Heat transport limitations and reaction scheme of partial oxidation of methane to synthesis gas over supported rhodium catalysts

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The partial oxidation of methane to synthesis gas over supported Rh catalysts is investigated, paying particular attention to removing heat transport limitations and identifying the reaction conditions within the kinetic-controlling regime. The results obtained suggest that the reaction follows the sequence of total oxidation to CO_2 and H_2O, followed by reforming reactions to synthesis gas.

Keywords: methane oxidation; synthesis gas; rhodium catalyst; heat transport

1. Introduction

Synthesis gas formation by direct oxidation of methane over supported metal catalysts has received significant attention during the past several years [1–10]. It has been well-established that the reaction between methane and oxygen over various supported metal catalysts produces synthesis gas with high selectivity to H_2 and CO. Conversions close to the equilibrium values can be achieved with considerable ease over supported Ni [1,4] or supported noble metals (Ru, Rh, Pd, and Pt) [2,3,5], although small differences in the conversion exist among various catalysts.

Concerning the reaction pathway of partial oxidation of methane to synthesis gas, two reaction schemes have been proposed: one is the sequence of total oxidation followed by reforming reactions (scheme I, reactions (2)–(4)), and the other is the direct conversion of methane to synthesis gas without the experience of CO_2 as reaction intermediate (scheme II, reaction (1)).

$$CH_4 + \tfrac{1}{2}O_2 \rightleftharpoons 2H_2 + CO \qquad \Delta H = -35.5\ \mathrm{kJ/mol}, \tag{1}$$

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O \qquad \Delta H = -801.7\ \mathrm{kJ/mol}, \tag{2}$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H = +247.5\ \mathrm{kJ/mol}, \tag{3}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H = +206.1\ \mathrm{kJ/mol}. \tag{4}$$

In studies of partial oxidation of methane to synthesis gas over supported Ni catalyst, Blanks et al. [1] and Dissanayake et al. [4] reported that the entrance to the reaction zone was dominated by the combustion reactions (reaction (2)) which consumed oxygen completely, while downstream from this zone, steam reforming and CO_2 reforming reactions overwhelmed the others. By studying the product distribution at various contact times, they found that CH_4 conversion was reduced while CO_2 selectivity was enhanced as contact time decreased, suggesting that the reaction follows the sequence scheme which involves CO_2 as the intermediate (i.e. scheme I). Experiments conducted by Ashcroft et al. [2] over mixed metal oxides of ruthenium ($Pr_2Ru_2O_7$, $Eu_2In_2O_7$, La_2MgPtO_7, $Bi_2Ru_2O_7$, $Yb_2Ru_2O_7$ and $Dy_2Ru_2O_7$) and over a group of supported transition metals (Ni, Ru, Rh, Pt, and Pd on Al_2O_3) [3] also implied that the production of CO and H_2 was the result of total oxidation of a fraction of methane, followed by the reforming reactions and the water–gas shift reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H = +41.4\ \mathrm{kJ/mol}. \tag{5}$$

Results showing that synthesis gas was formed via the direct conversion of methane (i.e. scheme II) were reported by Hickman and Schmidt [5,10,11]. Using Pt and Pt–Rh coated monoliths, the authors found that the direct oxidation of methane to synthesis gas was possible when the contact time applied was short, and claimed that the contact time was an important factor affecting the reaction schemes. According to these authors, the CO_2 product was either the secondary product of CO oxidation or the product of total oxidation of methane (reaction (2)), a reaction which proceeds in parallel with the direct oxidation to CO (reaction (1)). The direct conversion of methane to synthesis gas was also reported by Choudhary et al. [6–8], who observed that both, methane conversion and CO selectivity, increased with decreasing contact time when the reaction was carried out over Ni/Yb_2O_3, Co/rare-earth oxide, Co/MgO, and Ni/Al_2O_3 catalysts. Furthermore, they found that the concentrations of CO and H_2 obtained over these catalysts were in excess of those expected at thermodynamic equilibrium.

