# Partial oxidation of methane to synthesis gas via the direct reaction scheme over Ru / $TiO_2$ catalyst

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The partial oxidation of methane to synthesis gas has been investigated over various supported metal catalysts. The effects of operational variables on mass and heat transport resistances were investigated for defining the kinetic regime. It is observed that, in the absence of significant mass and heat transfer resistances, high selectivity (up to 65%) to synthesis gas is obtained over Ru / $TiO_2$ catalysts in the low methane conversion range ($X_{O_2} < 100\%$) whereas only negligibly small selectivity to synthesis gas is observed over all other catalysts investigated under similar conditions. This indicates that the Ru / $TiO_2$ catalyst possesses unique properties, offering high selectivity to synthesis gas formation via the direct reaction scheme, whereas the other catalysts promote the sequence of total oxidation of methane to $CO_2$ and $H_2O$, followed by reforming reactions to synthesis gas. An increase of selectivity to synthesis gas, in the presence of oxygen, is achieved over the Ru / $TiO_2$ catalyst by multi-feeding oxygen, which is attributed to suppression of deep oxidation of $H_2$ and CO.

**Keywords:** methane, partial oxidation of; natural gas, utilization; synthesis gas, production of; ruthenium, catalyst; titanium dioxide, catalyst carrier

## 1. Introduction

The process of steam reforming of methane is currently used in industry for the production of synthesis gas. The heat required is supplied by external heating of the tubular reactors by combustion of natural gas, thus making the production unit mechanically complex and environmentally harmful since undesired emissions ($CO_2$, $NO_x$ and $SO_x$) are produced and released into the atmosphere [1,2]. The catalytic partial oxidation of natural gas to synthesis gas combines the exothermic oxidation reaction(s) and endothermic reforming reactions within a single train. A major problem encountered in this process, however, is the highly uneven temperature profile along the catalyst bed, due to the fact that huge amounts of heat are produced by combustion reaction(s) at the entrance of the catalyst bed, which can bring the local temperature well above 1000°C. This results in several undesirable consequences, i.e. catalyst deactivation due to sintering, danger of explosion, and demand for special, high-temperature materials for reactor construction.

Green and co-workers [3,4] investigated the partial oxidation of methane over mixed metal oxides of ruthenium ($Ln_2RuO_7$, Ln = lanthanide). They reported that a very high yield (> 90%) to synthesis gas with a good stability can be obtained at reaction temperatures higher than 750°C. Lunsford and co-workers [5] studied the partial oxidation of methane in the temperature range of 450–900°C over a 25 wt% Ni / $Al_2O_3$ catalyst. Stable performance was not obtained unless an amount of oxygen higher than the stoichiometric requirement was supplied. A number of studies, using monolith-supported metals as catalysts for partial oxidation of methane, have been conducted by Schmidt and co-workers [6–8]. It has been found that Rh exhibits the best performance in terms of activity / selectivity and stability. Ni catalysts show similar conversion and selectivity, but deactivate with time on stream.

Concerning the reaction pathway, two mechanistic schemes have been proposed: one is the sequence of total oxidation of methane, followed by reforming of the unconverted methane with $CO_2$ and $H_2O$ which are formed primarily (designated as indirect scheme); the other is the direct partial oxidation of methane to synthesis gas without the experience of $CO_2$ and $H_2O$ as reaction intermediates. The majority of previous studies over numerous types of catalysts show that the partial oxidation of methane follows the indirect reaction scheme. This is supported by the observation that a sharp temperature spike occurs at the entrance of the catalyst bed which is attributed to the highly exothermic methane combustion and that essentially zero CO selectivity is obtained at low methane conversions (< 25%) where oxygen is not fully consumed [5,9].

Results showing that synthesis gas is formed via the direct conversion of methane were reported under conditions of extremely high space velocities, by Schmidt and co-workers [6–8] over monolith-supported metal catalysts at temperatures in the neighborhood of 1000°C. From the theoretical point of view, the direct partial oxidation to synthesis gas is thermodynamically permissible. From the practical point of view, it is of high industrial interest to develop a catalyst which promotes synthesis gas formation via the direct reaction scheme at temperatures much lower than 1000°C. However, this demands that the catalyst meets several stringent requirements in order to be able to effectively retard the deep oxidation of CO and $H_2$, which are thermodynamically more favorable. In the present study, results obtained over a $Ru/TiO_2$ catalyst, which demonstrate that it is capable of catalyzing the partial oxidation of methane with high selectivity to synthesis gas via the direct reaction scheme, are reported. This catalyst is found to be unique in this respect, among more than 20 catalysts investigated in this laboratory.

