Effect of support on the conversion of methane to synthesis gas over supported iridium catalysts

Kiyoharu Nakagawa [a,b], Kengo Anzai [a], Naoko Matsui [a], Naoki Ikenaga [a], Toshimitsu Suzuki [a,b,*], Yonghong Teng [c], Tetsuhiko Kobayashi [c] and Masatake Haruta [c]

[a] *Department of Chemical Engineering, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan*
[b] *High Technology Research Center, Kansai University, Suita, Osaka 564-8680, Japan*
[c] *Osaka National Research Institute, AIST, MITI, Ikeda, Osaka 563-8577, Japan*

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A partial oxidation of methane was carried out using iridium catalysts supported on several metal oxides. The productivity of the synthesis gas from methane was strongly affected by the choice of support oxides for the catalysts. The synthesis gas production proceeded basically via a two-step reaction consisting of methane combustion to give H_2O and CO_2, followed by the reforming of methane from CO_2 and steam. Although the combustion and the reforming of methane from steam did not depend upon the catalyst support, a large variation in the catalytic activity for the reforming of methane from CO_2 was observed over Ir catalysts with different supports. The support activity order in the reforming of methane from CO_2 with iridium catalysts was as follows: $TiO_2 \geqslant ZrO_2 \geqslant Y_2O_3 > La_2O_3 > MgO \geqslant Al_2O_3 > SiO_2$. The same order was observed in the synthesis gas production from the partial oxidation of methane.

Keywords: methane, partial oxidation, carbon dioxide, reforming, iridium, titania, synthesis gas

1. Introduction

The production of synthesis gas from methane has been studied in three reactions that attract industrial interest; the partial oxidation of methane (reaction (1)), steam reforming (reaction (2)), and CO_2 reforming (reaction (3)):

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

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298} = +206\ \text{kJ/mol} \qquad (2)$$

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

Among those, close attention has bee paid to the partial oxidation of methane, because the other two reactions are energy-consuming. Since the first report by Prettre et al. [1] in 1946, a large number of reports on the catalytic partial oxidation of methane have been published [2–4].

Two reaction paths for this reaction have been proposed. One is a direct path giving CO and H_2 over the catalyst. Schmidt et al. [5–7] have suggested the possibility of a direct path over Rh or Pt monoliths with a very short contact time for the reactants. The other route is a two-step process, where the complete oxidation of methane (reaction (4)) occurs as an initial step of the reaction, and the produced H_2O and CO_2 successively react with methane to give synthesis gas (reactions (3) and (4)). The latter two-step process is widely accepted for many catalytic systems [8]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H^0_{298} = -801\ \text{kJ/mol} \qquad (4)$$

Recently, we have reported the partial oxidation of methane with the use of supported Ir catalysts [9]. A distinct support effect was observed in the synthesis gas production. As a support of Ir, TiO_2 gave the highest productivity of the synthesis gas among the support materials tested. It is plausible that the two-step process, i.e., combustion and reforming, proceeds over the Ir/TiO_2 catalyst [10].

The transition metals of the group VIII supported on metal oxides have been widely examined as catalysts for the steam reforming [11–13] and the CO_2 reforming of methane [14,15], and in some cases the effect of the support on the catalytic activity has been reported. In the case of the steam reforming over Ru catalysts [13], Al_2O_3, SiO_2, and TiO_2 have shown a higher activity as supports than other support oxides. For the CO_2 reforming over Rh catalysts, the activity order in the supports has been reported to be $Al_2O_3 > TiO_2 > SiO_2$ [15]. Very recently, Solymosi et al. have reported that TiO_2 is a good support for the Ir catalyst in the CO_2 reforming of methane [16]. Their conditions are quite different from those of the partial oxidation of methane employed in our studies [9,10].