A survey of previous studies on partial oxidation of methane to synthesis gas shows that appropriate attention to eliminate or to minimize hot spots in the catalyst bed of this exothermic reaction system was not given, in many cases, as disclosed recently by Dissanayake et al. [9] and by Chang and Heinemann [12]. In addition, the kinetic behavior of the reaction was not studied under the kinetic-controlling regime, i.e. at conversions significantly lower than those expected at thermodynamic equilibrium [1–9] and at operating conditions under which the chemical rate constant, on a surface area basis, is significantly greater in magnitude than the mass transfer coefficient. Therefore, it is hard to reliably evaluate the reaction scheme from data obtained under conditions which are not well identified. In the present study, particular attention was paid to conducting the reaction within the kinetic-controlling regime and to eliminating hot spots in the catalyst bed. Kinetic behavior of partial oxidation of methane over Rh/Al_2O_3 catalysts was investigated under these conditions, and the resulting data are used to evaluate the reaction pathway with respect to the aforementioned reaction schemes.

2. Experimental

2.1. CATALYST PREPARATION

$x\%$ Rh/Al_2O_3 catalysts ($x = 0.2$ and 0.5 wt%) were prepared by the method of incipient wetness impregnation, using $RhCl_3 \cdot H_2O$ (Alfa Products) as the precursor compound for the metal [13]. 60–120 mg of $RhCl_3 \cdot H_2O$ were dissolved in 10 ml of distilled water at a temperature of 25°C, then 5–10 g of the γ-Al_2O_3 carrier (Akzo Chemicals) 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 range of 0.06–0.15 mm. The resulting catalysts were reduced in H_2 flow at 250°C for at least 1 h.

2.2. KINETIC APPARATUS AND MEASUREMENTS

The apparatus employed for kinetic measurements consists of a flow measuring and switching system, a heated quartz tube reactor and an on-line analytical system. Feed flow rates were measured and controlled by thermal mass flow meter (MKS Instruments). 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. Weighed amounts of catalyst (diluted with α-Al_2O_3) were placed in the middle of the reactor, supported by quartz wool. The length of the catalyst bed was typically 0.4 cm. The CH_4-to-O_2 partial pressure ratio applied in the present investigation was invariably 2. 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 at 500°C for at least 1 h.

Operating conditions with respect to total feed flow rate and average catalyst particle size were defined so as to eliminate intraphase and interphase transport resistances. In preliminary sets of experiments the maximum catalyst particle size, below which intraphase transport of mass and heat did not influence the observed rate, was determined. Similarly, the minimum feed flow rate, above which interphase transport resistances were minimised or eliminated, was also determined following standard procedures. These experiments were conducted at 650°C, which is the highest temperature employed in the kinetic studies, and with the catalyst with the highest metal loading (0.5 wt%). The kinetic experiments were conducted with an average catalyst particle diameter of approximately 0.1 mm and with feed flow rates larger than 100 cm^3/min.

Two chromel–alumel thermocouples close to the catalyst bed were applied for temperature measurement and control. One thermocouple was centered within the catalyst bed (T_r) and was used to control and measure the reaction temperature. The other thermocouple was placed at the entrance of the reactor, prior to the catalyst bed, (T_o), and was used to measure the difference (ΔT) between the temperatures prior to and at the catalyst bed. When He flow 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_o (ΔT up to ca. 300°C) upon switching the feed gas from He to CH_4/O_2 mixture. To directly measure the temperature of the catalyst surface (T_c) is difficult because the temperature gradient near the surface is rather steep for the exothermic reaction. However, the relationship of $T_c \geqslant T_r \geqslant T_o$ is always valid. The existence of large temperature difference between T_r and T_o implies that T_c is significantly higher than T_r. Therefore, ΔT can be conveniently used as an indicator for the presence of hot spots in the catalyst bed. In the following, T_r is used to represent the reaction temperature, while ΔT indicates the extent of overheating in the catalyst bed.

3. Results and discussion

3.1. ELIMINATION OF HOT SPOTS IN THE CATALYST BED

When highly exothermic reactions, as in the present case, 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. In the present work, 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 such 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 (ΔT) registered by two thermocouples, one within the catalyst bed and one prior to the catalyst bed, as explained in a previous section.

Fig. 1 shows the variation of ΔT as a function of contact time and He dilution (the ratio of CH_4-to-O_2 is invariable). It is shown that the magnitude of ΔT 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 rather concentrated feed stream (50% CH_4) and high space velocity, temperature differences larger

