Partial Oxidation of Methane to Synthesis Gas with Iridium-loaded Titania Catalyst

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Ir(5 wt%) supported on TiO_2 afforded a high activity for the partial oxidation of methane into CO and H_2 with the selectivity of above 80% at 600 °C.

Partial oxidation is an interesting and promising approach of producing synthesis gas from methane and oxygen or air, to give H_2 to CO ratio suitable for Fischer-Tropsch and methanol syntheses.

The first report of the partial oxidation of methane by using supported nickel catalyst was done by Prettre *et al.*[1] Ashcroft *et al.*[2-4] recently studied partial oxidation of methane using lanthanide ruthenium complex oxide catalysts ($Ln_2Ru_2O_7$) and supported group Ⅷ transition metals. Nakamura *et al.*[5] reported the same reaction over SiO_2-supported Rh, Ru and Ni catalysts and concluded that at 627-727 °C primary products of CO_2 and H_2O were further converted into CO and H_2 through the reactions of CH_4 with CO_2 and H_2O. Rh catalysts gave the highest synthesis gas yield of about 90% at 727 °C.

In this paper we will deal with the partial oxidation of methane on supported Ir catalysts. The conversions of methane with oxygen have been studied on using Ir-containing catalysts such as $Eu_2Ir_2O_7$[2-4] and also Al_2O_3[4]-supported Ir and Eu_2O_3[7]-supported Ir. We have found that the performance of the supported Ir catalysts in synthesis gas formation depended strongly upon the support materials. A high synthesis gas yield comparable to that of Rh catalysts was obtained, when TiO_2 is used as a catalyst support.

The reaction was carried out with a fixed-bed flow type quartz reactor (350 x 10 mm) at an atmospheric pressure. Using 60 mg of a catalyst, 25 ml/min CH_4 and 5 ml/min of O_2 were introduced at temperature ranges of 400-600 °C.

The catalyst supports used were Al_2O_3, SiO_2, TiO_2, ZrO_2 and Y_2O_3. The supported Ir catalysts containing 5 wt% Ir were prepared by the impregnation method with an aqueous solution of iridium tetrachloride to a respective support. Loaded catalysts were calcined at 600 °C for 5 h in the air prior to the reaction. The reaction was carried out by passing methane and oxygen mixture from 400 °C with increasing a temperature step of 50 °C up to 600 °C. The runs were conducted for 30 min and products were analyzed by a gas chromatograph.

Figure 1 shows effect of various supports of Ir on the conversion of methane at temperature ranges of 400 to 600 °C. The Ir-loaded TiO_2 exhibited the highest conversion of methane at 600 °C. However, this catalyst showed a very poor activity below 500 °C and the conversion of methane markedly increased above 550 °C. ZrO_2 and Y_2O_3 supports also exhibited high activities at 600 °C. Characteristic features of Al_2O_3 and SiO_2 supports were the higher conversions of methane below 500 °C. With these supports, only CO_2 and H_2O were obtained below 500 °C and apparently carbon deposition was observed. On the other hand, no carbon deposition was observed with TiO_2, ZrO_2 and Y_2O_3 supports. Carbon deposition through the Boudouard reaction or methane decomposition is thermodynamically favorable below about 900 °C.[8-9]

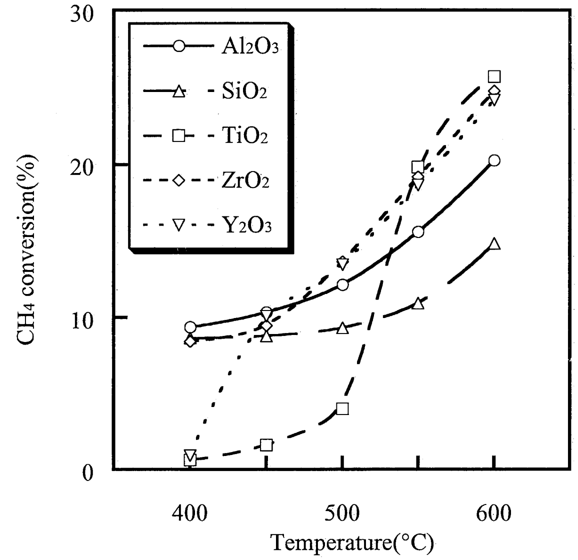

Figure 1. Effect of reaction temperature on the conversion of CH_4 over Ir-loaded catalysts.
Catalyst : 0.060 g, Space velocity=30000 h^{-1} · ml · g-cat^{-1}
Feed gas composition : CH_4 25 ml/min, O_2 5 ml/min.

Table 1 shows conversion and selectivity of the supported Ir catalysts. The order of the activity at the reaction temperature of 600 °C was $TiO_2 \geqq ZrO_2 \geqq Y_2O_3 > Al_2O_3 > SiO_2$. At 600 °C selectivities to CO and H_2 were the highest with the Ir-loaded TiO_2 catalyst being CO to H_2 ratio of 2.0 as expected from the stoichiometric reaction.