Such support effects reported in the catalytic reforming of methane motivated us to examine which elementary step is the most affected by the support materials in the Ir-catalyzed partial oxidation of methane [9]. In this paper, we will deal with the combustion, steam, and CO_2 reforming of methane over Ir catalysts supported on several metal oxides, and the results will be compared with the synthesis gas production by the partial oxidation of methane.

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[*] To whom correspondence should be addressed.

2. Experimental

The catalyst supports used were Al_2O_3, SiO_2 (JRC-ALO-4, JRC-SIO-4, the reference catalyst provided by the Catalyst Society of Japan), MgO (Ube Industry Co., Ltd.), TiO_2, ZrO_2 (Japan Aerosil Co.), Y_2O_3, and La_2O_3 (Nacalai Tesque, Inc.). The supported catalysts containing 5 wt% Ir metal were prepared by impregnation methods with an aqueous solution of $IrCl_4 \cdot H_2O$ (Mitsuwa Pure Chemicals) onto suspended supports, followed by evaporation-to-dryness. Loaded catalysts were calcined at 600 °C for 5 h in air. Prior to the reaction, the catalyst was reduced with H_2 at 400 or 600 °C for 1 h.

The reaction was carried out with a fixed-bed flow-type quartz reactor (350 × 10 mm) at 1 atm pressure. The conditions for partial oxidation were as follows: with 60 mg of a catalyst, 25 ml/min CH_4 and 5 ml/min of O_2 were introduced at 400–600 °C. For CO_2 reforming, using 100 mg of a catalyst and 300 mg of silica sand (Merck), 30 ml/min CH_4 and 30 ml/min of CO_2 were introduced at 600 °C. Silica sand was used as a heat buffer for a large endothermic reforming reaction. Steam reforming was tested using 60 mg of the catalyst at 600 °C with a mixture of $CH_4 : H_2O : N_2 = 1 : 1 : 23.3$ at a total flow rate of 30 ml/min.

The reaction products (H_2, CO, CH_4, and CO_2) were analyzed by a gas chromatograph directly connected to the outlet of the reaction tube with a thermal conductivity detector (model 802, Ohkura Riken), using columns packed with Molecular Sieve 5A, 13X and Porapak Q for the partial oxidation and steam reforming of methane. For the CO_2 reforming of methane, reaction products in the gas were analyzed by a gas chromatograph with a thermal conductivity detector (M200 chromato analyzer, Nippon Tyran Co.), which can separate H_2, CO, CH_4, and CO_2, within a few hundred seconds.

A thermal analysis system (SSC5200, Seiko Instruments, Inc.) was used for TG. The analyses were carried out with $CO_2 : CH_4 = 1 : 1$ at 1 atm pressure under isothermal conditions at 600 °C.

3. Results and discussion

3.1. Oxidation of methane

Table 1 shows the product distributions with various supported Ir catalysts. The support activity order at a 600 °C reaction temperature was $TiO_2 \geqslant ZrO_2 \geqslant Y_2O_3 > Al_2O_3 \geqslant La_2O_3 \geqslant MgO > SiO_2$. The performance of the catalyst depended strongly upon supports. At 600 °C, methane conversion and selectivities to CO and H_2 were the highest with the TiO_2-supported Ir catalyst, providing an H_2 to CO ratio of 2.0 as expected from the stoichiometric reaction. ZrO_2 and Y_2O_3 supports also exhibited high activities at 600 °C. Characteristic features of the Al_2O_3 and SiO_2 supports were the complete oxidation of methane (reaction (4)) and an apparent carbon deposition. On the other hand, no carbon deposition was observed with the other supports. Detailed studies on the reaction mechanism will be reported in a separate paper [10].