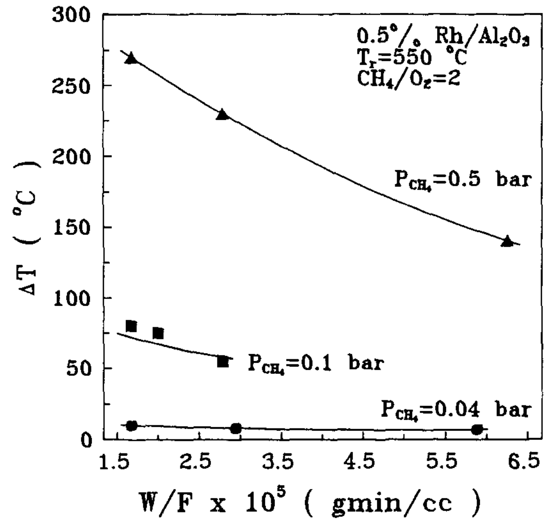

Fig. 1. Influence of contact time and gas dilution (He) on the temperature difference registered by a thermocouple inside the catalyst bed and one prior to the catalyst bed.

than 250°C were registered. Since oxygen conversions obtained under all conditions are high (> 70%), increased amount of heat is produced when high space velocities are applied, as would be expected. Recent results reported by Dissanayake et al. [9] 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. This suggests that the severe overheating problem in the catalyst bed is associated with both the supported Rh and the supported Ni catalysts, for the reaction of partial oxidation of methane.

In order to conduct the reaction under kinetic-controlling conditions (i.e., at conversions significantly lower than those expected at thermodynamic equilibrium), high space velocities or short contact times are required. 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 problem, as manifested in fig. 1. To deal with this problem, both feed gas and solid catalyst were heavily diluted so as to ensure the absence of hot spots in the catalyst bed. It was found that the value of ΔT can be negligibly small (< 15°C) over a wide range of contact times and reaction temperatures if 1 portion of catalyst is diluted with 2–5 portions of inert α-Al_2O_3, and the feed gas is heavily diluted with He, up to 94 vol%. These reaction conditions are essential in order to study the kinetic behavior of the reaction at various contact times and temperatures, without experiencing severe overheating problems in the catalyst bed.

Fig. 2 shows the influence of He dilution on the CO yield of the reaction. The solid lines describe results determined experimentally, while the dotted lines show the tendency predicted according to the equilibria of reactions (1)–(4). Regardless

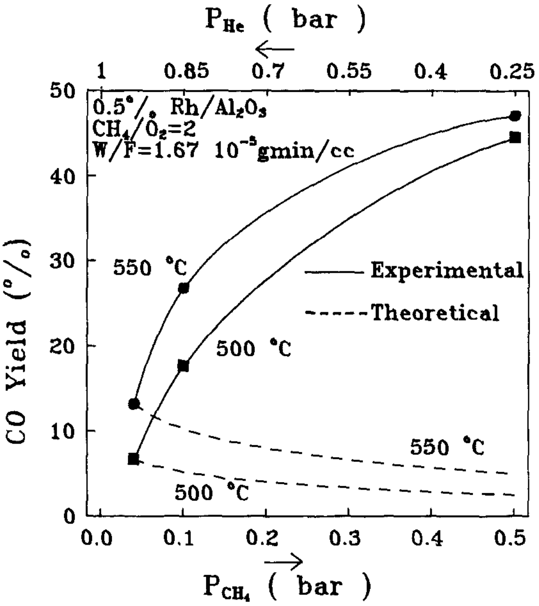

Fig. 2. Influence of He dilution on CO yield of partial oxidation of methane. The solid lines are experimental data while the dotted lines describe the tendency predicted theoretically.

of the actual reaction scheme, the conversion of methane to CO is always a volume-added reaction. Therefore, the CO yield of the reaction is theoretically expected to be reduced as the proportion of He diluent decreases, as shown by the dotted lines in fig. 2. However, the experimental data show the opposite tendency with decreasing partial pressure of He. This indicates that hot spots must exist in the catalyst bed in the case of undiluted feed gas and in the cases in which the feed gas is not diluted enough. In the absence of He diluent, the ΔT value is significant, as shown in fig. 1. Therefore, both methane conversion and CO selectivity are significantly higher than those expected thermodynamically, based on the temperature indicated by the thermocouple inside the reactor. As the proportion of He diluent increases, the amount of heat produced in the catalyst bed is reduced, and, consequently, the ΔT value is decreased, thereby the conversion and selectivity approach the values expected theoretically.

