C$, $P = 15$ bar, $CH_4:O_2:H_2O:N_2 = 1:0.5:1:1.887$.

The effect of steam on mitigation of carbon formation is very obvious. The total carbon deposition formed on the catalyst after 70 h reaction is 2.7 wt.% while 6.7 wt.% of carbon was measured for CPO without steam after only 24 h of reaction.

4. Conclusion

Compared with CPO, the OSRM reaction can increase methane conversion and thermal efficiency and decrease carbon formation dramatically at elevated pressure conditions.

The H_2:CO ratio in the final products is adjustable by varying the $H_2O:CH_4$ and/or $O_2:CH_4$ ratios. A higher $O_2:CH_4$ ratio may result in higher methane conversion but a lower H_2 yield. Methane conversion and syngas selectivity are dependent on the total GHSV. To achieve a higher H_2 yield, therefore, it is necessary to consider the balance between CH_4 conversion, H_2 yield and carbon deposition. Energy efficiency is balanced by carefully tuning the $H_2:CH_4$ and $O_2:CH_4$ ratios, GHSV and reaction temperature and pressure.

The supported 1 wt.% NiB catalyst exhibits high stability with 85% methane conversion at 15 bar and 800 °C during a 70 h time-on-stream reaction ($CH_4:O_2:H_2O:N_2 = 1:0.5:1:1.887$). The thermal efficiency is increased from 35.8% for CPO (without steam) to 55.6%. This is the first reported experimental OSRM reaction under elevated pressure and temperature.

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