The complete oxidation of methane (reaction (4)) occurred at 400 °C in all the supports examined (see table 1). Synthesis gas was not produced at 400 °C due to thermodynamic limitation [4], and CH_4 conversion and selectivity to synthesis gas increased with an increase in the temperature. The feed ratio of CH_4 and O_2 was set at 5 in order to prevent an explosion of the gas mixture. Thus, the CH_4 conversion was limited to 10%, if complete oxidation of CH_4 occurred. At 400 °C, as seen in table 1, only 8–9% of the CH_4 conversion was observed with a high selectivity to CO_2, indicating no support effect for the complete oxidation of methane with supported Ir catalysts under such

Table 1
Activities of supported Ir catalysts for the oxidation of methane.[a]

Catalyst	Temperature (°C)	Specific surface area ($m^2\,g^{-1}$)	Conversion	Selectivity			H_2/CO ratio
			CH_4 (%)	CO (%)	CO_2 (%)	H_2 (%)	
Ir/TiO_2	400	35.8	8.6	5.0	95.0	9.7	–
	600	35.8	25.7	81.8	18.2	83.4	2.0
Ir/ZrO_2	400	32.7	8.4	5.4	94.6	8.0	–
	600	32.7	24.8	78.5	21.5	82.8	2.1
Ir/Y_2O_3	400	2.2	9.3	1.3	98.7	9.3	–
	600	2.2	24.2	76.3	23.7	82.0	2.1
Ir/Al_2O_3	400	160.5	9.4	7.9	92.1	7.2	–
	600	160.5	20.3	71.2	28.8	72.0	2.0
Ir/La_2O_3	400	6.7	7.9	0.7	99.3	6.3	–
	600	6.7	19.9	59.9	40.1	75.8	2.5
Ir/MgO	400	53.2	8.8	0.3	99.7	1.2	–
	600	53.2	19.5	60.5	39.5	74.2	2.5
Ir/SiO_2	400	279.9	8.7	~ 0	100.0	2.0	–
	600	279.9	14.9	43.0	57.0	57.2	2.7

[a] Prior to the reaction, catalysts were reduced with H_2 at 400 °C for 1 h. Catalyst, 0.06 g; Ir loading, 5 wt%; flow rate, 30.0 ml/min ($CH_4/O_2 = 5.0$); space velocity = 30,000 h^{-1} ml g-cat^{-1}.

Table 2
Activities of supported Ir catalysts for the H_2O reforming at 600 °C.[a]

Catalyst	Conversion	Selectivity		H_2/CO
	CH_4 (%)	CO (%)	CO_2 (%)	ratio
Ir/Al_2O_3	49.9	84.5	15.5	4.2
Ir/Y_2O_3	49.8	94.6	5.4	3.5
Ir/La_2O_3	47.9	92.6	7.4	3.7
Ir/TiO_2	47.1	93.6	6.4	3.6
Ir/SiO_2	44.7	92.8	7.2	3.7
Ir/ZrO_2	44.6	90.1	9.9	3.9
Ir/MgO	43.7	87.7	12.4	4.0

[a] Prior to the reaction, catalysts were reduced with H_2 at 600 °C for 1 h. $P(N_2) = 696$ mm Hg, $P(CH_4) = 32$ mm Hg, $P(H_2O) = 32$ mm Hg, $CH_4/H_2O = 1.0$. Catalyst, 0.06 g; Ir loading, 5 wt%; $W/F = 448$ g-cat^{-1} min mol-CH_4^{-1}; reaction time, 1 h.

Table 3
Activities of supported Ir catalysts for the CO_2 reforming at 600 °C.[a]

Catalyst	Conversion		Yield		H_2/CO
	CH_4 (%)	CO_2 (%)	H_2 (%)	CO (%)	ratio
Ir/TiO_2	27.6	37.9	22.4	32.7	0.7
Ir/ZrO_2	21.7	27.1	19.1	24.4	0.8
Ir/Y_2O_3	17.7	28.4	12.3	23.1	0.5
Ir/La_2O_3	16.2	26.8	11.0	21.5	0.5
Ir/MgO	10.1	17.3	6.5	13.7	0.5
Ir/Al_2O_3	9.0	11.8	7.5	10.4	0.7
Ir/SiO_2	1.2	2.2	0.7	1.7	0.4

[a] Prior to the reaction, catalysts were reduced with H_2 at 600 °C for 1 h. Catalyst, 0.10 g; Ir loading, 5 wt%; silica sand, 0.300 g; flow rate, 60.0 ml/min ($CH_4/CO_2 = 1.0$); reaction time, 1 h; space velocity = 36,000 h^{-1} ml g-cat^{-1}.

conditions ($CH_4/O_2 = 5$). These results suggest that the partial oxidation of methane to synthesis gas would proceed via a two-step reaction path or the mechanism would be changed at an elevated temperature.

