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Effects of rhodium dispersion on catalytic behavior of Rh/active-carbon catalysts for H/D exchange reaction between CH_4 and D_2

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The H/D exchange reaction between CH_4 and D_2 was carried out over Rh/active-carbon catalysts, which were prepared from RhCl₃ and Rh(NO₃)₃. In the case of the catalysts prepared from RhCl₃, Rh species were homogeneously dispersed on the support from external surface to the inside of pores. Metallic particles of Rh were found to be the predominant species on the catalysts prepared from Rh(NO₃)₃ in the low Rh-loading region of <2 wt.%, whereas the number of highly dispersed Rh species remarkably increased with an increase in the amount of Rh-loading in the region of >2 wt.%. The reaction rate per unit gram of catalyst and the product distribution in methane reflected well the Rh-dispersion on the catalysts. The catalysts which contained the highly dispersed Rh species as predominant species were found to be more active for the H/D exchange reaction than the catalysts with relatively large metal particles of Rh. On the former, the ratio of CH_3D/CD_4 was observed to be much higher than that on the latter.

Introduction

For the evaluation of noble metal dispersion on the support, the chemisorption of carbon monoxide (CO) has frequently been used, where adsorption of one CO molecule on each surface metal atom was assumed. Although such 1: 1 stoichiometry has been pointed out to be questionable in the case of a highly dispersed phase of noble metal, 1-3 the amount of CO adsorbed would strongly reflect the dispersion. We have already reported that Rh supported on active-carbon prepared from rhodium trichloride (denoted by Rh(C)/AC) adsorbed a very large amount of CO compared with that from rhodium trinitrate (denoted by Rh(N)/AC).⁴⁻⁶ The transmission electron microscope (TEM) measurements showed that the dispersion of Rh species on Rh(C)/AC was very high compared with Rh(N)/AC.7 On the other hand, metallic Rh species were found to be the main species on Rh(N)/AC. Thus, the Rh compound used in the preparation of the Rh/AC catalyst strongly affected the dispersion of Rh. However, the effects of the amount of Rh-loading on the dispersion with respect to the two kinds of Rh compounds, $RhCl_3$ and $Rh(NO_3)_3$, have not been clarified.

Kemball and co-workers have studied extensively the H/D exchange reaction between methane (CH₄) and D₂ over various kinds of single-component metal catalysts and bimetallic alloy catalysts.⁸ In the literature, CD₄ was found to be the main product at the early stage of the reaction on Rhfoil. On the other hand, CH₃D was the main product on Rh/SiO₂ catalysts.^{9,10} In the case of highly dispersed supported noble metal catalysts, *e.g.*, Pt/Al₂O₃, CH₃D was found to be the predominant product at the early stage of the reaction.³ Multiple and stepwise exchange processes were proposed to be the reaction routes for CD₄ and CH₃D formation, respectively.⁸ Thus, the catalytic behavior in the exchange reaction between CH₄ and D₂ may reflect the difference in the Rh dispersion on the Rh/AC catalysts.

In the present work we have studied the dispersion of Rh on active-carbon support by means of CO chemisorption and

X-ray photoelectron spectroscopy (XPS). In addition, the H/D exchange reaction between CH_4 and D_2 was studied on the two kinds of catalyst, Rh(C)/AC and Rh(N)/AC.

Experimental

The active-carbon support (obtained from Wako Pure Chemical Ind., Ltd, specific surface area = 930 m² g⁻¹, average pore diameter (d_{av}) = 4 nm) was immersed in 0.1 mol dm⁻³ of hydrochloric acid solution and then thoroughly washed with de-ionized water. Rh/AC catalysts with Rh loading from 1.0 wt.% (97 × 10⁻⁶ mol g(cat)⁻¹) to 4.0 wt.% (389 × 10⁻⁶ mol g(cat)⁻¹) were prepared by a conventional impregnation method, where rhodium trichloride trihydrate (RhCl₃ · 3H₂O) or rhodium trinitrate (Rh(NO₃)₃) was deposited on the support from the appropriate aqueous solution. The solid was dried at 383 K for 12 h in an oven.

