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Catalytic performance and characterization of Rh–CeO_2/MgO catalysts for the catalytic partial oxidation of methane at short contact time

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ABSTRACT

The addition of an optimum amount of CeO_2 (Ce/Rh = 4) to 1.0 wt% Rh/MgO promoted the catalytic partial oxidation (CPO) of methane with N_2 dilution. At the same time, it can suppress the temperature increase at the catalyst bed inlet during the CPO of methane without N_2 dilution. The Rh–CeO_2/MgO (Ce/Rh = 4) has the ability to maintain a more reduced state in the CPO of methane, and this may be related to the high ability to activate methane by the synergy of Rh metal surface and partially covering Ce species. The catalyst bed of the CPO of methane consists of the initial oxidation zone and the subsequent steam reforming zone. The catalyst with higher resistance to the oxidation of Rh gives larger zone for the steam reforming and it also enables the overlap of the exothermic oxidation zone with the endothermic steam reforming zone.

1. Introduction

Conversion of natural gas to synthesis gas is important for the production of methanol, dimethyl ether, and Fischer–Tropsch liquids, and a more compact and energy-efficient process for syngas production than conventional steam reforming is needed [1,2]. Much attention has recently been paid to the catalytic partial oxidation (CPO) of methane, where high methane conversion and syngas yield have been obtained at millisecond contact times under autothermal conditions [3]. Therefore, CPO makes the reactors simple and compact and it also enables fast responses and low heat capacity. It has been confirmed that noble-metal-based catalysts are highly active for the CPO of methane, and Rh is one of the suitable components [3–7]. It has been known that rhodium is applied to various catalytic reactions other than partial oxidation of methane, and modification of Rh catalysts with CeO_2 promoted many reactions such as deNOx [8,9], CO oxidation [10], reforming of hydrocarbons [11,12], gasification of biomass [13–15], catalytic partial oxidation and autothermal reforming of ethanol [16,17], and catalytic wet air oxidation of gasoline oxygenates [18]. In the CPO of methane, Schmidt and co-workers have reported that the effect of the washcoat and Ce addition was investigated over Rh + CeO_2-based catalysts supported on α-Al_2O_3 foam monoliths using the spatial analysis of gas composition and temperature profiles in the catalyst bed [19–21]. In the present study, the effect of CeO_2 addition to Rh/MgO is investigated in the CPO of methane at short contact time. In the case of the practical application of the CPO of methane, the reaction pressure will be higher such as 1 MPa, although the CPO performance has been evaluated under atmospheric pressure or below. Under pressurized conditions, the suppression of carbon deposition will be more important. MgO is known to be an effective support to the suppression of carbon deposition in the production of synthesis gas by the reforming reactions [22,23]. The addition of CeO_2 to MgO decreased the amount of carbon deposition in the CPO of methane under pressurized condition [24]. In addition, it has been reported that the MgO support suppressed the sintering of Rh metal particles [25–27].

In this article, we investigated the dependence of the added amount of CeO_2 over 1 wt% Rh/MgO on the CPO of methane with or without dilution. In particular, the effect of CeO_2 addition on the catalyst structure and the reaction zones of CPO are discussed on the basis of the catalyst bed temperature measured by the infrared thermographical observation and catalyst characterization results.

2. Experimental

2.1. Catalyst preparation

A Rh/MgO catalyst was prepared by impregnating MgO with an aqueous solution of $RhCl_3{\cdot}3H_2O$ (Soekawa Chemicals). The MgO

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support was prepared by calcining MgO (UBE Material Industries Ltd., Japan) at 1423 K for 3 h. After the impregnation, the solvent was evaporated at 353 K and the sample was dried at 383 K for 12 h and then calcined at 773 K in air for 3 h. Rh–CeO_2/MgO catalysts were prepared by impregnating MgO with the mixed aqueous solution of $RhCl_3{\cdot}3H_2O$ and $Ce(NH_4)_2(NO_3)_6{\cdot}H_2O$ (Wako Pure Chemical Industries) in the co-impregnation method. After the co-impregnation, the solvent was evaporated at 353 K. The sample was dried at 383 K for 12 h and then calcined at 773 K for 3 h. The loading amount of Rh on Rh/MgO and Rh–CeO_2/MgO was 1.0 wt%. The loading amounts of CeO_2 on Rh–CeO_2/MgO were represented as the molar ratio of Ce to Rh (Ce/Rh) in parentheses as Rh–CeO_2/MgO (Ce/Rh = 4). The weight content of the CeO_2 is listed out in Table 1. As a reference, CeO_2/MgO was also prepared by the impregnation method. The loading amount of CeO_2 was adjusted to the corresponding Rh–CeO_2/MgO. Catalysts in powder form were pressed, then crushed and sieved into granules of 0.13–0.18 mm.

2.2. Characterization of catalysts

Temperature-programed reduction (TPR) profiles were measured in a fixed-bed quartz reactor, and the procedures were the same as those mentioned in the previous report [28]. Before TPR measurement, the catalysts were treated in O_2 at 773 K for 0.5 h and then in Ar at 773 K for 0.5 h to remove adsorbed species such as CO_2. The sample weight was 50 mg, and the heating rate was 10 K min^{-1} from room temperature to 1123 K, and 5% H_2 diluted in Ar (30 cm^3 min^{-1}) was used. Consumption of hydrogen was estimated from the integrated peak area of the profiles.