Table 1. Conversion and selectivity of supported Ir(5 wt%) catalysts for the partial oxidation of CH_4 at 600 °C

catalyst	CH_4 Conv.	Selectivity / %		ratio
	%	CO[a]	H_2[b]	H_2/CO
Ir/TiO_2	25.7	81.8	83.4	2.0
Ir/ZrO_2	24.8	78.5	82.8	2.1
Ir/Y_2O_3	24.2	76.3	82.0	2.1
Ir/Al_2O_3	20.3	71.2	72.0	2.0
Ir/SiO_2	14.9	43.0	57.2	2.7

Catalyst : 0.060 g, Space velocity=30000 h^{-1} · ml · g-cat^{-1}
Feed gas composition : CH_4 25 ml/min, O_2 5 ml/min.
[a] CO selectivity =(amount of CO in products)/(amount of ($CO+CO_2$) in products).
[b] H_2 selectivity =(amount of H_2 in products)/(2 × amount of ($CO+CO_2$) in products).

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298} = -38 \text{ kJ/mol} \qquad (1)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^0_{298} = -801 \text{ kJ/mol} \qquad (2)$$

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \qquad \Delta H^0_{298} = +247 \text{ kJ/mol} \qquad (3)$$

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \qquad \Delta H^0_{298} = +206 \text{ kJ/mol} \qquad (4)$$

Methane seemed to be converted into CO_2 and H_2O at the first stage of the reaction. Due to a large CH_4 to O_2 ratio (5: 1) in the present study, methane conversion should be limited to 10%, if complete oxidation (reaction 2) was assumed. A concurrence of reforming reactions (reactions 3, 4) may increase the conversion of methane up to 40%. Although oxygen conversion reached to 100% at 600 ℃, the observed conversions of methane were lower than 40% (Table 1).

According to the thermodynamics reported for the methane-oxygen system (CH_4:O_2=2:1),[9] the formations of CO_2 and H_2O are dominant at temperatures lower than about 550 ℃ and the synthesis gas formation becomes favorable at higher temperatures. However, temperatures higher than 700 ℃ are thermodynamically required for a high methane conversion (>90%) and a high synthesis gas selectivity (>90%). Such an equilibrium limitation might be the reason for the observed methane conversion of about 25% at 600 ℃ (Table 1) but not 40%.

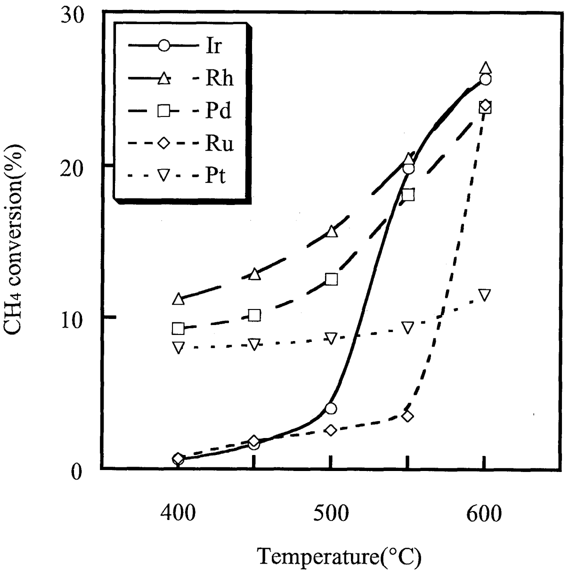

Figure 2. Effect of reaction temperature on the conversion of CH_4 over TiO_2-supported transition metal catalysts.
Catalyst : 0.060 g, Space velocity=30000 h^{-1} · ml · g-cat^{-1}
Feed gas composition : CH_4 25 ml/min, O_2 5 ml/min.

Figure 2 shows the conversions of methane over TiO_2 -supported group Ⅷ metal (5 wt%) catalysts. The conversion of methane was affected by the metal species and its order of activity was Rh ≧ Ir > Ru ≧ Pd > Pt. In the case of the Rh-loaded TiO_2 catalyst, the observed high performance was maintained even if Al_2O_3 or SiO_2 was used as the catalyst support, indicating a weak support effect in the Rh catalysts. TiO_2-supported noble metal catalysts are known to exhibit strong metal support interaction (SMSI),[10] in which characteristics of the catalyst changed drastically with a high temperature reduction. After the reaction between methane and oxygen at 600 ℃, the used Ir-loaded TiO_2 catalyst was again tested in the same reaction with increasing temperatures from 400 to 600 ℃. The second run gave a different temperature conversion dependence from that of the fresh Ir catalyst, but similar to that of the Ir-loaded ZrO_2 catalyst (Figure 1) or the Rh-loaded TiO_2 catalyst (Figure 2). This fact suggests that active species of the Ir-loaded TiO_2 catalyst seems to be metallic iridium. In the first run, the oxidic iridium species stabilized on titania could not bring about a high activity until it is reduced to metallic one in the reaction above 550 ℃. On the other hand, Rh, Pd, and Pt would be reduced to metallic species even at a low temperature, and complete oxidation of CH_4 occurred at 400 ℃.

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