The samples for the CO chemisorption measurements were prepared as follows. The solid pretreated with H₂ at 573 K for 3 h in a conventional flow system was transferred into a glass cell, and it was re-treated with H₂ at 573 K for 1 h before the chemisorption measurement. The amounts of CO adsorbed on the catalysts were measured at 296 K by a conventional static method using a glass-made apparatus connected to a vacuum line. The first CO adsorption run was followed by the second run after the evacuation of the sample for 10 min at room temperature. The sum of physical and chemical adsorption was estimated by extrapolating the flat part of the first adsorption isotherm to the zero of the equilibrium pressure for adsorption. The amount of physically adsorbed CO was estimated from the second isotherm in the same way for the estimation of the total adsorption. The amount of chemically adsorbed CO (denoted by $q_{\rm CO}$) was estimated by subtracting the physical adsorption from the total adsorption. The value for $q_{\rm CO}$ on the active carbon support itself ($<1 \times 10^{-6}$ mol $g(cat)^{-1}$) was found to be much less than those on the Rh/AC catalysts.

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The H/D exchange reaction between CH_4 and D_2 was carried out using a glass-made apparatus with a re-circulation system (350 cm³) connected to a vacuum line. The catalyst (0.100 g, pretreated with H_2 at 573 K for 3 h in the flow system) placed in the reactor was treated with H_2 at 573 K for 1 h, and cooled to the temperature at which the reaction was performed. Introduction of 0.50×10^{-3} mol each of CH_4 , D_2 and Ar (as diluent) into the system was followed by the reaction. A small portion of the reaction gas mixture was periodically taken out from the reaction system to analyze the D-distribution in methane by mass spectrometry, using a ULVAC-STANDOM-200R spectrometer.

XPS measurements were carried out using a Rigaku XPS-7000 spectrometer employing Al K α X-radiation; adhesive tape on the sample holder was used to support a Rh/AC sample in a fine powder form. Binding energy values are referenced to the peak at 285.0 eV for C 1s. To evaluate the Rh concentration by XPS, the peak intensities for C 1s were normalized to be 100 000 counts per second (cps).

Results and discussion

Results on the CO adsorption measurements are shown in Figs. 1 and 2 for Rh(C)/AC and Rh(N)/AC, respectively. In the case of Rh(C)/AC, the amount of CO chemisorbed per unit gram of catalyst (q_{CO}) almost linearly increased with an increase in Rh-loading, as shown by open circles in Fig. 1. The value for (q_{CO})/(Rh-loaded) obtained was around 1.3, indicating that the Rh dispersion on Rh(C)/AC was very high. In fact, no formation of metallic particles of Rh was observed on Rh(C)/AC even after the H₂ pretreatment by X-ray diffraction



Fig. 1 Effects of Rh-loading on the CO adsorption on Rh(C)/AC (\bigcirc , reduced; \bigcirc , treated with CO after reduction with H₂).



Fig. 2 Effects of Rh-loading on the CO adsorption on Rh(N)/AC (\triangle , reduced; \blacktriangle , treated with CO after reduction with H₂).

(XRD) and TEM measurement.⁷ In the case of Rh(N)/AC, q_{CO} on the samples with 1 and 2 wt.% Rh was found to be much less than those on the corresponding samples of Rh(C)/AC. On the Rh(N)/AC samples, the formation of metallic particles of Rh was observed. However, q_{CO} increased significantly in a region of high Rh-loading, as shown by open triangles in Fig. 2, indicating that the amount of highly dispersed Rh species increased in this region on Rh(N)/AC samples.