Measurement of H_2 chemisorption was carried out in a high-vacuum system using a volumetric method, and the procedures were the same as those mentioned in the previous report [28]. Before the adsorption of H_2, the catalysts were treated in H_2 at 1123 K for 0.5 h in a fixed-bed reactor. After this pretreatment, the sample was transferred to a cell for adsorption measurements under air atmosphere. Before each measurement, H_2 pretreatment at 773 K was carried out for 0.5 h in the cell. After evacuation at 773 K, the sample was cooled to room temperature. The total amount of H_2 adsorption was measured at room temperature with a H_2 pressure at adsorption equilibrium of about 1.0 kPa. The dead volume of the apparatus was 63.5 cm^3 and the sample weight was 150 mg.

The catalysts were observed using a transmission electron microscope (TEM) (JEOL JEM-2010) at an accelerating voltage of 200 kV. Catalysts after the H_2 reduction pretreatment at 1123 K for 0.5 h and after the activity test were dispersed in ethanol using supersonic waves. Then they were put on Cu grids for TEM observation under air atmosphere. Average particle size in the form of a surface mean diameter (d_s) is calculated by $d_s = \sum n_1 d_1^3 / \sum n_1 d_1^2$ (n_i, number of pieces; d_i, particle size) [29–31].

Rh *K*-edge EXAFS were measured at BL01B1 station in SPring-8 with support from the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2006A1058, 2007A1156), and the measurement method and the beam conditions were the same as those reported previously [28]. The catalyst powder (750 mg) was treated using H_2 at 1123 K for 0.5 h in a fixed-bed reactor and the sample was pressed into a self-supporting 7-mm-diameter wafer under atmosphere, followed by treatment with H_2 at 773 K for 0.5 h in a cell. After this pretreatment, the sample wafer was transferred to the measurement cell using a glove box filled with nitrogen to prevent exposure of the sample disk to air. The analysis method for the EXAFS spectra was carried out in the same way as that in the previous report [28].

2.3. Partial oxidation of methane with or without N_2 dilution

Activity tests for the catalytic partial oxidation (CPO) of methane with N_2 dilution were carried out using a tubular fixed bed flow reactor made of quartz. The reactor setup was the same as that in the previous report [28]. The dilution of the reactant gases with N_2 ($CH_4/O_2/N_2$ = 4/2/94) was applied to suppress the temperature increase of the catalyst bed due to exothermic reactions. The catalyst weight was 10 mg, and the height of the catalyst bed was about 1.4 mm. Catalysts were reduced with hydrogen at 1123 K for 0.5 h before each activity test. The temperature on the reactor was monitored with a thermocouple at the bottom of the catalyst bed, and it was denoted as T_{TC}. The total flow rate of the gases was 1500 cm^3 min^{-1}, and the contact time was as short as 0.4 ms. The temperature profile of the catalyst bed during the CPO of methane with the N_2 dilution was measured by using the infrared thermography, and the profile is shown in Fig. S1. The bed temperature was only 20 K higher than the T_{TC}, indicating that the effect of the temperature increase in the CPO of methane with N_2 dilution is

Table 1
Properties of catalysts and results of activity test in partial oxidation of methane with N_2 dilution.

Catalyst	Loading of CeO_2 (wt%)	BET surface area (m^2 g^{-1})	H_2 adsorption (μmol g_{cat}^{-1})[a]	Rh metal particle size (nm)[b]	Dispersion		Partial oxidation of methane[c]			
					H_2 adsorption (H/Rh)	TEM[d]	CH_4 conversion (%)	H_2 selectivity (%)	CO selectivity (%)	TOF (s^{-1})[e]
Rh/MgO	–	6.9	11.2	5.6 ± 0.3	0.24	0.20	69	83	81	125
Rh–CeO_2/MgO (Ce/Rh = 4)	6.4	9.8	6.0	4.1 ± 0.3	0.13	0.27	81	93	90	274
Rh–CeO_2/MgO (Ce/Rh = 8)	12.8	11.5	4.8	–	0.10	–	72	88	84	303
Rh–CeO_2/MgO (Ce/Rh = 12)	19.2	12.8	4.0	–	0.09	–	70	87	84	352
Rh–CeO_2/MgO (Ce/Rh = 18.7)	30.0	15.0	4.0	3.2 ± 0.3	0.09	0.34	64	87	80	323
6.4 wt% CeO_2/MgO[f]	6.4	10.2	–	–	–	–	0.3	28	12	–
30 wt% CeO_2/MgO[f]	30.0	14.6	–	–	–	–	0.5	36	9	–

[a] H_2 adsorption at 298 K.

[b] Rh particle size (surface-averaged) is calculated from TEM images.

[c] Reaction conditions: $CH_4/O_2/N_2$ = 4/2/94, total flow rate 1500 cm^3 min^{-1}; T_{TC} = 973 K; total pressure 0.1 MPa; catalyst weight 10 mg; contact time 0.4 ms.

[d] Dispersion from TEM is calculated from (1.098/(Rh particle size [nm])) [34].

[e] Turnover frequency (TOF) in partial oxidation of methane is calculated on the basis of methane conversion rate and the amount of H_2 adsorption at 298 K.

[f] Loading amounts of CeO_2 on 6.4 and 30 wt% CeO_2/MgO were equal to those on Rh–CeO_2/MgO (Ce/Rh = 4 and 18.7), respectively.