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Role of support in reforming of CH_4 with CO_2 over Rh catalysts

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The reforming of CH_4 with CO_2 over supported Rh catalysts has been studied over a range of temperatures (550–1000 K). A significant effect of the support on the catalytic activity was observed, where the order was $Rh/Al_2O_3 > Rh/TiO_2 > Rh/SiO_2$. The catalytic activity of Rh/SiO_2 was promoted markedly by physical mixing of Rh/SiO_2 with metal oxides such as Al_2O_3, TiO_2, and MgO, indicating a synergetic effect. The role of the metal oxides used as the support and the physical mixture may be ascribed to the promotion in dissociation of CO_2 on the surface of Rh, since the $CH_4 + CO_2$ reaction is first order in the pressure of CO_2, suggesting that CO_2 dissociation is the rate-determining step. The possible model of the synergetic effect was proposed.

Keywords: CO_2 reforming of CH_4; supported Rh catalyst; support effect; CO_2 activation

1. Introduction

Great attention has been paid to the reforming of CH_4 with CO_2 ($CH_4 + CO_2 \rightarrow 2CO + 2H_2$ 59.1 kcal/mol) on account of the following two backgrounds. Firstly, the reaction is a promising process as an alternative route to synthesis gas [1–8]. The industrial interest in the $CH_4 + CO_2$ reaction is related to the CO/H_2 ratio of unity which is less than that obtained by steam reforming of CH_4. In fact, the CO_2 reforming has been used in conjunction with steam reforming by addition of CO_2 to the feed gas to obtain a suitable $H_2/(CO + CO_2)$ ratio for a hydrogenation of CO such as methanol synthesis. Secondly, the $CH_4 + CO_2$ reaction has been investigated from a viewpoint of energy transfer or storage by use of the great heat of reaction and the reversibility between the forward and the reverse reaction [9–11]. In the Eva–Adam process operated in Germany, steam reforming of CH_4 is adopted for the energy transfer. The products of CO/H_2 are transported to remote sites where the reverse reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, is performed, and then CH_4 is sent back after removing H_2O from the product mixture. The advantages of the $CH_4 + CO_2$ reaction in the application to the heat transfer are due to the heat of reaction (59.1 kcal/mol) which is higher than that of steam reforming of CH_4 (49.3 kcal/mol) and to the fact that no liquid products that need excess energy for vaporization are formed.

Most of the group VIII metals (Rh, Ru, Ni, Pd, Pt, Ir, Co, Fe) except Os are known to catalyze more or less the $CH_4 + CO_2$ reaction. The serious problem is deactivation of the catalyst by carbon deposition on the surface of the catalyst and the subject of worldwide research interest is currently to develop catalysts which can efficiently conduct the CO_2 reforming without coking. The conventional Ni-based steam reforming catalysts tend to be coked due to the formation of stable nickel carbide on the surface of Ni catalysts [3]. Among the metals having catalytic activity, Rh is a superior component in respect of the high activity and the coking-free nature. The combination of metal and support also influences the catalytic activity as well as the extent of carbon deposition, where Al_2O_3 is an excellent support for Pd and Pt catalysts while MgO is suitable for Ni catalysts. In this paper, we report the support effect of Rh catalysts for the $CH_4 + CO_2$ reaction and propose a model for the role of the support played in the activation of CO_2.

2. Experimental

The supports used here were Al_2O_3 (JRC-ALO4), SiO_2 (JRC-SIO7), and TiO_2 (JRC-TiO4) supplied by the Catalyst Society of Japan and MgO manufactured by Wako pure chemical industries, Ltd, and calcined at 1073–1173 K before preparation of catalysts. The supported catalysts with 0.5 wt% loading of Rh were prepared by an impregnation method using rhodium chlorides. The catalysts were dried at 383 K for ca. 2 h and calcined at 723 K for 3 h in air. Prior to the reaction, the catalysts were reduced with H_2 at 773 K for 1 h in a flow reactor. The reforming of CH_4 with CO_2 was conducted using mixtures of $CH_4 : CO_2 : N_2 = 3.4 : 3.4 : 93.2$ at total flow rates of 50 ml/min. The total pressure is 1 atm. Reaction products were analyzed by an on-line gas chromatograph. The dispersion of Rh was determined by static measurement of H_2 chemisorption using the post-reaction catalysts. The reaction rate was determined by changing W/F value, where W and F were weight of the catalysts and flow rate of reactant, respectively. Turnover frequency (TOF) was calculated from the reaction rate and dispersion.

3. Results and discussion

The reaction of CH_4 with CO_2 was carried out over Rh/Al_2O_3, Rh/SiO_2, and Rh/TiO_2 between 600 and 1100 K. The results of the reaction at 893 K for these catalysts and the dispersions of Rh are summarized in table 1. The conversion of CH_4 and CO_2 and the reaction rate on the basis of the unit 10^{-4} mol/s g clearly indicate the significant effect of the support on the catalytic activity where its order of supports was $Al_2O_3 > TiO_2 > SiO_2$ and Rh/Al_2O_3 was 18 times more active than

Table 1

	Dispersion[a]	Conversion[b]		Yield[b]			Reaction rate[c]	
		CH_4 (%)	CO_2 (%)	H_2 (%)	CO (%)	H_2/CO ratio	10^{-4} mol /s g	TOF /s site
Rh/Al_2O_3	0.514	83.8	85.7	66.2	78.3	0.85	632	25.5
Rh/TiO_2	0.068	88.7	88.2	80.7	82.4	0.98	123	37.5
Rh/SiO_2	0.121	5.8	5.1	4.4	5.4	0.81	35.7	6.1

[a] The dispersions were determined using post-reaction catalysts.