## 2. Experimental

### 2.1. Catalyst preparation

Supported metal catalysts (M = Rh, Ru, Pd, Ir, and Ni) were prepared by the method of incipient wetness impregnation, using metal chloride and/or metal nitrate as the precursor compound for the metal [10]. 60–120 mg of the precursor compound were dissolved in 10 ml of distilled water at 25°C, then 5–10 g of the carrier ($\gamma$-$Al_2O_3$, $\alpha$-$Al_2O_3$, $SiO_2$, $TiO_2$, yttria-stabilized $ZrO_2$ (YSZ)) were added to the solution under continuous stirring at the same temperature. When the water evaporated, the solid material was dried in an oven at 110°C for 24 h. It was subsequently crashed and sieved in the particle size range of ca. 40 $\mu$m. The resulting catalysts were reduced in $H_2$ flow at 250°C for at least 1 h. $H_2$ chemisorption at room temperature was used to measure metal dispersion assuming that each surface metal atom chemisorbs one hydrogen atom.

### 2.2. Kinetic apparatus and measurements

The apparatus employed for kinetic measurements consists of a flow measuring system, a heated quartz tube reactor and an on-line analytical system. Feed flow rates were measured and controlled by a thermal mass flow meter. Analysis of the feed and of the reaction mixtures was achieved by a gas chromatograph connected on-line to the reactor apparatus via a gas sampling valve. The TC detector was used to analyze $H_2$, $N_2$, $O_2$, CO, $CH_4$, $CO_2$ and $H_2O$, separated by a Carbosieve S-II 100/120 mesh column.

The reactor was a 4 mm i.d. quartz tube, immersed in an electrically-heated furnace. Temperature was measured by a thermocouple inserted into a thermowell which is placed at the center and runs along the length of the reactor. Weighed amounts of catalyst (diluted with $\alpha$-$Al_2O_3$) were placed in the middle of the reactor, supported by quartz wool. Contact time was altered by adjusting the total flow rate and amount of catalyst. Before reaction was initiated, the catalyst sample was pretreated in $H_2$ flow for at least 1 h. Operating conditions with respect to total feed rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances.

## 3. Results and discussion

The main objective of this communication is to report on the unique catalytic performance of the $Ru/TiO_2$ catalyst, which is capable of exhibiting relatively high selectivity to synthesis gas at low methane conversions ($X_{O_2} < 100\%$). First, the effects of heat and mass transfer limitations were studied in order to define the kinetic regime. Then, differences in catalytic performance between the $Ru/TiO_2$ and other catalysts, including Ru dispersed on other carriers, were evaluated under various reaction conditions. The influence of $CH_4/O_2$ ratio on catalytic performance, and the beneficial effect of oxygen multi-feeding were also investigated.

### 3.1. Heat and mass transfer limitations

When highly exothermic reactions are carried out in experimental reactors, hot spots of significant magnitude can develop within the catalyst bed. Under such conditions, erroneous results concerning the kinetic behavior of the reaction system may be obtained. As described above, two possible routes (i.e. direct and indirect) exist for the partial oxidation of methane. The problem of heat transfer limitations is more dramatically encountered when the reaction follows the indirect scheme. In the present work, Rh catalysts were chosen for defining the kinetic regime with respect to the aspects of heat transfer limitations because Rh is one of the most active catalysts for the partial oxidation of methane [3,8,10] and, furthermore, the reaction over Rh has been demonstrated to follow the indirect reaction scheme [10]. Therefore, if the operating conditions which eliminate heat and mass transport resistances are defined over the Rh catalyst, it is certain that over other less active catalysts the same operating conditions will be within the kinetic regime. Several factors affecting the presence and magnitude of hot spots, under conditions of partial oxidation of methane over $Rh/Al_2O_3$ catalysts, were investigated. The most important of these factors are contact time, solid dilution, gas dilution, and metal loading of the catalyst. The magnitude of the hot spot is quantified by the temperature difference ($\Delta T$) registered by two thermocouples, one within the catalyst bed ($T_r$) and one just prior to the catalyst bed ($T_o$). Both thermocouples were placed within a thermowell which was running along the length of the reactor. When He passed through the reactor, $T_r$ and $T_o$ were approximately equal. However, the value of $T_r$ was sharply increased and became significantly higher than that of $T_0$ upon switching the feed gas from He to $CH_4/O_2$ mixture.

