Catalytic partial oxidation of methane to synthesis gas over γ-Al_2O_3-supported rhodium catalysts

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The partial oxidation of methane was studied over γ-Al_2O_3-supported catalysts for Rh loadings between 0.01 and 5.0 wt%. It was found that the activity and selectivities for loadings between 0.5 and 5.0 wt% are almost the same. As an example, detailed information is presented for the 1.0 wt% Rh/γ-Al_2O_3, which provides at 750 °C (furnace temperature) an activity of 82% and selectivities of 96% to CO and 98% to H_2, at a gas hourly space velocity (GHSV) of 720000 ml g^{-1} h^{-1}. Its activity remained stable during our experiment which lasted 120 h. Possible explanations for this high stability are proposed based on TPR and XRD experiments. Pulse reactions with small pulses of CH_4 and CH_4/O_2 (2/1) were performed over the reduced and unreduced Rh catalysts to probe the mechanistic aspects of the reaction. The partial oxidation of methane to syngas was found to be initiated by metallic rhodium sites, since the CO selectivity increased with increasing number of such sites.

Keywords: methane partial oxidation, syngas, rhodium, alumina

1. Introduction

An effective pathway to utilize methane is its transformation into the synthesis gas (a mixture of CO and H_2), from which, further, hydrocarbons and methanol can be prepared. Currently, steam reforming is the dominant commercial process employed to produce the synthesis gas [1,2]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^0_{298} = 206 \text{ kJ/mol} \quad (1)$$

However, this process is extremely endothermic and provides a syngas with a too high H_2/CO ratio for the Fischer–Tropsch and methanol syntheses. Recently, the partial oxidation of methane has attracted attention due to its mild exothermicity and suitable H_2/CO ratio [3–23]:

$$CH_4 + (1/2)O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298} = -36 \text{ kJ/mol} \quad (2)$$

The synthesis gas thus produced is an ideal feed stock for methanol and Fischer–Tropsch syntheses.

The catalysts that have been reported to be active and selective towards the partial oxidation of methane to syngas are mainly supported noble metals, such as Rh, Ru, Pd, Pt [3–10], and supported Ni catalysts [11–18], as well as some pyrochlore type oxides, such as $Ln_2Ru_2O_7$ [19,20], and perovskite type oxides, such as $LaMO_3$ (M = Ni, Rh, Co, Cr) [21–23]. While the reaction mechanism was examined in [24–35], no unified point of view has yet been reached.

The scope of the present paper is to report the results obtained over the γ-Al_2O_3-supported Rh catalysts. The effects of Rh loading, reaction temperature, and time on stream are investigated. The nature of the active sites is examined on the basis of pulse reaction experiments with CH_4 and with CH_4/O_2 (2/1).

2. Experimental

2.1. Catalyst preparation

The supported rhodium catalysts were prepared by impregnating γ-Al_2O_3 (Alfa, 60.9 m^2/g) with an ethanol solution of $Rh(NO_3)_3 \cdot 2H_2O$ (Alfa); this was followed by overnight drying at 110 °C and calcination in air at 800 °C for 4 h. The calcined catalysts are denoted Rh(O)/γ-Al_2O_3, while the reduced catalysts, prepared via the reduction of the calcined ones with H_2, are denoted Rh/γ-Al_2O_3. Rh loading means the wt% of Rh in the reduced catalyst.

2.2. Continuous reaction

The experiments were carried out in a continuous-flow reactor at atmospheric pressure. A 3 mm ID quartz tube immersed in an electronically heated furnace was used as reactor. 5.0 mg of catalyst of about 2.5 mm height were placed in the middle of the reactor, supported on quartz wool. A thermocouple was inserted in the center of the catalyst bed to measure the temperature of the catalyst. Another thermocouple located after the quartz wool layer was used to measure the temperature in the gas phase. The analysis of the reactants and products was carried out with an on-line gas chromatograph, equipped with a thermal conductivity detector (TCD) and with Porapak Q and 5A molecular sieve columns. Before reaction, the calcined catalyst was heated in a H_2 flow (20 ml/min) up to 750 °C at a rate of 20 °C/min, after which H_2 was switched to a CH_4/O_2

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(2/1) mixture, at a gas hourly space velocity (GHSV) of 720000 ml g^{-1} h^{-1}.

