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Support effect of metal oxide on Rh catalysts in the CH_4–CO_2 reforming reaction

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Rhodium supported on various metal oxides was studied in the dry reforming reaction using methane and carbon dioxide, in order to reveal the effect of support on the catalytic activity of Rh. The TOF (turnover frequency) based on exposed Rh decreased in the following sequence of support: $TiO_2 > La_2O_3 \fallingdotseq CeO_2 > ZrO_2 \fallingdotseq MgO \fallingdotseq SiO_2 \fallingdotseq$ MCM-41 $> \gamma$-Al_2O_3. The different TOF could be correlated with the stabilized species of Rh atom. It was concluded that the supports influenced the electronic state of Rh atoms, and that Rh metal catalyzed this reaction as a prominent active species.

KEY WORDS: carbon dioxide reforming; Rh-supported catalyst; structure-sensitive reaction; support effect.

1. Introduction

Recently, carbon dioxide reforming of methane (reaction (1)) has received attention from the viewpoint of global-warming prevention because this reaction uses only methane and carbon dioxide, which are greenhouse gases. The ratio of CO/H_2 of the gas produced by this reaction is low and suitable for reactants of the Fischer–Tropsch synthesis and hydroformylation [1,2]. Furthermore, this endothermic reaction is one of the candidates for chemical energy transmission systems [3–5]. The products of this reaction can be transported to another location where energy is required, and the exothermic reversed reaction is carried out and the energy is released again:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^0_{298} = 274\,\mathrm{kJ/mol}. \quad (1)$$

Previously, various metals and the support components have been examined as catalysts for carbon dioxide reforming of methane [6–8]. A highly active and durable catalyst has been desired, because the catalyst often deactivates due to carbon deposition caused by the dehydrogenation of methane (reaction (2)) and the Boudouard reaction (reaction (3)):

$$CH_4 \rightarrow C + 2H_2 \quad (2)$$

$$2CO \rightarrow C + CO_2. \quad (3)$$

Among the various catalysts examined, a Rh-supported catalyst exhibited a high durability [9–11]. This is due to the suppression of carbon deposition on Rh, as reported by Ashcroft and Rostrup-Nielsen [9,10]. Many researchers have examined the support effect of various kinds of metal oxide on the catalysis of Rh. However, the structure sensitivity of Rh as well as the role of the support in the reaction has been under controversy up to now. For example, Maier noted that the rate of CH_4–CO_2 reaction per unit Rh surface area was constant over a wide dispersion range of Rh [12]. In contrast, Tsipouriari claimed that the reaction was highly structure sensitive, where the TOF of the reaction has profoundly changed, depending on the kinds of support [13,14].

In this paper, in order to reveal the active Rh species and the effect of the support, various kinds of oxide were employed as supports, while fixing the Rh loading at 0.5 wt%. The low loading of Rh was necessary for the purpose of emphasizing metal–support interaction. The catalytic performance of Rh was correlated with the data from various characterization techniques, including specific surface area, Rh dispersion by CO adsorption and XAFS (X-ray absorption fine structure).

2. Experimental

2.1. *Catalyst preparation and catalytic test*

γ-Al_2O_3 (reference catalyst, Catalysis Society of Japan, JRC-ALO-4), CeO_2 (Nacalai tesque), ZrO_2 (Nacalai tesque), La_2O_3 (Nacalai tesque), MgO (Nacalai tesque), SiO_2 (Fuji silysia chemical), TiO_2 (Wako chemicals) and MCM-41 were used for supports of Rh. The MCM-41 was hydrothermally synthesized according to the method previously reported [15]. Rhodium chloride (Wako chemicals) was impregnated on these supports, followed by drying at 383 K. The loading of Rh was fixed at 0.5 wt%. Prior to the reaction, the catalysts were pretreated at 773 K for 2 h in H_2 flow.

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The catalytic reaction was carried out in a fixed-bed continuous-flow reactor at atmospheric pressure. A reaction mixture consisting of $CO_2/CH_4/Ar = 25:25:50$ was fed to the reactor with a flow rate of 100 ml/min. All gases were passed through a deoxidation column. The products were analyzed by online gas chromatography using a thermal conductivity detector. The catalytic activities were measured in the temperature range between 773 and 973 K.