Table 1 shows the variation of $\Delta T$ as a function of contact time and He dilution. It is shown that the magnitude of $\Delta T$ is significant when the feed gas contains more than 10% $CH_4$. It increases significantly with increasing $CH_4$ partial pressure in the feed and decreases with decreasing space velocity or increasing contact time. Under conditions of undiluted feed stream (66% $CH_4$) and high space velocity, temperature differences larger than 300°C were registered. Since oxygen conversions obtained under all conditions are high (> 70%), increased amounts of heat are produced when high space velocities are applied, as would be expected. Recent results reported by Dissanayake et al. [11] also indicate that the temperature of the catalytic sites over a supported nickel catalyst might be as much as 300°C higher than the temperature measured by a thermocouple located only a short distance from the catalyst bed, when high space velocities are applied. In order to conduct the fast reaction in the kinetic regime without mass transfer limitations, high space velocities or short contact times are required. However, the application of high space velocity would result in production of a large amount of heat within the catalyst bed, which may lead to severe overheating problems, as shown in table 1. To deal with this problem, both feed gas and solid catalyst should be heavily diluted so as to ensure the absence of severe hot spots in the catalyst bed. It was found that the value of $\Delta T$ can indeed become negligibly small (< 15°C) over a wide range of contact times and reaction temperatures if one portion of the catalyst is diluted with at least five portions of inert $\alpha$-$Al_2O_3$, and the feed gas is heavily diluted with He, up to 94 vol% (table 1).

Due to the fast reaction of partial oxidation of methane, the problem of external mass transfer could also be readily encountered. Fig. 1 shows the influence of flow rate on methane conversion and CO selectivity obtained under conditions where mass transfer limitations are expected to occur. In these experiments contact time was held constant at $W/F = 5.56 \times 10^{-5}$ ($g_{cat}$ min/ml) by changing the flow rate and the catalyst mass. It is observed that methane conversion and CO selectivity increase upon increasing flow rate from 45 to 180 ml/min. When the flow rate exceeds ca. 200 ml/min, methane conversion and CO selectivity tend to be stable. This indicates that at low flow rates the reaction is limited by external mass transfer effects. As flow rate increases, the mass transfer coefficient increases, which leads to a higher diffusion rate of the reactants, from the gas phase to the catalytic sites. As a consequence, enhancement of the overall reaction rate is observed. The increase of CO selectivity, resulting from the increase of the mass transfer coefficient, is attributed to enhanced rate of diffusion of the products from the catalyst surface to the gas phase which prevents the oxidation of CO to $CO_2$. When the flow rate applied is above ca. 200 ml/min, the mass transfer limitations are removed due to sufficiently high transport rates. Thus, the kinetic regime, as defined in the present study, is characterized by a dilute reactant mixture, consisting of $CH_4/O_2/He = 4/2/96$ vol%, total flow rates exceeding 200 ml/min, and catalyst of an average particle diameter of 40 $\mu$m, diluted with 5 portions of $\alpha$-$Al_2O_3$ (of the same particle size).

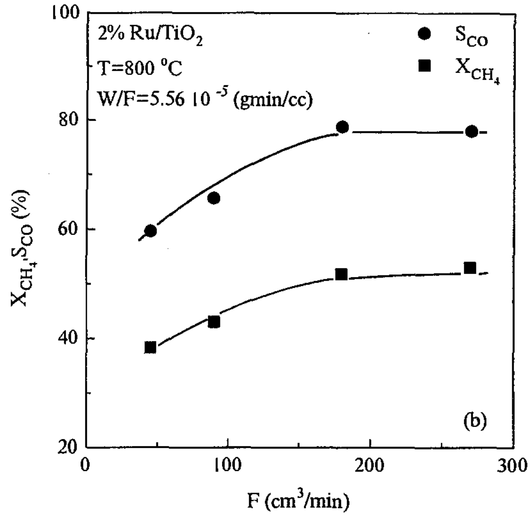

Fig. 1. Influence of total flow rate on methane conversion and CO selectivity obtained over a 2 wt% $Ru/TiO_2$ catalyst. $T = 800$°C, $W/F = 5.56 \times 10^{-5}$ g min/ml; $CH_4/O_2/He = 4/2/94$ vol%.