Methane (99.97% purity, from Matheson) and oxygen (99.9% purity, from Cryogenic) were used without further purification. The gases were premixed before they were introduced into the reactor.

2.3. Pulse reaction

A quartz tube (4 mm inside diameter) was used as reactor. The catalyst powder was held on quartz wool. Helium (35 ml/min), which was purified using Hydro-Purge II and Oxy-Trap columns, was employed as the carrier gas. In the experiments, a reactant gas mixture was injected via a six-way sampling valve into the carrier gas, which was flowing through the reactor. In each run, 50.0 mg of catalyst were used and the pulse volume was 50 μl for both CH_4 and CH_4/O_2 (2/1). For the pulse reaction over the reduced catalyst, the calcined catalyst was reduced in a flow of H_2 (20 ml/min) at 600 °C for 0.5 h (unless otherwise stated). The reactants and products were analyzed with an on-line gas chromatograph equipped with a TCD and a Porapak Q column.

2.4. Catalyst characterization

2.4.1. Surface area

The surface area of the calcined catalyst was determined by nitrogen adsorption, using a Micromeritics ASAP2000 instrument, and the results are presented in table 1. The sample was degassed at 200 °C for at least 5 h in high vacuum prior to nitrogen adsorption.

2.4.2. Dispersion of metal

CO chemisorption was conducted in a pulse reaction apparatus at room temperature. The uptake of CO was used to estimate the initial (before the catalytic process) Rh dispersion and the particle size, by assuming an adsorption stoichiometry of CO : Rh = 1 : 1 and a hemisphere model for the crystallites. The results are listed in table 1. A certain amount of catalyst powder held on quartz wool was reduced in a H_2 flow (20 ml/min) at 600 °C for 1.5 h, then purged with an ultra-high purity helium flow (35 ml/min) at the same temperature for 1 h. After the sample was cooled to room temperature in He, CO (10 μl per pulse) was pulsed over the catalyst until chemisorption saturation was reached. The CO left during the chemisorption experiment was determined quantitatively with a TCD. Both the hydrogen and helium were purified using Hydro-Purge II and Oxy-Trap columns.

Table 1
Physical data for γ-Al_2O_3-supported rhodium catalysts.

Rh loading (wt%)	Surface area (m^2/g)	Dispersion (%)	Particle diameter (nm)
0.01	63.3	100[a]	1.1
0.05	61.4	60.5	1.7
0.2	63.9	32.2	3.3
0.5	63.5	27.6	3.9
1.0	59.3	15.3	7.0
2.0	59.0	9.8	10.9
5.0	59.1	8.5	12.6

[a] Assumed.

2.4.3. Temperature-programmed reduction (TPR)

The TPR of the catalyst was carried out by heating the sample from 50 to 850 °C at a rate of 20 °C/min in a flow of 2.5% H_2/Ar mixture (35 ml/min). The hydrogen consumption in TPR was monitored using a TCD.

2.4.4. X-ray powder diffraction (XRD)

A Siemens D500 X-ray diffractometer was used to identify the phases in a calcined catalyst containing 5.0 wt% Rh. Cu Kα operated at 40 kV and 30 mA was used as the X-ray source.

3. Results

3.1. Continuous reaction

A CH_4/O_2 gas mixture with a molar ratio of 2/1 was used as the feed gas and the partial oxidation of methane was conducted at atmospheric pressure, at 750 °C (furnace temperature) and at a GHSV of 720000 ml g^{-1} h^{-1} over γ-Al_2O_3-supported Rh catalysts. As shown in figure 1, both the methane conversion and the selectivities to CO and H_2 rose notably when the Rh loading was increased from 0.01 to 0.2 wt%, and lightly when it increased from 0.2 to 0.5 wt%; they remained, however, almost unchanged for Rh loadings $\geqslant$0.5 wt%.