[b] Catalyst weight, 10 mg; reaction temperature, 893 K.

[c] The rates were determined by changing *W*/*F* value.

Rh/SiO_2 at 893 K. The activities were also compared by turnover frequency (TOF) for CH_4 conversion considering the dispersion of Rh particles, and the order of activity was found to be $TiO_2 > Al_2O_3 > SiO_2$, where Rh/TiO_2 was 6 times more active than Rh/SiO_2 at 893 K. Arrhenius plots of the TOF for these three catalysts are shown in fig. 1. The activation energies for Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 were given as 15, 21 and 20 kcal/mol, respectively.

The significant effect of support may be due to a direct activation of CH_4 or CO_2 by metal oxides used as support. Another possibility of the support effect is related to the difference of particle size of Rh, since a so-called "structure sensitive" reaction is influenced by dispersion of metal on the support. To evaluate the role of the support, the $CH_4 + CO_2$ reaction was performed over Rh/SiO_2 catalysts mixed physically with metal oxides such as Al_2O_3, TiO_2, and MgO. Fig. 2 shows

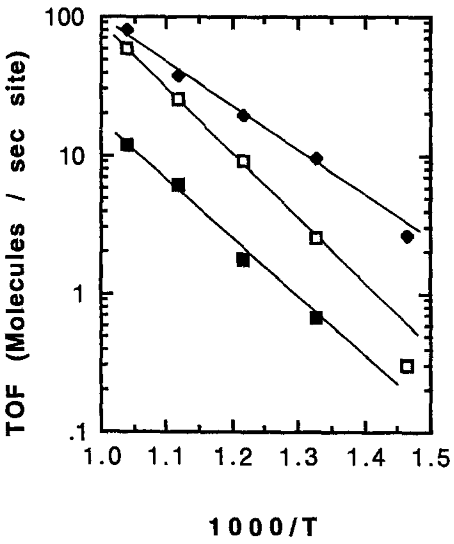

Fig. 1. Arrhenius plots of turnover frequency (TOF) for CH_4 conversion over (◆) Rh/TiO_2, (□) Rh/Al_2O_3, and (■) Rh/SiO_2.

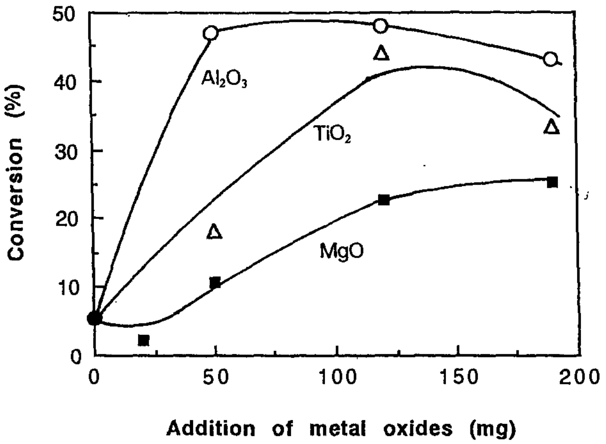

Fig. 2. Effect of metal oxides mixed with Rh/SiO_2 on conversion of CH_4. Reaction temperature is 893 K. Rh/SiO_2 (10 mg) + metal oxide (x mg)+SiO_2($190 - x$ mg). Total amount of the mixtures is 200 mg. (○) Al_2O_3, (△) TiO_2, (■) MgO, (●) none.

the conversions of CH_4 at 893 K as a function of the amount of metal oxides mixed with 10 mg of Rh/SiO_2. The equilibrium conversion is 84.9% under this reaction condition. It is clear from the results in fig. 2 that each of the metal oxides, Al_2O_3, TiO_2, and MgO, promotes the catalytic activity of Rh/SiO_2 remarkably. Although the addition of Al_2O_3 promoted the catalytic activity of Rh/SiO_2 by an order of magnitude, no activity of Al_2O_3 alone was observed for the $CH_4 + CO_2$ reaction. This indicates a synergetic effect of Rh metal and metal oxide on the catalytic activity for the $CH_4 + CO_2$ reaction.