Table 1
Variation of $\Delta T$ as a function of contact time and He dilution, obtained over a 0.5% $Rh/\gamma$-$Al_2O_3$ catalyst [a]

| $P_{He}$ (bar) | $W/F \times 10^5$ ($g_{cat}$ min/cm³) | $\Delta T$ (°C) |
|---|---|---|
| 0.94 | 1.67 | 15 |
|  | 2.90 | 12 |
|  | 5.80 | 7 |
| 0.70 | 0.67 | 80 |
|  | 2.00 | 75 |
|  | 2.78 | 55 |
| 0.25 | 1.67 | 270 |
|  | 2.78 | 230 |
|  | 6.25 | 140 |

[a] The $CH_4/O_2$ feed ratio is invariably 2. One portion of catalyst is diluted with five portions of $\alpha$-$Al_2O_3$.

### 3.2. Kinetic study

### 3.2.1. Influence of methane conversion on CO selectivity

Detailed studies were carried out for evaluating the kinetic behavior of the $Ru/TiO_2$ and other conventional catalysts which include Ni-, Rh-, Pd- and Ir-based catalysts and Ru catalysts supported on carriers other than $TiO_2$. Fig. 2 shows CO selectivity as a function of methane conversion, which is varied by changing contact time. Attention is focused on the low methane con-

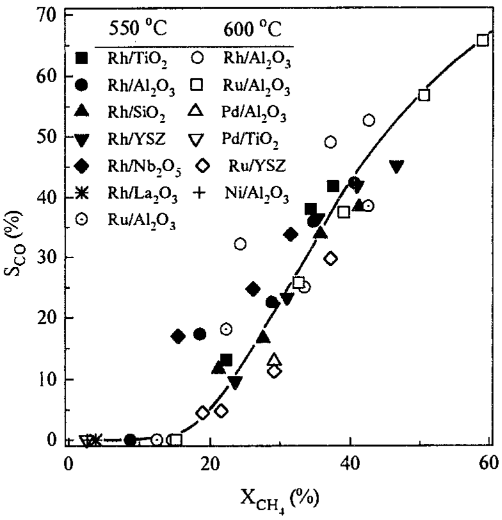

Fig. 2. CO selectivities obtained over various supported metal catalysts as a function of methane conversion. ($T = 550$ and 600°C; $CH_4/O_2/He = 4/2/94$ vol%; catalyst mass: 5–10 mg; solid dilute: 45–90 mg; total feed flow rate: 200–800 ml/min.)

version range where oxygen conversion is less than 100%. Due to the presence of oxygen, the metal surface is anticipated to be oxidized or partially oxidized, which makes the rate of reforming reactions negligibly small as compared to those of oxidation reactions. In this range, any synthesis gas formation is mainly attributed to the direct partial oxidation of methane. It is shown in fig. 2 that CO selectivity is negligibly low when methane conversion is lower than ca. 20%, but selectivity to CO increases rapidly with increasing methane conversion when it exceeds ca. 25%. The selectivity to CO approaches the equilibrium value as conversion of methane reaches that expected thermodynamically. A similar tendency for $H_2$ selectivity was also observed. These results can be well explained by a reaction sequence according to which methane is first deeply oxidized to $H_2O$ and $CO_2$, and, as oxygen is completely consumed, corresponding to ca. 25% of methane conversion ($CH_4/O_2 = 2$), reforming of the unconverted methane with $H_2O$ and $CO_2$ occurs to give synthesis gas. The absence of selectivity to CO at low methane conversions suggests that CO is not the primary product of the reaction. The above observation is in harmony with previous studies [3–5] which shown that the partial oxidation of methane to synthesis gas follows an indirect reaction scheme.