The effect of time on stream, up to 120 h, is presented in figure 2 for the 1.0 wt% Rh/γ-Al_2O_3 catalyst. As shown in figure 2, during the 1st hour both methane conversion and selectivities to CO and H_2 increased with time, while during the next 7 h the methane conversion increased slowly;

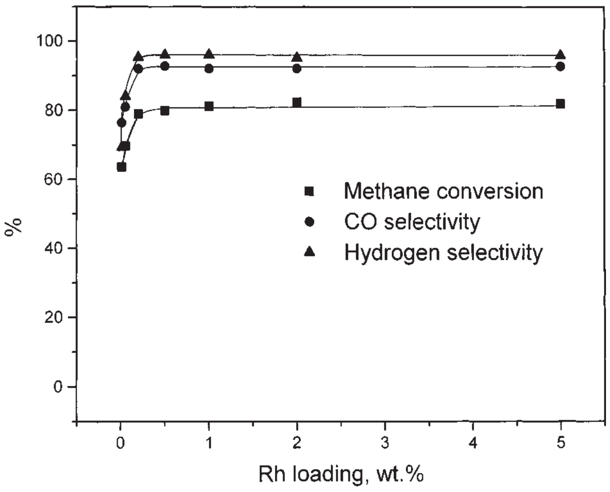

Figure 1. Effect of Rh loading on the performance of rhodium supported on γ-Al_2O_3. $P = 1$ atm, $T_{furnace} = 750$ °C, $CH_4/O_2 = 2.0$, GHSV = 720000 ml g^{-1} h^{-1}. (Remark: data obtained after 10 h of reaction.)

starting with the 8th hour, the methane conversion and selectivities to CO and H_2 remained almost unchanged during the entire experimentation time (120 h). The 1.0 wt% Rh/γ-Al_2O_3 catalyst provided about 82% methane conversion, 96% CO selectivity and 98% H_2 selectivity, with very high stability.

The effect of reaction temperature over the 1.0 wt% Rh/γ-Al_2O_3 is summarized in table 2. One can note that the temperature of the catalyst bed was higher than that of the furnace, but that their difference notably decreased with increasing furnace temperature. With the increase in the catalyst bed temperature, both the conversion and the selectivities to CO and H_2 increased. At each temperature, a syngas with a H_2/CO ratio of about 2 was produced, as expected from the stoichiometry of the reaction.

3.2. Pulse reaction

3.2.1. Reaction between CH_4 pulses and the calcined Rh(O)/γ-Al_2O_3 catalyst

The reaction between methane pulses and Rh(O)/γ-Al_2O_3 was investigated at 700 °C. The amount of surface carbon formed during reaction was calculated from the carbon balance. Figure 3 plots the methane conversion and the selectivities to CO, CO_2 and $\underline{C}$ (surface carbon) as a function of rhodium loading during the first methane pulse. Due to the small volume of a pulse, the methane conversion was 100% over the catalysts with Rh loadings $\geqslant$0.5 wt%. Over the catalyst with a 0.05 wt% Rh loading, the methane conversion was about 40%. With an increase in rhodium loading from 0.05 to 5.0 wt%, the selectivity to CO decreased from 100 to 0%, while that to CO_2 increased from 0 to 100%. Over the 0.05 wt% Rh catalyst only CO was formed as a carbon-containing product. In addition, in the latter case the oxygen balance indicated that the oxygen contained in rhodium oxide constituted only 65% of the oxygen needed for the formation of CO during the first pulse. It is clear that a part of the oxygen has its origin in the OH groups and/or in some low-coordinated oxygen of the support.

Figure 4 provides the methane conversion and the yield of surface carbon over Rh(O)/γ-Al_2O_3 catalysts as a function of the number of methane pulses. The methane conversion was much lower over the 0.05 wt% Rh catalyst than over those with a Rh loading $\geqslant$0.5 wt% (figure 4(a)). However, no carbon deposition occurred over the 0.05 wt% catalyst for as much as 25 pulses (figure 4(b)). Over the catalysts with $\geqslant$0.5 wt% Rh loading (figure 4(b)), the yield