The effects of Rh-loading on the XPS intensity (peak area for Rh) are shown in Fig. 3. Although all samples were pretreated with H₂, they were exposed to air during the transfer of them from the sample tube to the sample holder. Therefore, we focussed solely on the concentration of Rh by XPS, but not on the oxidation number of Rh on the samples. In the case of Rh(C)/AC samples, the intensity was increased with an increase in the amount of Rh-loaded. In the case of Rh(N)/AC, however, the increase in the peak intensity was very small in the region from 1 to 4 wt.% Rh. The concentration of Rh by XPS on the Rh(C)/AC(1 wt.%) was observed to be much lower than that on the Rh(N)/AC(1 wt.%), indicating that the dispersion of Rh species on the former was very high throughout the whole active-carbon support, *i.e.*, from the external surface to the inside of the pores. On the other hand, Rh species on the Rh(N)/AC(1 wt.%) were mainly present at the external surface and/or in the pores near the entrance at low Rh contents. However, the amount of CO chemisorption remarkably increased with an increase in Rh-loading as shown in Fig. 2, suggesting an increase in the amount of a highly dispersed phase of Rh species in the pores at high Rhloading on Rh(N)/AC.

The H/D exchange reaction between CH_4 and D_2 was performed on the two kinds of Rh/AC catalyst. Typical time courses of the exchange reaction over Rh(C)/AC(2 wt.%) and Rh(N)/AC(2 wt.%) are shown in Figs. 4 and 5, respectively. The main product at the early stage of the reaction was found to be CH₃D, indicating that the stepwise exchange process was predominant on these catalysts. On Rh(N)/AC, however, the amount of CD_4 was more than the amounts of CH_2D_2 and CHD₃, which is similar to the results on Rh/SiO₂ reported by Kemball and co-workers,^{9,10} indicating the presence of the Rh sites for the multiple exchange process. It is noteworthy that the formation of CD_4 was much less than CH_2D_2 on Rh(C)/AC. Namely, the amount of relatively large metal particles, which contribute to the multiple exchange process to form CD₄, was extremely low on Rh(C)/AC. These results correspond well with the results of CO chemisorption and XPS. In the present work, the rates for the exchange reaction between CH_4 and D_2 per unit gram of catalyst (denoted by r) are estimated from the data for the products formed during the reaction time of 1 h using the equation $\sum i CH_{4-i}D_i$.



Fig. 3 Effects of Rh-loading on the XPS intensity of Rh(C)/AC (O) and Rh(N)/AC (Δ).



Fig. 4 Exchange reaction between CH_4 and D_2 over Rh(C)/AC(2.0 wt.%) at 413 K (\bigcirc , CH_4 ; \bullet , CH_3D ; \blacktriangle , CH_2D_2 ; \lor , CHD_3 ; \blacksquare , CD_4).



Fig. 5 Exchange reaction between CH_4 and D_2 over Rh(N)/AC(2.0 wt.%) at 453 K (\bigcirc , CH_4 ; \bigcirc , CH_3D ; \bigstar , CH_2D_2 ; \blacktriangledown , CHD_3 ; \blacksquare , CD_4).



Fig. 6 Effects of reaction temperature on the rate of exchange reaction between CH_4 and D_2 (\bigcirc , Rh(C)/AC; \triangle , Rh(N)/AC).