The effect of the support on the steam and CO_2 reforming reactions of methane was examined in order to clarify the reaction mechanisms.

3.2. Steam reforming

Table 2 shows the product distributions with various supported Ir catalysts for the steam reforming of methane to synthesis gas at 600 °C. A much higher CH_4 conversion as compared to CO_2 reforming was observed in all the catalysts employed, although H_2O and CH_4 were diluted with a large amount of N_2. Little support effect was observed in the CH_4 conversion. The CH_4 conversion is almost equal to the equilibrium conversion, and the reactivity of steam is higher than that of CO_2, as described later. The higher H_2/CO ratio expected from the stoichiometry indicates a water–gas shift reaction, as evidenced by the considerable formation of CO_2. These findings did not give positive information about the differences in the catalytic activity among the supports of Ir-loaded catalysts for the partial oxidation of methane.

3.3. CO_2 reforming

Effect of supports on the partial oxidation of methane seemed to be related to the catalytic activity of the CO_2 reforming reaction. CO_2 reforming was carried out with supported iridium catalysts, and the relation between the activity in partial oxidation and CO_2 reforming was examined. Table 3 shows the product distributions in the CO_2 reforming of methane with various supported Ir catalysts. CH_4 and CO_2 conversions were greatly affected by the support of iridium. In all cases, the CO_2 conversion was higher than that of CH_4. The support activity order among the supports evaluated from CH_4 and CO_2 conversions at the 600 °C reaction temperature is as follows: $TiO_2 \geqslant ZrO_2 \geqslant Y_2O_3 > La_2O_3 > MgO \geqslant Al_2O_3 > SiO_2$. This order is the same order as that observed in the partial oxidation of methane (see table 1). No carbon deposition was observed for the TiO_2-, ZrO_2-, Y_2O_3-, La_2O_3-, and MgO-loaded cases. Carbon deposition was apparently observed for Al_2O_3- and SiO_2-supported catalysts. The significant effect of the support might be ascribed to the activation of CO_2 with metal oxides used as a support. Similar results have been obtained in the CO_2 reforming of heptane or CH_4 using a ruthenium-loaded catalyst. In the ruthenium-loaded catalyst, La_2O_3, Y_2O_3, and ZrO_2 exhibited high catalytic activity for the CO_2 reforming of heptane or methane [16,17].

Figures 1 and 2 show the effect of time on stream on the CH_4, CO_2 conversions and CO, H_2 yields in the CO_2 reforming at 600 °C. TiO_2, ZrO_2, and MgO maintained initial activity for at least 2 h. The CH_4 and CO_2 conversions with Y_2O_3- and La_2O_3-supported catalysts increased slightly with time on stream. To achieve a higher activity in the CO_2 reforming, the activation of CO_2 on the support would be one important factor, in addition to the activation of methane on the transition metal surface. Nakamura et al. [15] have reported the effects of supports on catalytic activity in the CO_2 reforming of methane. They achieved an enhanced catalytic activity by mixing MgO with Rh/SiO_2, concluding that this activity promoted the dissociation of CO_2 on the surface of Rh enriched with the CO_2 adsorbed on MgO. This suggests that CO_2 dissociation is the rate-determing step of this reaction. On the other hand, CH_4 conversion with Al_2O_3- and SiO_2-supported catalyst decreased gradually with increasing reaction time, presumably due to the accumulation of carbonaceous material on the catalyst surface. Carbon deposition through the Boudouard reaction (reaction (5)) or methane decomposition (reaction (6)) is thermodynamically favorable below 900 °C [4,11]:

$$2CO \rightleftharpoons C + CO_2 \quad \Delta H^0_{298} = -173 \text{ kJ/mol} \tag{5}$$

$$CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H^0_{298} = +75 \text{ kJ/mol} \tag{6}$$