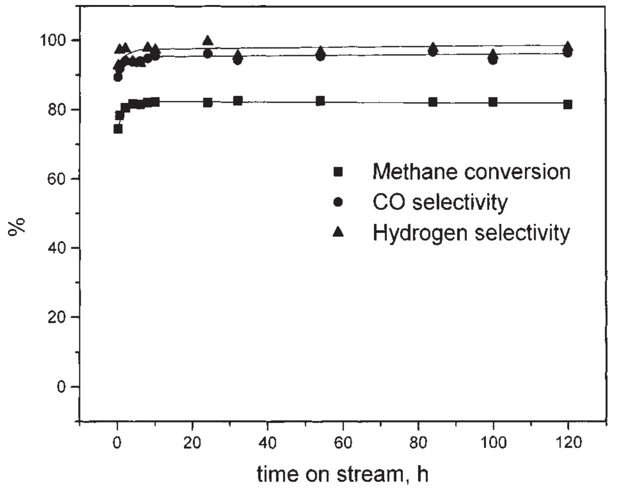

Figure 2. Effect of time on stream on performance of 1.0 wt% Rh/γ-Al_2O_3. $P = 1$ atm, $T_{\text{furnace}} = 750\,^\circ C$, $CH_4/O_2 = 2.0$, GHSV $= 720000\ \text{ml}\,\text{g}^{-1}\,\text{h}^{-1}$.

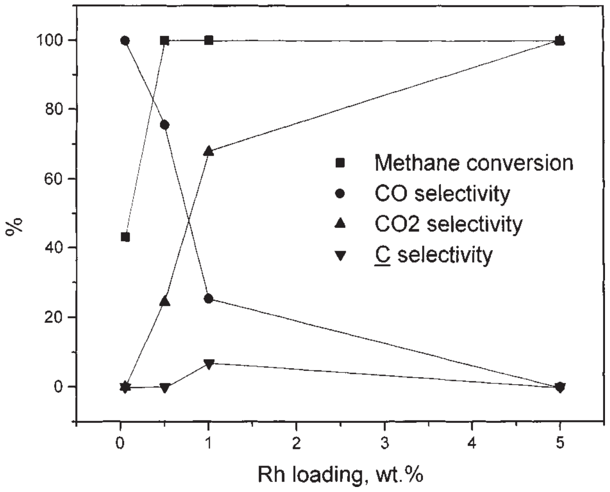

Figure 3. Methane conversion and selectivities to CO, CO_2 and $\underline{C}$ against Rh loading in the reaction between methane and calcined Rh(O)/γ-Al_2O_3 catalysts during the first pulse at 700 °C.

Table 2

Effect of temperature on the performance of 1.0 wt% Rh/γ-Al_2O_3.[a]

Temp. (°C)		CH_4 conv. (%)		CO selec. (%)		H_2 selec. (%)		H_2/CO ratio	
Furnace	Bed	Exp.	Equil.[b]	Exp.	Equil.[b]	Exp.	Equil.[b]	Exp.	Equil.[b]
600	670	70.0	71.4	90.5	79.3	92.2	88.4	2.00	2.28
700	735	79.6	83.0	94.0	91.0	97.2	94.0	2.06	2.07
750	772	84.5	87.8	96.1	94.3	99.2	95.8	2.06	2.03
800	811	88.7	92.3	97.1	97.2	100.0	97.4	2.06	2.00
850	857	92.0	94.9	98.1	98.2	100.0	98.2	2.05	2.00

[a] Data obtained after 2 h of reaction.

[b] Thermodynamic equilibrium data at the temperatures of the catalyst bed (the data have been interpolated from those provided by [37]).