Fig. 3 shows the influence of space velocity (or contact time) on methane conversion and CO selectivity of the reaction in the absence ($\Delta T < 15°C$) and presence ($\Delta T = 50–270°C$) of hot spots in the catalyst bed. An increase in both methane conversion and CO selectivity is observed with increasing contact time in the case in which hot spots are not present in the catalyst bed ($P_{CH_4} = 0.04$ bar). However, again, the opposite tendency, i.e. both methane conversion and CO selectivity decreasing with increasing contact time, is observed in cases in which the catalyst bed is associated with a severe overheating problem ($P_{CH_4} = 0.5$ bar). As was revealed by temperature measurements (fig. 1), the ΔT values were significant when the feed gas was not diluted enough, and they were enlarged as contact time

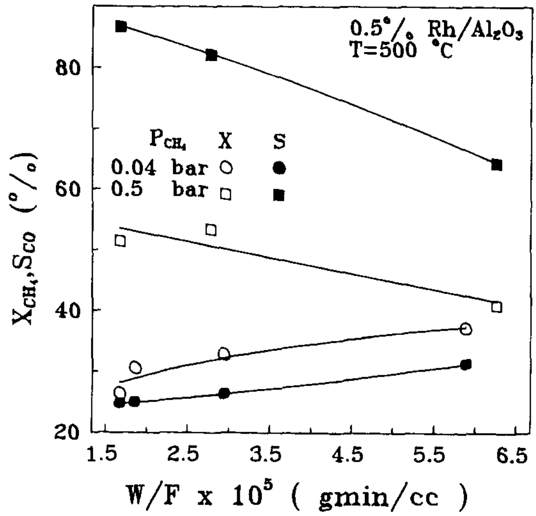

Fig. 3. Influence of contact time on methane conversion and CO selectivity under conditions of partial oxidation of methane.

decreased. Therefore, the results obtained in the case in which the feed gas was diluted with only 25 vol% He ($P_{CH_4} = 0.5$ bar) are deceiving.

In summary, the above results (figs. 1–3) clearly show that a severe overheating problem in the catalyst bed is associated with the partial oxidation of methane to synthesis gas over supported Rh catalysts. A heavy dilution of feed gas with He and of the catalyst solid with inert α-Al_2O_3 can efficiently minimize hot spots in the catalyst bed, which allows the study of the kinetic behavior of the reaction at various contact times and temperatures, without experiencing severe hot-spot problems in the catalyst bed.

3.2. KINETIC PARAMETERS EVALUATED IN THE KINETIC-CONTROLLING REGIME

3.2.1. Influence of reaction temperature

Fig. 4 shows the sensitivity of methane conversion and CO selectivity on reaction temperature, obtained over the 0.5 wt% Rh/Al_2O_3 and 0.2 wt% Rh/Al_2O_3 catalysts in the kinetic-controlling regime, i.e. in the absence of hot spots in the catalyst bed and conversions lower than those expected at thermodynamic equilibrium. When the temperature was below 450–500°C, both conversion and selectivity did not increase appreciably with stepwise increasing reaction temperature. A further increase in reaction temperature, however, resulted in an abrupt increase in both parameters which continued to increase with further increasing temperature. When the reaction was initiated at high temperatures (>700°C) and temperature was reduced stepwise, conversion and selectivity were found to be coincident, down to temperature between 500 and 550°C, depending on metal load-

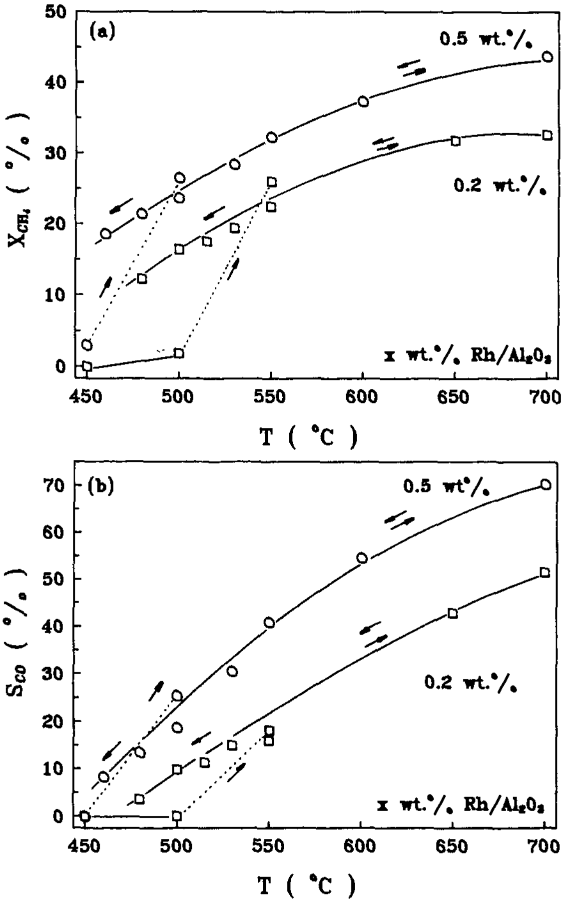

Fig. 4. Influence of reaction temperature on (a) CH_4 conversion; and (b) CO selectivity over Rh/Al_2O_3 catalysts ($CH_4/O_2 = 2$, $P_{CH_4} = 0.04$ bar, $W/F = 1.67 \times 10^{-5}$ g min/cm^3).