In contrast, the $Ru/TiO_2$ catalyst is found to exhibit unique kinetic behavior. Fig. 3a shows CO selectivity obtained over a 0.5 wt% $Ru/TiO_2$ catalyst as a function of methane conversion. It is evident that significantly high CO selectivity is obtained over the $Ru/TiO_2$ catalyst at low methane conversions. The value of CO selectivity is almost constant, even at methane conversions approaching zero. This suggests that CO is partially formed as a primary product. Increasing reaction temperature from 550 to 750°C results in a sharp increase in

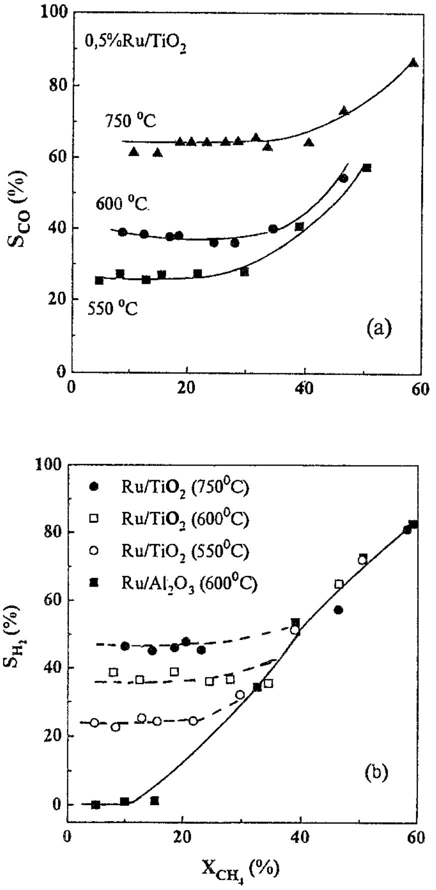

Fig. 3. CO selectivity (a) and $H_2$ selectivity (b) over supported Ru catalysts as a function of methane conversion at 550, 600 and 750°C. (Other conditions as in fig. 2.)

CO selectivity from ca. 25 to 65% over the $Ru/TiO_2$ catalyst at the low methane conversion region, indicating that higher temperatures favor direct CO formation. When $H_2$ selectivity is plotted versus methane conversion (fig. 3b), approximately the same pattern is observed, i.e. negligible $H_2$ selectivity over the other catalysts at low methane conversions, whereas significantly high $H_2$ selectivity is obtained over the $Ru/TiO_2$ catalyst. $H_2$ selectivity is also found to increase with increasing reaction temperature. It is noted that the value of $H_2$ selectivity is slightly lower than that of CO selectivity, particularly at the high temperature. This could be explained by the stoichiometric ratio of production of the two molecules ($H_2/CO = 2$), which implies that $H_2$ has a higher probability to be oxidized than CO does.

When oxygen conversion approaches 100%, methane conversions as high as 60–65% are achieved over the $Ru/TiO_2$ catalyst at 750°C. This implies that, by increasing selectivity to synthesis gas via the oxidation reaction(s), the load of the reforming section (in the middle and downstream of the catalyst bed) can be significantly reduced. The fact that CO selectivity is practically independent of methane conversion (as long as oxygen conversion is below 100%) leads to the suggestion that under the present reaction conditions, CO and $CO_2$ are formed in parallel by oxidation reactions, possibly via two different sites of different natures. It can be concluded from the results shown in fig. 3 that in the low methane conversion region, to a large extent, synthesis gas ($CO + H_2$) is formed over the $Ru/TiO_2$ catalyst through the direct partial oxidation scheme. As oxygen is consumed at higher contact times, the contribution to synthesis gas formation from reforming reactions, which occur at the later part of catalyst bed, increases.

The unique kinetic performance of the $Ru/TiO_2$ catalyst could also be explained assuming that the rate of methane reforming with $CO_2$ and $H_2O$ over this catalyst is higher than the rate of combustion of methane. To test this hypothesis, the relative rates of partial oxidation of methane and $CO_2$ reforming of methane were determined over the $Ru/TiO_2$ catalyst under identical conditions. The reactant feed composition in the $CO_2$ reforming reaction was adjusted so as to mimic the composition of reaction mixtures obtained under conditions of partial oxidation, at low methane conversions, without, of course, oxygen ($CH_4/CO_2/He = 3.5/0.3/96.2$). In another set of experiments, equimolar mixtures of methane and $CO_2$ were used. It was determined that the rate of partial oxidation of methane is nearly two orders of magnitude larger than the rate of $CO_2$ reforming of methane. Furthermore, it must be realized that under reforming conditions the catalyst surface is fully reduced, offering high rates, while under partial oxidation conditions the catalyst surface is partially oxidized, offering reduced rates. Thus, under conditions of partial oxidation, the difference between the rates of oxidation and reforming reactions is probably larger than the two orders of magnitude estimated by the present experiments. It is highly unlikely, therefore, that the high selectivities to CO and $H_2$ formation which are observed at low methane conversions over the $Ru/TiO_2$ catalyst are due to very rapid methane reforming reactions.