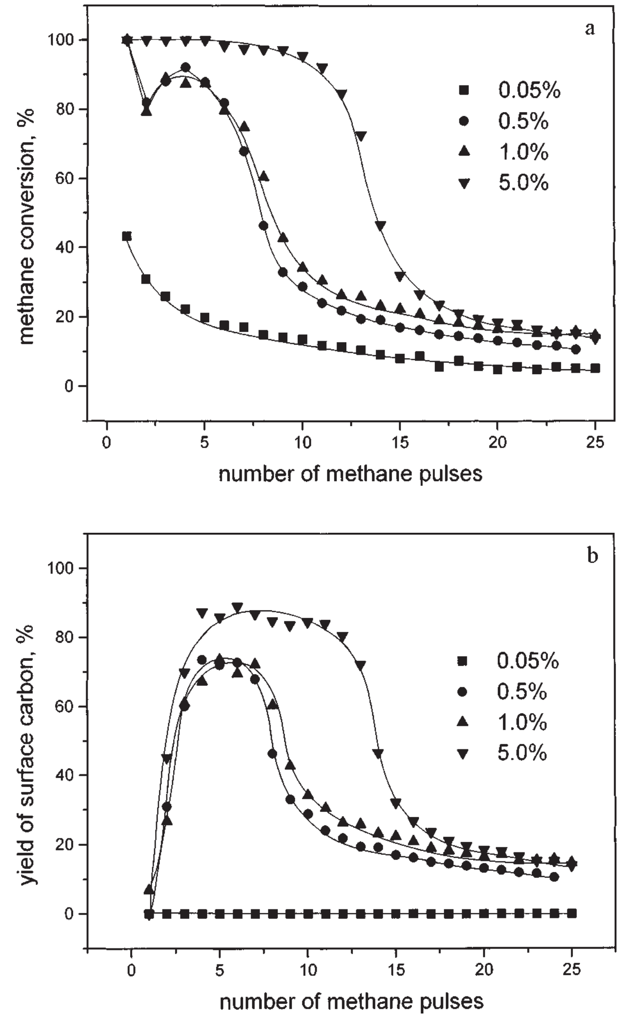

Figure 4. Methane conversion (a) and $\underline{C}$ yield (b) against the number of methane pulses over the calcined Rh(O)/γ-Al_2O_3 catalysts at 700 °C.

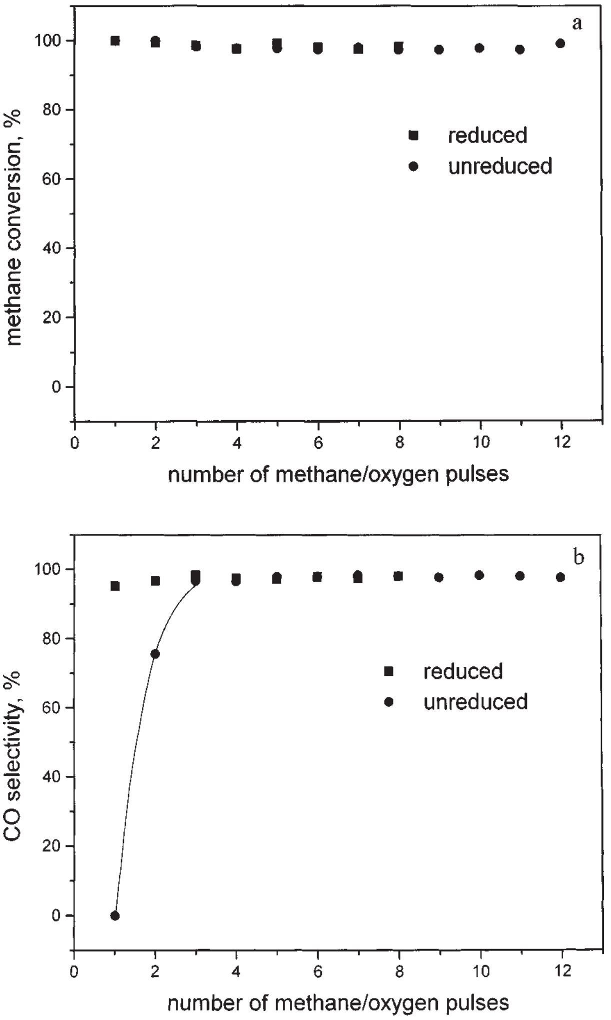

Figure 5. Methane conversion (a) and CO selectivity (b) against the number of CH_4/O_2 (2/1) pulses over the reduced 1.0 wt% Rh/γ-Al_2O_3 and unreduced 1.0 wt% Rh(O)/γ-Al_2O_3 at 700 °C.

of surface carbon increased notably with increasing number of pulses, passed through a maximum and then decreased. The 5.0 wt% Rh catalyst provided the highest carbon deposition, while those with 0.5 and 1.0 wt% Rh loadings had comparable carbon depositions (figure 4(b)).