In order to clarify which molecule, CH_4 or CO_2, is activated by the mixing of metal oxides with Rh/SiO_2, it is necessary to get information on the rate determining step of the $CH_4 + CO_2$ reaction. We hereby examined the dependence of TOF over Rh/SiO_2 at 823 K on the pressures of CO_2 and CH_4 which were varied between 26 and 130 Torr. As shown in fig. 3, the reaction was found to be 1.0 order in CO_2 and -0.6 order in CH_4. The rise of CH_4 pressure leads to a decrease of reaction rate for the $CH_4 + CO_2$ reaction. This suggests that dissociation of CO_2 on Rh/SiO_2 is the rate-limiting step and proceeds faster than dissociation of CH_4, which is consistent with the results of surface science studies on dissociation of CO_2 and CH_4 over Rh surface. It is known that CH_4 dissociates easily on Rh surface [12,13], while the dissociation of CO_2 is a slow step [14,15]. The dissociation probabilities of CH_4 and CO_2 at 823 K are estimated to 1×10^{-4} and 2×10^{-5}, respectively, which are calculated from the data measured by Ehrlich [13] and Goodman [14]. It is concluded from the results of the pressure dependences that the role of metal oxides such as Al_2O_3, TiO_2, and MgO for the promotion of the activity of Rh/SiO_2 shown in fig. 2 is ascribed to the activation of a CO_2 related step.

It is known that CO_2 can adsorb on the surface of Al_2O_3, TiO_2, and MgO above room temperature as carbonate or formate in the presence of hydrogen. The carbo-

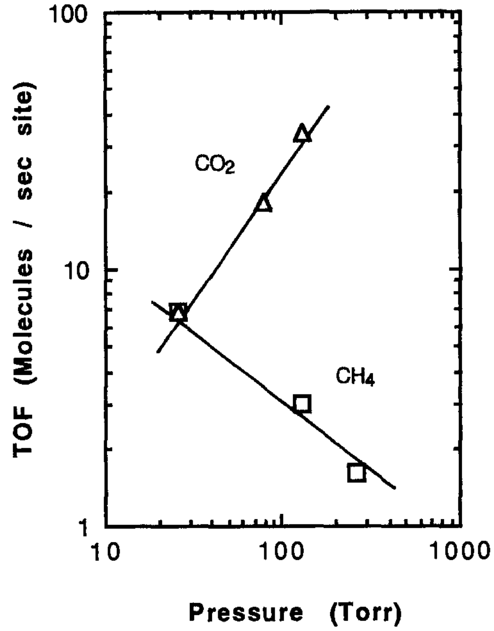

Fig. 3. Dependence of TOF on the partial pressure of (△) CO_2 and (□) CH_4 in the $CH_4 + CO_2$ reaction over Rh/SiO_2 at 893 K. The constant pressure of CH_4 or CO_2 is 26 Torr. The TOF values for the CH_4 and CO_2 pressure dependence are calculated from CO yield and CH_4 conversion, respectively.

nates on Al_2O_3 [16], TiO_2 [17], and MgO [18] decompose in vacuum at 350, 420, and 580 K, respectively. As for formate [19] on Al_2O_3, TiO_2, and MgO, the peak tops of temperature programmed desorption for CO_2 are 650, 540, 730 K, respectively, which are higher than the decomposition temperature of carbonate. We have confirmed the formation of formate on Al_2O_3 during the reaction of CO_2 and H_2, the reverse water–gas shift (RWGS) reaction, over the catalyst $Rh/SiO_2 + Al_2O_3$ using in situ FT IR. No carbonate or formate, however, is formed on SiO_2 [20] which is the only metal oxide that has no promotional effect for the $CH_4 + CO_2$ reaction in this study, suggesting that formation of carbonate or formate may be responsible for the enhancement of the reaction rate shown in fig. 2. Since the formate on Al_2O_3 is known to be intermediate species for the RWGS reaction [21], H_2O should be formed on Al_2O_3 by the RWGS reaction during the $CH_4 + CO_2$ reaction. We have also reported that TOF for steam reforming of CH_4 is greater than that for the $CH_4 + CO_2$ reaction by a factor of 6 at 823 K [22]. Thus, we tentatively propose a mechanism for the role of metal oxide where a part of CO_2 is once converted to H_2O by the RWGS reaction via formate intermediates over Al_2O_3 and the H_2O then reacts with CH_4 to form CO and H_2 over Rh. The formate on Al_2O_3 may be produced by either the reaction between hydrogen splitover from Rh onto Al_2O_3 and CO_2 on Al_2O_3 or the spillover of formate from Rh onto Al_2O_3 [23]. We will report in more detail on this mechanism elsewhere.

Solymosi et al. [6] reported the CO_2 pressure dependence in the $CH_4 + CO_2$ reaction over supported Rh catalysts and the support effect on the catalytic activity. The dependence of the rates for CO and H_2 formations on the pressure of CO_2 were 0.23 and 0.31, respectively, which were lower than the value in our case. Furthermore, no significant support effect was observed in the reaction of $CH_4 + CO_2$ over supported Rh catalysts, Rh/Al_2O_3, Rh/TiO_2, and Rh/SiO_2. The different results from ours on the pressure dependence and the support effect is probably due to the pressure condition that the CO_2 and CH_4 reaction is performed at atmospheric pressure in their experiment, while each pressure of CO_2 and CH_4 is 26 Torr in this study. The different feature of the pressure dependence at 26 Torr and atmospheric pressure suggests that the kinetic balance for CO_2 and CH_4 dissociation and RWGS reaction is changed at the pressure region.

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