### *3.2.2. Influence of surface reducibility on catalytic performance*

As shown in figs. 2 and 3, the $Ru/TiO_2$ catalyst is the only one, among more than 20 catalysts investigated in this laboratory, showing high selectivity to synthesis gas at low methane conversions ($X_{O_2} < 100\%$). It is believed that the unique performance of the $Ru/TiO_2$ catalyst is related to its reducibility characteristics under working conditions. Most of the metal catalysts tend to be oxidized under the $CH_4/O_2$ reaction conditions, when oxygen conversion is less than 100%. This explains the observation that the conventional catalysts exhibit low activity and no or small selectivity to synthesis gas in the low methane conversion range. For the $Ru/TiO_2$ catalyst, the high selectivity to synthesis gas obtained in the presence of oxygen seems to be due to a unique surface state which is different from the oxidized or reduced states. Although the nature of such a new state is unclear at the present moment, it seems that this new state is maintained as a result of the equilibrium between the interaction of $CH_4$ (reducing agent) and oxygen (oxidizing agent) with the ruthenium surface. This kind of a state should only exist within a rather narrow range of operating conditions and should be sensitive to the reducibility of the catalyst surface.

Fig. 4 illustrates how conversions of methane and oxygen and CO selectivity over the $Ru/TiO_2$ and $Ru/\gamma$-$Al_2O_3$ catalysts are altered by a stepwise increase and then decrease of reaction temperature. At low reaction temperatures, both conversion and selectivity are low, due to the fact that the catalyst surface is at the oxidized state. As reaction temperature increases, conversion increases gradually. After oxygen is fully consumed, at ca. 800°C for the $Ru/TiO_2$ and at ca. 700°C for the $Ru/\gamma$-$Al_2O_3$ catalysts, both conversion and selectivity increase sharply, primarily due to reduction of the catalyst surface and, secondarily due to the elevated temperatures. The pronounced difference between the $Ru/\gamma$-$Al_2O_3$ and $Ru/TiO_2$ catalysts is revealed during the stepwise reduction of reaction temperature. For the former catalyst, a sharp drop in conversion and selectivity

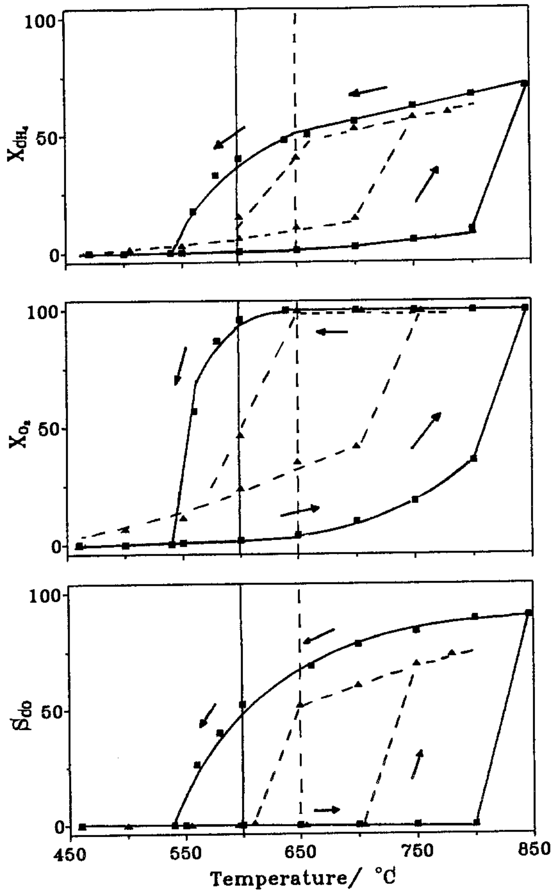

Fig. 4. Alteration of conversions of methane and oxygen, and CO selectivity as a function of reaction temperature, first stepwise increasing and then stepwise decreasing. $CH_4/O_2/He = 4/2/94$ vol%, $W/F = 1 \times 10^{-5}$ g min/ml. (■) $Ru/TiO_2$, (▲) $Ru/\gamma$-$Al_2O_3$.