ing of the catalyst. At lower temperatures, however, conversion and selectivity were found to be significantly higher than those observed when the experiment was conducted in an ascending temperature sequence. The same phenomenon was also observed in the case of undiluted feed gas in which case the temperature at which abrupt changes of conversion and selectivity occur shifted towards higher values (not shown). A recent study conducted in this laboratory [14] showed that the phenomenon described above is also present during the reaction of methane reforming with carbon dioxide (an endothermic reaction). From these results, it can be concluded that this phenomenon is not related to parameters of heat transport in the catalyst bed but is due to alterations in the chemical state of the catalyst surface, induced at higher temperatures.

It was observed that conversion of oxygen was low at temperatures below 450–500°C, but was abruptly increased (>80%) when the temperature exceeded 450–500°C. It can be reasoned from this observation that, when the supported Rh catalyst is exposed to the CH_4/O_2 mixture, the Rh surface tends to be oxidized by oxygen contained in the feed, at the temperature applied. The oxidized Rh surface is relatively unreactive to methane, resulting in low conversions. However, when the oxygen at the feed is nearly consumed by reaction with methane to carbon oxides, by increasing reaction temperature, the oxidized Rh surface can then be reduced by the unconverted methane. The reduced Rh surface, which is more active towards methane activation, in turn, significantly promotes methane conversion, presumably with the participation of carbon dioxide and steam. As a consequence, a sharp enhancement in methane conversion is observed. A similar phenomenon was reported earlier by Dissanayake et al. [4] over supported Ni catalyst but under reaction conditions which resulted in equilibrium conversions. They found that an abrupt increase in methane conversion occurs at a temperature as high as ca. 800°C. Apparently, the significant difference between the supported Ni and supported Rh catalysts in the temperature at which the abrupt increase in methane conversion occurs is related to the different reducibility of the oxidized metal (Ni and Rh) by methane as a reducing agent. The above results suggest that the reaction of partial oxidation of methane is favoured on the reduced metallic sites.

Values of the apparent activation energies for CO_2 formation, CO formation and for methane conversion obtained over Rh/Al_2O_3 catalysts are reported in table 1. For comparison, values of the activation energies for methane reforming with carbon dioxide [14–16] and for methane reforming with steam [17] over supported Rh catalysts are also included. It should be mentioned that the data given in table 1 in are obtained in the methane conversion range of 15–25%. This is because there is practically no CO formation when the conversion is lower than 10%. Although these reaction conditions do not strictly conform to a differential mode of operation, the conversions obtained (15–25% at 400–500°C) are still far away from those expected thermodynamically. Therefore, the tendencies presented in table 1 are considered to be valid, although the absolute values of the apparent activation energies may differ somewhat. The value of the apparent activation energy for CO_2 formation amounts to ca. 34 kJ/mol. This value is close to that of methane conversion (ca. 38 kJ/mol), which is an expected result because the main product

Table 1
Apparent activation energy for production of CO and CO_2 from methane over supported Rh catalysts

Reactants	Product	Activation energy (kJ/mol)	Ref.
CH_4/O_2	CO	85–109	this work
CH_4/O_2	CO_2	ca. 34	this work
CH_4/O_2	CO_x [a]	ca. 38	this work
CH_4/CO_2	CO	85–105	[14–16]
CH_4/H_2O	CO	ca. 105	[17]

[a] Activation energy for methane conversion to carbon oxides (CO_x, $x = 1$ and 2).

of methane conversion is CO_2 at the temperatures applied. It is noted that the apparent activation energy for CO formation amounts to ca. 85–109 kJ/mol, which is significantly higher than that for CO_2 formation. This implies that CO_2 is not a secondary product originating from CO. Since the value of the apparent activation energy for CO formation from partial oxidation of methane is close to the values for CO production from methane reforming with carbon dioxide or with steam (table 1 and refs. [14,16–18]), it is suggested, from a energetic point of view, that the scheme of partial oxidation of methane to synthesis gas initially involves total oxidation to CO_2 and H_2O, followed by reforming reactions of methane with CO_2 and H_2O to produce synthesis gas.