2.2. *Rh-dispersion measurement*

The Rh dispersion of the reduced catalyst was measured by CO adsorption at room temperature. A 100 mg catalyst was reduced with H_2 at 773 K for 2 h, and CO (50 μL per pulse) was injected over the catalyst until no further adsorption of CO was detected. The CO desorbed from the surface was quantified with a mass spectrometer.

2.3. *XAFS measurement and analysis*

Rh K-edge XAFS was measured at the BL01B1 of the Japan Synchrotron Radiation Research Institute (SPring-8) in a transmission mode at room temperature. An Si(311) single crystal was used to obtain a monochromatic X-ray beam. Two ion chambers filled with Ar and Kr were used as detectors of I_0 and I, respectively. An *in situ* reactor was used for the treatment and XAFS measurement. After pretreatment of the catalyst in the fixed-bed flow reactor at 773 K for 2 h in H_2 flow, the CH_4–CO_2 reforming reaction was carried out. After the reaction, reaction gases were switched to Ar gas. Rh K-edge XAFS was measured after the sample was cooled down at room temperature. XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption fine structure) data were analyzed, using REX 2000 programs produced by RIGAKU. The curve-fitting analysis was carried out using Rh foil as the standard.

3. Results and discussion

3.1. *Catalytic activity*

The specific surface area and Rh dispersion measured by CO adsorption are listed in table 1. The Rh dispersion was relatively low on the support with the small surface area, and it became high by increasing the surface area. Figure 1 shows the TOF of CH_4 conversion calculated based on the exposed Rh measured by CO adsorption. The TOF for CH_4 conversion decreased in the following order of support, *i.e.*, $TiO_2 > La_2O_3 \fallingdotseq CeO_2 > ZrO_2 \fallingdotseq MgO \fallingdotseq SiO_2 \fallingdotseq$ MCM-41 $> \gamma$-Al_2O_3. Rh supported on TiO_2 and Al_2O_3 exhibited the highest and the lowest TOF value, respectively.

Table 1
Specific surface area, dispersion and TOF of 0.5 wt% Rh-supported catalysts.

Support	Specific surface area (m^2/g)	Dispersion (%) [a]	TOF for CH_4 conversion (s^{-1}) [b]
TiO_2	38.9	6.8	80.5
La_2O_3	3.5	14.4	28.1
CeO_2	1.4	15.4	26.1
ZrO_2	9.5	38.5	14.3
MgO	5.2	28.5	13.7
SiO_2	327	51.4	11.5
MCM-41	1185	67.6	9.58
γ-Al_2O_3	139	102	5.00

[a] Rh dispersion determined by CO adsorption.
[b] TOF measured at 973 K.

Figure 2 shows the relationship between Rh dispersion and TOF for CH_4 conversion measured at 973 K. The TOF decreased with increasing dispersion of Rh. Thus, a simple relation was observed between Rh dispersion and TOF for CH_4 conversion.

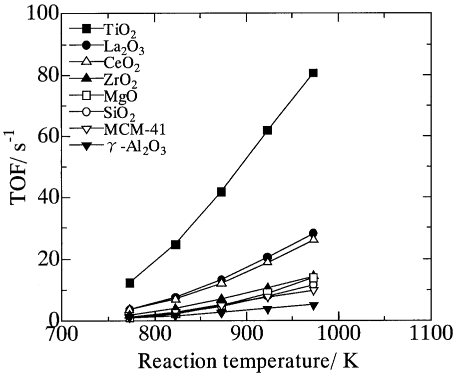

Figure 1. Dependence of TOF for CH_4 conversion of 0.5 wt% Rh-supported catalyst related to reaction temperature. Catalyst: 0.5 wt% Rh/support 0.05 g; Feed gas: $Ar/CO_2/CH_4 = 50/25/25$ ml/min, atmospheric pressure.