3.2.2. Reactions of CH_4/O_2 pulses over the calcined 1.0 wt% Rh(O)/γ-Al_2O_3 and the reduced 1.0 wt% Rh/γ-Al_2O_3

The reaction of methane and oxygen over the unreduced (calcined) and reduced catalysts was investigated by using CH_4/O_2 pulses with a feed molar ratio of 2/1. The products contained CO, H_2, CO_2 and H_2O. The carbon balance indicated that no carbon was deposited on the catalyst. In figure 5, the reactivities of CH_4/O_2 over the 1.0 wt% Rh(O)/γ-Al_2O_3 and the 1.0 wt% Rh/γ-Al_2O_3 catalysts are compared at 700 °C. Over both catalysts, O_2 was completely converted during each pulse and the methane conversion was equal or close to 100% (figure 5(a)). During the first pulse, no CO and H_2 were formed over the unreduced catalyst, CO_2 being the only carbon-containing product. In contrast, the CO selectivity was as high as about 95% over the reduced catalyst (figure 5(b)). Starting with the second pulse, CO was formed over the unreduced catalyst and its selectivity increased with the number of CH_4/O_2 pulses until a steady state was reached (figure 5(b)). Both catalysts had almost the same CO selectivity from the third pulse onward (figure 5(b)).

The effect of the extent of reduction on the CO selectivity during the reaction of methane and oxygen was investigated at 700 °C. Before the mixture of CH_4/O_2 (2/1) was pulsed over the catalyst, 0–400 μl H_2 were pulsed over the original calcined catalyst in order to attain various extents of reduction. Figure 6 plots the CO selectivity as a function of the amount of H_2 pulsed. Under the reaction conditions adopted, the methane was completely converted. When the amount of H_2 pulsed was $\leqslant 50$ μl, the hydrogen was completely consumed and the extent of reduction of the catalyst was proportional to the amount of H_2 pulsed. At zero H_2 pulsed, no CO was formed; with the increase of the amount of H_2 from 0 to 50 μl, the CO selectivity increased notably;

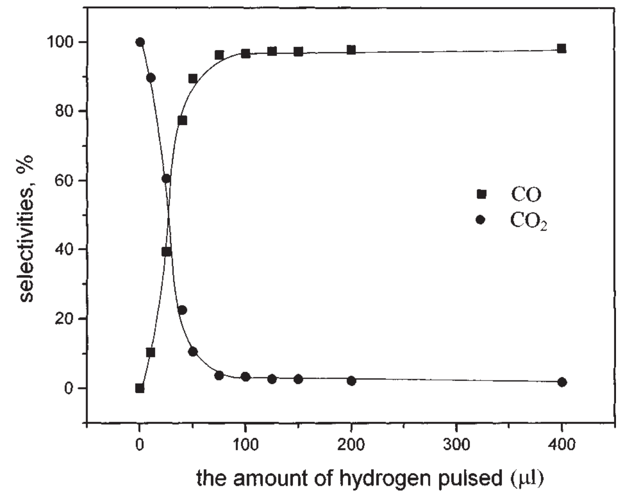

Figure 6. CO selectivity against the amount of H_2 pulsed over the calcined 1.0 wt% Rh(O)/γ-Al_2O_3 at 700 °C.

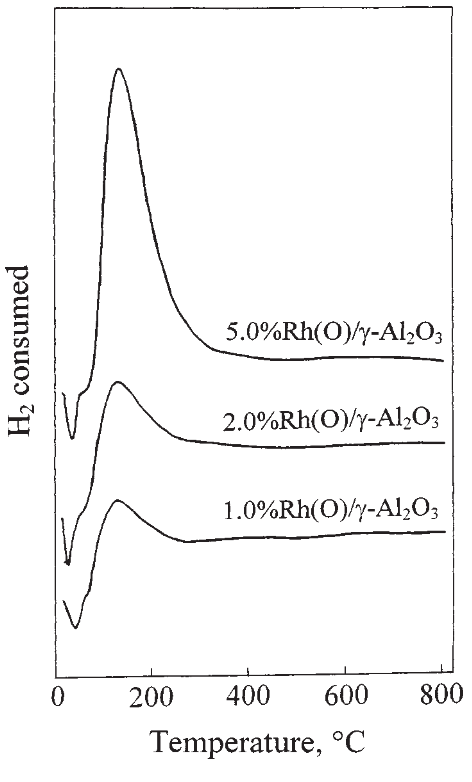

Figure 7. TPR profiles of Rh(O)/γ-Al_2O_3.

it increased only slightly from 50 to 75 μl H_2 and a further increase of the amount of H_2 pulsed had almost no effect on the CO selectivity.