Kinetically, both the Boudouard reaction (reaction (5)) and the methane decomposition reaction (reaction (6)), which give undesirable carbon, are known to be exceptionally

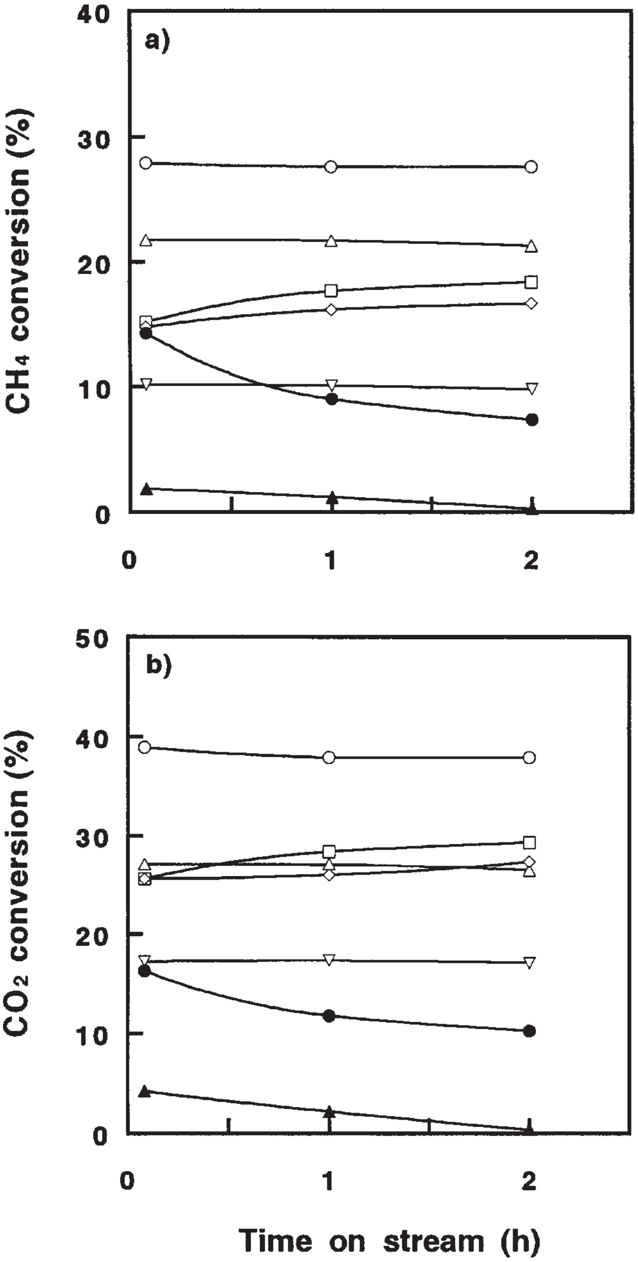

Figure 1. Effect of time on stream on the conversion of CH_4 and CO_2 over supported Ir catalysts: (○) TiO_2; (△) ZrO_2; (□) Y_2O_3; (◇) La_2O_3; (▽) MgO; (●) Al_2O_3; (▲) SiO_2. Reaction conditions: reaction temperature, 600 °C, $CH_4 : CO_2 = 1 : 1$, flow rate = 60 ml/min. Catalyst: 100 mg, silica sand: 300 mg, SV = 36,000 h^{-1} ml/g-cat.