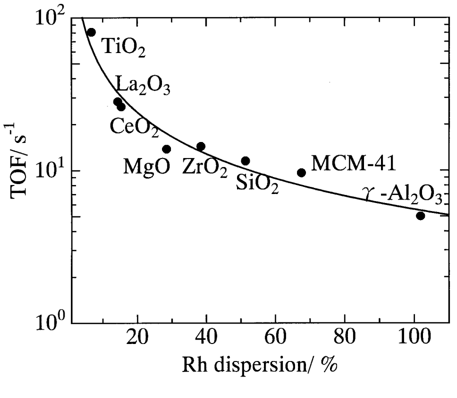

Figure 2. Dependence of TOF for Rh dispersion. Catalyst: 0.5 wt% Rh/support 0.05g; Feed gas: $Ar/CO_2/CH_4 = 50/25/25$ ml/min, atmospheric pressure; Reaction temperature: 973 K.

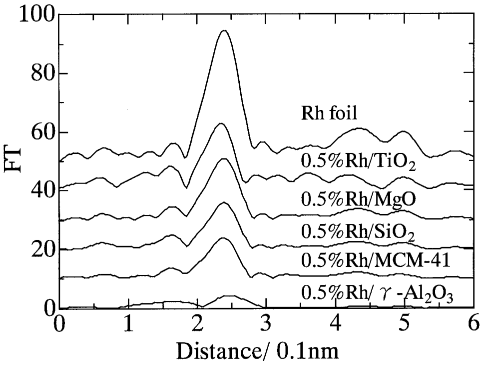

Figure 3. Rh K-edge EXAFS Fourier transforms for Rh-supported catalysts.

Table 2
Curve-fitting analysis of Rh K-edge EXAFS data for 0.5% Rh-supported catalysts measured after reaction at room temperature.

Support	CN[a]	r (nm)[b]	ΔE_0 (eV)[c]	σ (nm)[d]
TiO_2	10.0	0.266	−4.51	0.0081
MCM-41	6.5	0.266	−2.55	0.0082
MgO	8.6	0.268	−1.52	0.0077
SiO_2	6.7	0.268	−2.43	0.0078
γ-Al_2O_3	4.3	0.269	1.96	0.0110

[a] Coordination number.
[b] Bond distance.
[c] Difference in the origin of photoelectron energy between the reference and the sample.
[d] Debye–Waller factor.

3.2. XAFS studies

Figure 3 shows Fourier transforms of EXAFS spectra measured after the CH_4–CO_2 reforming reaction over various kinds of catalyst. The spectrum for Rh foil was attached for a comparison. XAFS on the measured samples showed a major feature at 0.24 nm (phase shift uncorrected), which was straightforwardly ascribed to the nearest neighbor Rh–Rh bond in Rh metal. The peak intensity of the Rh–Rh depended on the support. This fact suggested that the loaded Rh was coordinated to the neighbor Rh to different extents. The coordination number was calculated from the signal intensity and is shown in table 2. This value could be compared with 12 of the coordination numbers of the reference Rh metals, from which the size of Rh loaded on the support was estimated. The peak intensity of the nearest neighbor Rh–Rh bond on the Rh/γ-Al_2O_3 was smaller than that on Rh on TiO_2, MgO, SiO_2 and MCM-41. This fact suggested that the dispersion of Rh was high on γ-Al_2O_3 compared with Rh over other supports, which was confirmed from the data of the curve-fitting analysis (table 2). The relationship between Rh–Rh coordination number and Rh dispersion is plotted in figure 4. A linear relationship was obtained between these parameters. The reliability of the measurement of Rh dispersion was thus confirmed.

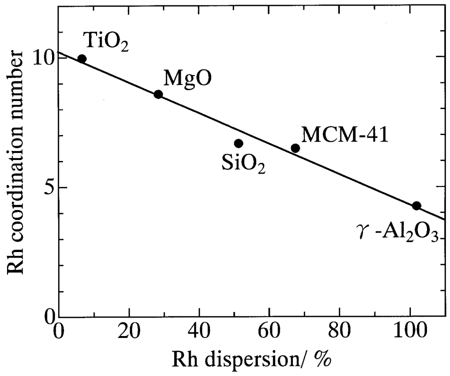

Figure 4. Dependence of Rh coordination number for Rh dispersion.