3.3. Physico-chemical characterization

After the calcined catalysts were reduced in H_2, the initial dispersions of Rh were determined by CO chemisorption. Table 1 shows that the dispersion of Rh increased notably with decreasing Rh loading.

TPR experiments were performed for the catalysts with Rh loading $\geqslant$1.0 wt%. As shown in figure 7, only a TPR peak around 160–170 °C was observed for the three catalysts investigated.

Table 3
Data and assignments of XRD patterns.

Catalyst	d (Å)	Assignment
5.0 wt% Rh(O)/γ-Al_2O_3	1.39, 1.98	γ-Al_2O_3
	2.56, 2.73, 1.70, 3.73	Rh_2O_3

XRD analysis was conducted for the 5.0 wt% Rh(O)/γ-Al_2O_3 catalyst. As shown in table 3, only Rh_2O_3 was detected as a rhodium-containing compound.

4. Discussion

4.1. Continuous reaction

4.1.1. Effect of Rh loading

It was found that for γ-Al_2O_3-supported Rh catalysts the activities and selectivities in the continuous partial oxidation were almost the same for metal loadings between 0.5 and 5.0 wt%; they increased, however, with increasing Rh loading for metal loadings between 0.01 and 0.5 wt% (figure 1). Though the Rh loading of the 0.01 wt% Rh/γ-Al_2O_3 catalyst is very low, it provided about 64% methane conversion, 76% CO selectivity and 69% H_2 selectivity at the high GHSV of 720000 ml g^{-1} h^{-1}. This means that the partial oxidation reaction on Rh proceeds rapidly.

4.1.2. Effect of time on stream

As shown in figure 2, the 1.0 wt% Rh/γ-Al_2O_3 catalyst provided a very stable catalytic activity for the partial oxidation of methane, its activity and selectivity remaining the same for a long time. As identified by the XRD experiment (table 3), only Rh_2O_3 was present as a rhodium-containing compound over the 5.0 wt% Rh(O)/γ-Al_2O_3. The ease of reduction of rhodium oxide over the γ-Al_2O_3-supported Rh catalysts, as indicated by the low-temperature reduction peak (figure 7), means that no strong interactions occur between rhodium oxide and γ-Al_2O_3. However, the γ-Al_2O_3-supported Rh catalyst was stable. A possible explanation is based on the observation that the atmosphere in the reactor was both reductive and oxidative due to the coexistence of reductive (CH_4, CO and H_2) and oxidative (O_2, CO_2 and H_2O) compounds. Sintering is stimulated by the reductive atmosphere, while the oxidative atmosphere may favor redispersion [36]. When on average they compensate each other, a quasi-stable steady state is expected to occur. Another possible explanation is that, for Rh loadings $\geqslant$0.5 wt%, the reaction rate is diffusion limited. This can explain both the independence of the activity of Rh loading for loadings greater than 0.5 wt% as well as the stability of the 1 wt% Rh catalyst.

4.1.3. Effect of temperature

It is well known that a hot spot can be generated during the continuous partial oxidation of methane [37], which increases the temperature of the catalyst bed above that of the furnace. However, as noted by Dissanayake et al. [37], the temperature measured by a thermocouple in the bed only a short distance from the hot spot can be much lower than that of the hot spot. The thermodynamic equilibrium data for methane oxidation at the temperatures measured in the catalyst bed are listed in table 2. Except at the bed temperature of 670 °C, the conversions and the selectivities to CO and H_2 were found to be close to the equilibrium values (the conversions are a little smaller, but the selectivities are a little larger than those at equilibrium). At 670 °C, the conversion and the selectivity to H_2 were close to the equilibrium values, whereas the CO selectivity was much higher than the equilibrium value. Even though hot spots have been observed visually, the conversions have been always a little lower than the equilibrium ones at the measured temperatures of the bed. This probably occurred because at the high space velocity employed, the contact time with the hot spot was short and the equilibrium at the hot spot temperature could not be reached. The CO selectivity at 670 °C of the catalyst bed was much greater than the thermodynamic one for kinetic reasons.