is observed when oxygen conversion is less than 100%. In the presence of oxygen ($X_{O_2}$ < 100%), no or only low selectivity to synthesis gas is observed. This drop in activity and selectivity corresponds to the transformation of the catalyst surface from the reduced to the oxidized state. The perpendicular lines (solid line for the $Ru/TiO_2$, and dotted line for the $Ru/\gamma$-$Al_2O_3$) demarcate the regions where oxygen conversion is below (left side region) and equal to 100% (right side region). In contrast to the case of the $Ru/\gamma$-$Al_2O_3$ catalyst, both methane conversion and CO selectivity over the $Ru/TiO_2$ catalyst decrease smoothly with reducing reaction temperature, even when oxygen conversion is much lower than 100%. This indicates that the working surface state of the $Ru/TiO_2$ catalyst is very different from that of the $Ru/\gamma$-$Al_2O_3$ catalyst. It should be mentioned that the temperature at which oxygen conversion reaches 100% is dependent on the nature of the catalyst, and the operating conditions. Fig. 4 only shows an exemplary result which reveals the intrinsic difference between the conventional supported metal catalysts and the $Ru/TiO_2$ catalyst.

### 3.2.3. *Influence of feed composition*

As described earlier, one of the major problems encountered in the process of partial oxidation of methane to synthesis gas is the large temperature spike at the entrance of the catalyst bed, due to methane combustion. This imposes risks of explosion, as well as other disadvantages which may eventually render the process not feasible. Increasing selectivity to synthesis gas via the direct reaction scheme is the most efficient way to reduce the amount of heat produced at the entrance of the catalyst bed. Distributing the feed of oxygen over the entire length of the catalyst bed might be helpful in reducing the risks of explosion as well as the probability of non-selective gas-phase reactions.

Fig. 5 shows the influence of $CH_4/O_2$ ratio on CO selectivity as a function of methane conversion obtained over a 0.5 wt% $Ru/TiO_2$ catalyst. It is observed that CO selectivity in the low methane conversion region ($X_{O_2}$ < 100%) is significantly increased from ca. 63 to 85% when the $CH_4/O_2$ feed ratio is increased from the stoichiometric value of 2 to 6. This indicates that a high $CH_4/O_2$ ratio suppresses $CO_2$ formation either via surface reactions or via gas-phase reactions. This observation implies that if oxygen is fed along the length of the catalyst bed instead of only at the entrance (as, for example, by multipoint feeding or by feeding via a porous membrane) and its local partial pressure is maintained at low levels, CO selectivity via the direct reaction scheme may be increased by attenuating oxidation of methane to $CO_2$. This requires that the reaction between the newly-fed oxygen and CO and/or $H_2$ already produced, is not very rapid. Unlike conventional catalysts which favour the oxidation reactions between $O_2$ and CO and/or $H_2$, the $Ru/TiO_2$ catalyst is capable of suppressing CO and $H_2$ oxidation even in the presence of significant amounts of oxygen (see figs. 2 and 3), thus meeting the demands described above.

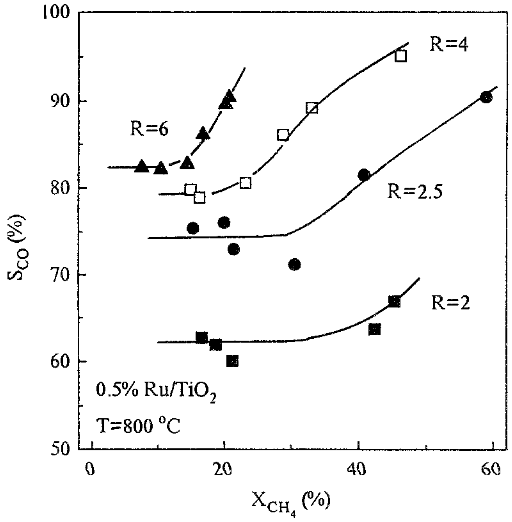

Fig. 5. CO selectivity vs. methane conversion obtained over a 0.5% $Ru/TiO_2$ catalyst as a function of $CH_4/O_2$ feed ratio. $T = 800$°C, $P_{tot} = 1$ bar, $P_{CH_4} = 0.04$ bar.