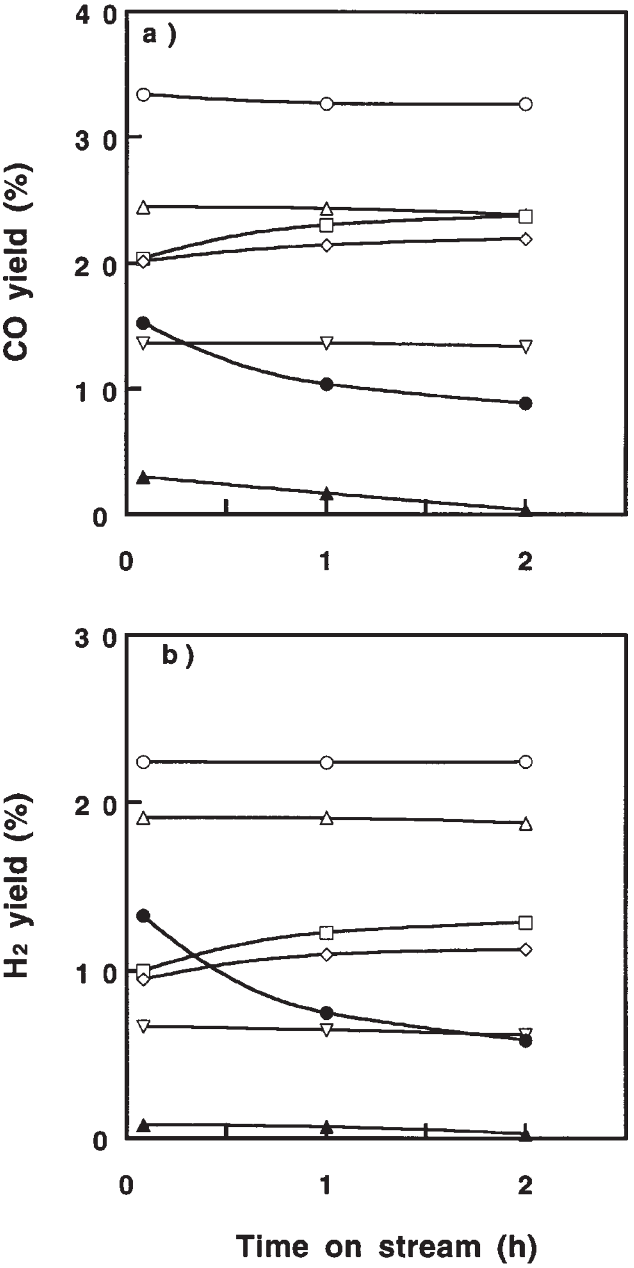

Figure 2. Effect of time on stream on the CO and H_2 yields over supported Ir catalysts: (○) TiO_2; (△) ZrO_2; (□) Y_2O_3; (◇) La_2O_3; (▽) MgO; (●) Al_2O_3; (▲) SiO_2. Reaction conditions: reaction temperature, 600 °C, $CH_4 : CO_2 = 1 : 1$, flow rate = 60 ml/min. Catalyst: 100 mg, silica sand: 300 mg, SV = 36,000 h^{-1} ml/g-cat.

slow in the absence of a catalyst, but both can be readily catalyzed by many transition metals. Carbon deposition on supported Ir catalysts was measured under an isothermal reaction at 600 °C with a TG, and the results are shown in table 4. Carbon deposition was not detected with a TiO_2-supported Ir catalyst in the reaction for 2 h. In contrast, carbon deposition was measured on an Al_2O_3 support, indicating that the Al_2O_3-supported Ir catalyst was deactivated by carbon deposition.

Figure 3 shows the effect of time on stream on the H_2/CO ratio with iridium catalysts loaded on various sup-

Table 4
TG analyses of Ir catalysts at 600 °C.[a]

Catalyst	Carbon deposition rate (C μmol/(g-cat min))	Carbon deposition (C μmol)
Ir/TiO_2	nd	nd
Ir/Al_2O_3	1.2	1.7

[a] Prior to the reaction, catalysts were reduced with H_2 at 600 °C for 1 h. Ir loading, 5 wt%. Flow rate, 30.0 ml/min (CH_4/CO = 1.0); reaction time, 2 h. nd, not detected.