Figure 5 shows Rh K-edge XANES spectra measured after reaction at 773 K. The spectra of Rh foil and Rh_2O_3 were attached in the figure. As can be seen in the figure,

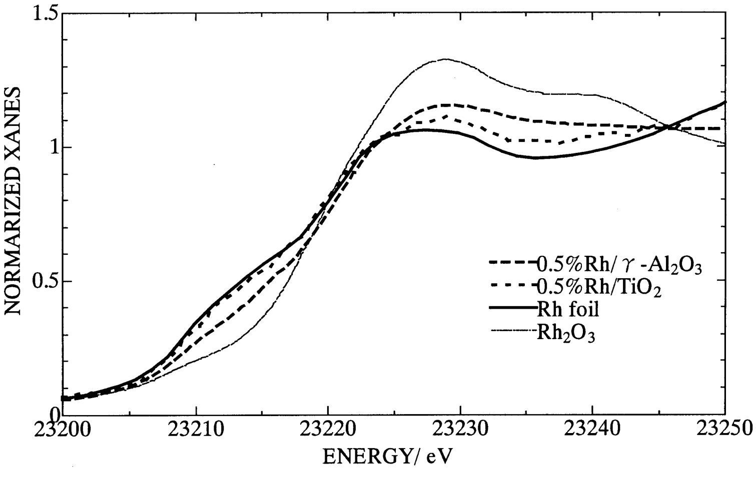

Figure 5. Rh K-edge XANES spectra for Rh-supported catalysts.

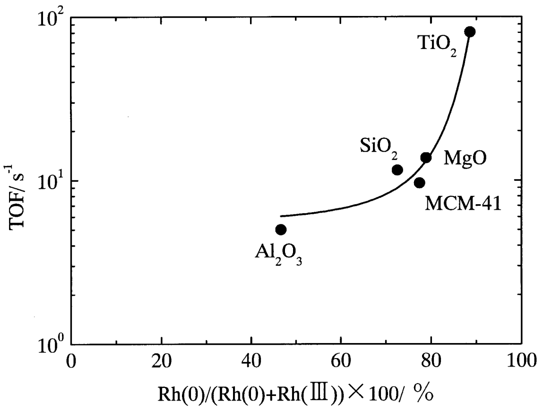

Figure 6. Dependence of TOF on the Rh(0)/(Rh(0) + Rh(III)) ratio determined by pattern fitting of XANES spectra. Catalyst: 0.5 wt% Rh/support 0.05 g; Feed gas: $Ar/CO_2/CH_4 = 50/25/25$ ml/min, atmospheric pressure; Reaction temperature: 973 K.

the shape of the spectrum of Rh/TiO_2 was similar to that of Rh foil, implying that the Rh metal was kept on the TiO_2 surface during the reaction. On the other hand, the XANES spectrum of the Rh supported on γ-Al_2O_3 shifted to the higher energy, which was intermediate between Rh foil and Rh_2O_3. The data suggested that Rh on Al_2O_3 possessed a cationic character. This fact was consistent with the data of IR measurement of adsorbed CO, where the generation of dicarbonyl Rh species was observed upon the exposure of CO onto Rh/γ-Al_2O_3, especially at low Rh loadings [16].

Figure 6 shows the relationship between the Rh metal concentration and TOF for CH_4 conversion measured at 973 K. The Rh metal concentration was calculated by fitting the XANES spectra of Rh foil and Rh_2O_3 to that of catalysts. The TOF increased by increasing the Rh metal concentration. These facts suggested that Rh metal exhibited a higher activity than Rh with cationic character. It was revealed that the catalytic activity of Rh has changed through the electronic interaction between support and Rh.

4. Conclusions

It was found that the catalytic performance of Rh for CO_2–CH_4 reaction was significantly affected by the kinds of support. The TOF for methane conversion decreased in the following order: $TiO_2 > La_2O_3 \fallingdotseq CeO_2 > ZrO_2 \fallingdotseq MgO \fallingdotseq SiO_2 \fallingdotseq$ MCM-41 $> \gamma$-Al_2O_3. The highest TOF of Rh was observed on TiO_2, where the metal Rh was kept during reaction. On the other hand, Rh supported on an Al_2O_3 surface exhibited low TOF. The cationic Rh was generated on Al_2O_3 as proved by XANES characterization. It was concluded that the Rh was structure sensitive in the CO_2–CH_4 reaction. The structure sensitivity was caused by the electronic interaction between Rh and support surface.

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