Table 2 reports a comparison between the results obtained over the $Ru/TiO_2$ catalyst with single and dual feed points of oxygen. The total amount of oxygen fed through the two feed points is equal to that of the single feed point. Also, the position of the second feed point was adjusted to be near where the oxygen fed from the first feed point was fully consumed. By making the oxygen accessible to nearly all catalyst sites along the catalyst bed (although the concentration of oxygen along the catalyst bed differs), the reforming reactions are suppressed. It is shown in table 2 that dual feed point of oxygen indeed improves selectivity to CO, as compared to the single feed operation. It is expected that further improvement of selectivity to synthesis gas (via the direct partial oxidation scheme) will occur when the same amounts of oxygen are fed from more than two feeding points. This will lead to flattening of the temperature profile along the catalyst bed.

## 4. Concluding remarks

The present study demonstrates that the $Ru/TiO_2$

Table 2
Methane conversion and CO and $H_2$ selectivity obtained over 0.5% $Ru/TiO_2$ catalyst using single and dual oxygen feed at 750°C [a]

| Feed points | $CH_4/O_2$ | $X_{CH_4}$ (%) | $X_{O_2}$ (%) | $S_{CO}$ (%) | $S_{H_2}$ (%) |
|---|---|---|---|---|---|
| one | 2 | 40 | 95–99 | 65 | 55 |
| two | 2 | 42 | 95–99 | 74 | 59 |

[a] In all cases, $CH_4/O_2/He = 4/2/94$ vol%.

catalyst exhibits unique performance, as compared to other conventional catalysts, under conditions of partial oxidation of methane to synthesis gas. In the kinetic regime (absence of mass and heat transfer limitations), high selectivity to synthesis gap (up to 65%) is obtained over the Ru/$TiO_2$ catalyst in the low methane conversion region ($X_{O_2} < 100\%$). The fact that high selectivity to synthesis gas is maintained even at methane conversions approaching zero indicates that synthesis gas is, to a large extent, formed via the direct partial oxidation scheme. Probably, CO and $CO_2$ are formed by parallel routes via two different catalytic sites. Of course, a fraction of CO originates from methane reforming with $CO_2$. It has been estimated, using isotopic labeling experiments, that the amount of CO produced by reforming corresponds to less than 8% of total CO produced, when the reaction takes place at 550°C with a methane conversion of 10% [12]. The high activity and selectivity of the Ru/$TiO_2$ catalyst towards conversion of $CH_4/O_2$ to synthesis gas in the presence of oxygen may be related to unique oxidation/reduction characteristics of the surface of the Ru/$TiO_2$ catalyst, which averts complete oxidation of the metal surface. This property may be ascribed to an interaction beween Ru and $TiO_2$, generating a new type of surface state.

Feeding of oxygen at multiple points along the catalyst bed is a good way to decrease the hot-spot near the entrance of the reactor and to reduce the risks of explosion. However, the synthesis gas already formed, might be oxidized by newly-introduced oxygen over conventional catalysts. As shown in fig. 3, the Ru/$TiO_2$ catalyst meets the stringent requirement of retarding the deep oxidation of CO and $H_2$, even in the presence of significant amounts of oxygen. Thus, the concept of oxygen-multifeeding might be very beneficial with the Ru/$TiO_2$ catalyst. The advantages of such an operation are expected to be more pronounced under industrial operating conditions where high risks of explosion are often encountered due to high temperatures and pressures.

It should also be mentioned that the amount of heat produced by the reaction is determined by conversion and selectivity. As long as high selectivity to synthesis gas at low methane conversions is achieved, the amount of heat released by the oxidation reaction(s) at the entrance of the catalyst bed will be small, regardless of the reaction scheme which is followed. This means that the serious problem of temperature run-away associated with the process of partial oxidation of methane to synthesis gas can be largely removed by employing the Ru/$TiO_2$ catalyst. The reduction of the temperature spike at the entrance of the catalyst bed leads to reduced risks of explosion and catalyst sintering, it favors autothermal operation, and lengthens the lifetime of the reactor materials.

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