4.2. Pulse reaction

4.2.1. CH_4 decomposition

As shown in figure 3, during the first CH_4 pulse, the following three kinds of reactions occurred between methane and the calcined catalyst: (i) the total oxidation of methane to CO_2 and H_2O, (ii) the partial oxidation of methane to CO and H_2, and (iii) the decomposition of methane to surface carbon and H_2. Over the catalysts with loadings $\geqslant$0.5 wt% Rh, during the first pulse, the selectivity to CO_2 increased with increasing Rh loading (figure 3); it is therefore obvious that rhodium oxide is responsible for the formation of CO_2. For catalysts with Rh loadings $\geqslant$0.5 wt% Rh, the yield of surface carbon first increased with the number of pulses, because of the generation of metallic Rh sites, then decreased after passing through a maximum, because of the gradual coverage of the Rh sites by carbon.

Obviously, the generation of surface carbon from pure methane over the metallic rhodium sites follows the pyrolysis mechanism [5,6]:

$$CH_{4,s} \rightarrow CH_{3,s} + H_s \qquad (3)$$

$$CH_{3,s} \rightarrow CH_{2,s} + H_s \qquad (4)$$

$$CH_{2,s} \rightarrow CH_s + H_s \qquad (5)$$

$$CH_s \rightarrow C_s + H_s \qquad (6)$$

Over the 0.05 wt% Rh calcined catalyst, only CO was formed as a carbon-containing compound during the pulse reaction with methane. The oxygen balance indicated that even for the first pulse the amount of oxygen included in the CO was greater than that present in the Rh_2O_3. Obviously, the OH groups and/or some surface oxygen of the support participated to the CO formation. Similar observations were reported by Buyevskaya et al. [24], who suggested that the OH surface groups of the support were involved in the conversion of CH_x to CO via a reaction with OH over the 1% Rh/Al_2O_3 catalyst.

4.2.2. Active site for CH_4 partial oxidation

As shown in figure 5, during the first pulse of CH_4/O_2 (2/1) over the unreduced (calcined) catalyst, both oxygen and methane were completely consumed and CO_2 was the only carbon-containing product. The oxygen balance indicated that a part of oxygen was provided by the catalyst. It can be inferred that during the first pulse the reaction $4Rh_2O_3 + 3CH_4 \rightleftharpoons 8Rh + 3CO_2 + 6H_2O$ took place, leading to the generation of metallic rhodium. The amount of metallic rhodium increased with the number of pulses until a steady state was reached. With the generation of metallic rhodium, the partial oxidation started to take place. With increasing amount of metallic rhodium, the catalytic activity and the product distribution became close to those over the reduced catalyst. As shown in figure 5 (a) and (b), almost the same reactivities were obtained over these two catalysts from the third pulse onward. This clearly indicates that the metallic rhodium is the active site for the partial oxidation of methane. As shown in figure 6, the CO selectivity increased with increasing amount of H_2 pulsed over the unreduced catalyst until a steady state was reached. It can be reasoned that the greater the amount of H_2 pulsed, the larger the number of metallic rhodium sites generated (before a steady state is reached). This again indicates that the metallic rhodium is responsible for the partial oxidation of methane to syngas.

5. Conclusion

(i) For γ-Al_2O_3-supported Rh catalysts the activities and selectivities are almost the same for metal loadings between 0.5 and 5.0 wt%. (ii) The 1.0 wt% Rh catalyst remained stable during our experiment that lasted 120 h. (iii) No carbon deposition was generated during the pulse reaction between CH_4 and the catalyst with a 0.05 wt% Rh loading; notable amounts of carbon were, however, formed on the catalysts with Rh loadings $\geqslant$0.5 wt%. (iv) The CO selectivity was directly proportional to the extent of reduction of the catalyst achieved by pulsing different amount of H_2; this indicates that the metallic Rh sites are responsible for the partial oxidation of methane.

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