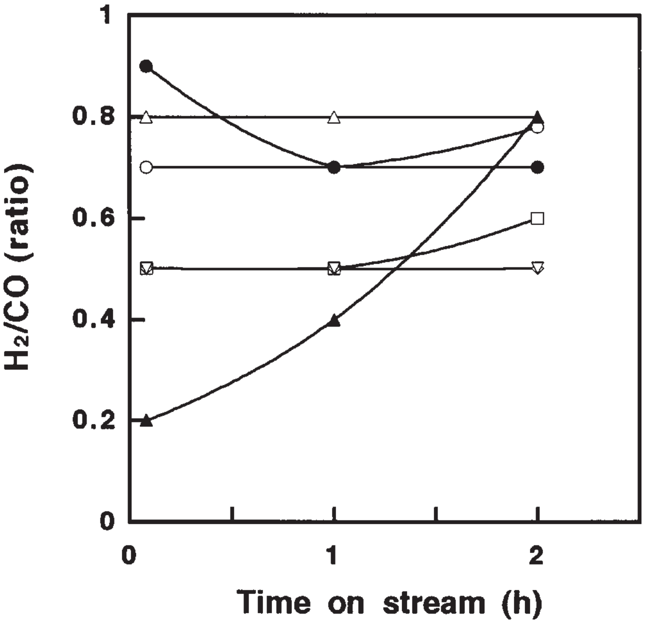

Figure 3. Effect of time on stream on the H_2/CO ratio over supported Ir catalysts: (○) TiO_2; (△) ZrO_2; (□) Y_2O_3; (◇) La_2O_3; (▽) MgO; (●) Al_2O_3; (▲) SiO_2. Reaction conditions: reaction temperature, 600 °C, $CH_4 : CO_2 = 1 : 1$, flow rate = 60 ml/min. Catalyst: 100 mg, silica sand: 300 mg, SV = 36,000 h^{-1} ml/g-cat.

ports. At 600 °C, all the supported Ir catalysts afforded a lower H_2/CO ratio than the stoichiometric ratio of unity. Low H_2/CO ratios over supported Ir catalysts could be attributed to the reverse water–gas shift reaction shown below:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H^0_{298} = +41 \text{ kJ/mol} \qquad (7)$$

The excess CO may come from this reaction, and H_2 was consumed to increase CO_2 conversion. This reaction seems to be faster than the CH_4–CO_2 reaction. In the partial oxidation of methane, H_2 and CO were produced with a suitable H_2/CO ratio of 2.0 at 600 °C over TiO_2 and ZrO_2 supports which exhibited high CH_4 conversions. On the other hand, La_2O_3, MgO, and SiO_2, which exhibited lower CH_4 conversions, showed higher H_2/CO ratios (above 2.5) [9]. The stoichiometric H_2/CO ratio is unity in the CO_2 reforming, and 3 in the steam reforming. In order to obtain an H_2/CO ratio of 2 in the partial oxidation, CO_2 and steam reforming need to occur at the same reaction rate. The higher H_2/CO ratios with La_2O_3, MgO and SiO_2 can be explained by the lower rate of the CO_2 reforming reaction. This strongly supports the possibility that a two-step reaction path is operative in the partial oxidation of methane to synthesis gas with supported Ir catalysts.

4. Conclusions

The partial oxidation and CO_2 reforming of methane with supported Ir catalysts are strongly affected by support oxides. In contrast, the steam reforming reaction is not affected by the supports. The support activity orders in the partial oxidation and the CO_2 reforming are in good agreement. This indicates that the partial oxidation of methane with a supported Ir catalyst proceeds in a two-step mechanism involving the complete oxidation of methane to give CO_2 and H_2O, followed by CO_2 and steam reforming, which might be the slowest elementary step.

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