3.2.2. Selectivity versus conversion

The influence of methane conversion (in the absence of any severe hot spots in the catalyst bed) on selectivity towards CO formation was extensively studied over supported Rh catalysts at various reaction temperatures and typical results are shown in fig. 5. The variation of methane conversion was realized by altering contact time at a fixed temperature. It is observed that selectivity to CO is enhanced as the methane conversion is increased, under all temperatures investigated (530–650°C). At low methane conversion ($X_{CH_4} < 10\%$), the selectivity to CO formation is essentially zero. This leads to the conclusion that CO_2 is not the secondary product from deep oxidation of CO, while CO is very likely to be a secondary product from CO_2 (reactions (2)–(4)), as would be expected, based on the fact that the value of the apparent activation energy for CO formation is much higher than that for

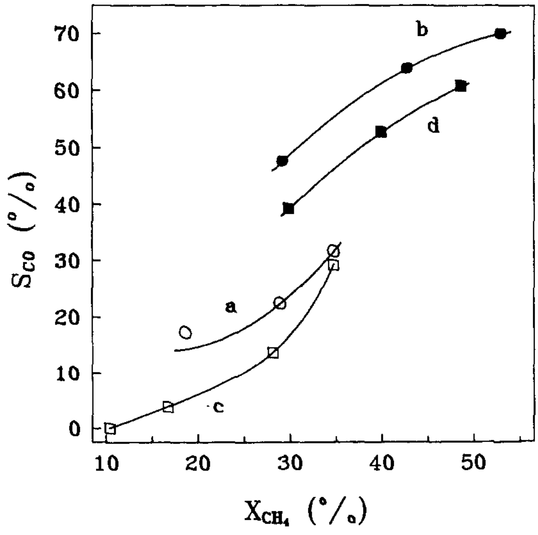

Fig. 5. Influence of CH_4 conversion on CO selectivity, obtained at selected temperatures ($CH_4/O_2 = 2$, $P_{CH_4} = 0.04$ bar). (a) over 0.5 wt% Rh/Al_2O_3, at 550°C, (b) over 0.5 wt% Rh/Al_2O_3, at 650°C, (c) over 0.2 wt% Rh/Al_2O_3, at 550°C, and (d) over 0.2 wt% Rh/Al_2O_3, at 650°C.

CO_2 formation. Although CO may also be formed via a reaction which occurs in parallel with CO_2 (reactions (1) and (2)), such a route is considered improbable. If it is assumed that the CO and CO_2 products are formed by two parallel reaction routes, the CO selectivity would be expected to either decrease or to practically remain constant with increasing methane conversion, considering the fact that the reaction proceeds via a route associated with lower activation energy. Obviously, the present results, i.e. CO selectivity increasing (CO_2 selectivity decreasing) with increasing methane conversion, does not conform to the parallel reaction scheme. The most probable reaction scheme for synthesis gas formation is through the reactions of methane reforming with CO_2 and H_2O which result from the initial deep oxidation of methane. As would be expected, the reforming reactions to synthesis gas are promoted when the concentrations of CO_2 and H_2O are increased, due to increased methane conversion.

4. Conclusions

The following conclusions can be drawn from the results of the present study:

(1) Partial oxidation of methane to synthesis gas over supported Rh catalysts is associated with severe hot-spots in the catalyst bed when operating under usual reaction conditions, which may lead to erroneous conclusions concerning kinetic and mechanistic aspects.

(2) Dilution of the feed gas with up to 94 vol% He, and of the catalyst bed with 2–5 portions of inert solid (α-Al_2O_3) can essentially eliminate hot spots in the catalyst bed, which allows the study of the kinetic behavior of the reaction at various contact times and temperatures, without experiencing severe overheating problems.

(3) The apparent activation energy for CO formation over Rh catalysts amounts to 85–109 kJ/mol, which is significantly higher than that for CO_2 formation, amounting to only ca. 34 kJ/mol.

(4) Both CO selectivity and methane conversion are found to increase with increasing contact time (or decreasing space velocity). CO selectivity is enhanced with increasing methane conversion.

(5) The results of the present study strongly suggest that partial oxidation of methane to synthesis gas over supported Rh catalysts follows the sequence of total oxidation to CO_2 and H_2O, followed by reforming reactions to synthesis gas.

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