The effects of reaction temperature on r over the Rh/AC(2)wt.%) catalysts are shown in Fig. 6. The rate at 433 K on Rh(C)/AC ($r = 9.8 \times 10^{-6}$ mol min⁻¹ g(cat)⁻¹) was observed to be very high compared with that on Rh(N)/AC(2 wt.%) $(r = 1.8 \times 10^{-6} \text{ mol min}^{-1} \text{ g(cat}^{-1}))$. The value of the apparent activation energy (denoted by E) calculated on Rh(N)/AC is 90 kJ mol⁻¹. This value is close to that on Rh/SiO_2 , already reported to be 103 kJ mol^{-1,10} On the other hand, the value for E on Rh(C)/AC (51 kJ mol⁻¹) was observed to be much lower than that on Rh(N)/AC. Partial pressure dependencies of r on CH_4 and D_2 were observed to be ca. 0.6 and -0.3, respectively, on Rh(C)/AC as shown in Table 1. On Rh(N)/AC, the D₂ partial pressure dependency at 453 K was obtained as -0.4. This value is slightly negative compared with that on Rh(C)/AC at 413 K, indicating the stronger adsorption of D_2 on Rh(N)/AC. These results indicate that the nature of the active sites on Rh(C)/AC is different from those on Rh(N)/AC. Although we have not determined the number of highly dispersed Rh species as well as the number of the surface Rh atoms on the metal particles, turnover frequency (TOF) values at 433 K may roughly be estimated as follows. When the value for %-exposed of Rh was assumed to be 100%, the TOF was calculated to be $5.1 \times 10^{-2} \text{ min}^{-1}$ for the highly dispersed Rh species. In the case of Rh(N)/AC(2 wt.%), the value for %-exposed of Rh was estimated to be 20% on the assumption that each surface Rh atom could adsorb one molecule of CO. By using the value for %-exposed, the TOF at the Rh site on metallic particles was estimated to be 4.6×10^{-2} min⁻¹. Thus, the difference in TOF values between the two types of active site is not large, indicating that the difference in the activity (r) at the reaction temperatures around 433 K mainly corresponded to the difference in the number of active sites.

As previously described, the amount of CO adsorbed on Rh(C)/AC was observed to be very large. However, the catalyst once treated with CO at temperatures >433 K did not show a high ability for the CO adsorption.^{5,7} On Rh/Al₂O₃ and Rh/SiO₂ catalysts, agglomeration of dispersed Rh species into metal particles took place when the sample was exposed to CO.¹¹⁻¹⁵ We also showed by means of TEM that the transformation of dispersed Rh species into metallic particles of Rh was induced by the treatment of the samples with CO at 473 K.7 As can be seen from Fig. 1, the amount of CO chemisorbed on the Rh(C)/AC with the CO treatment was observed to be much lower than that on the corresponding sample without the CO treatment. The effects of the CO treatment on r are shown in Fig. 7. It is noteworthy that the treatment of Rh(C)/AC with CO at 473 K remarkably reduced r. In addition, the apparent activation energy on Rh(C)/AC with the CO treatment (68 kJ mol⁻¹) was higher than that on the catalyst without the CO treatment (51 kJ mol⁻¹). As shown in Fig. 8, the amount of CD_4 was observed to be more than the amounts of CH₂D₂ and CHD₃ on the former catalyst. These results clearly showed that some portions of the dispersed Rh species were converted into the relatively large metallic particles of Rh through the CO treatment.

The effects of Rh loading on r are shown in Fig. 9. The rate on Rh(C)/AC was almost proportional to the amount of Rh-loading. The rate on Rh(N)/AC with 2.0 wt.% Rh was much low compared with that on Rh(C)/AC with the same Rh-loading. The rate on Rh(N)/AC, however, remarkably

Table 1 Comparison of kinetic behavior of Rh/AC catalysts for the exchange reactions between CH_4 and D_2

		Partial pressure dependency		
Catalyst	Reaction temp./K	$\overline{\mathrm{CH}_4}$	D_2	$E/kJ mol^{-1}$
Rh(C)/AC(2.0 wt.%) Rh(N)/AC(2.0 wt.%)	413 453	0.6 0.6	-0.3 -0.4	51 90



Fig. 7 Effects of the CO treatment of Rh(C)/AC on the rate for the exchange reaction between CH_4 and D_2 (\bigcirc , Rh(C)/AC reduced; \bigcirc , Rh(C)/AC treated with CO at 473 K).

increased with an increase in the amount of Rh-loading as shown in Fig. 9. As shown in Fig. 10, the apparent activation energy on Rh(N)/AC with 4.0 wt.% Rh was calculated to be 70 kJ mol⁻¹. This value is much lower than the value of E on



Fig. 8 Product distribution in methane formed during the exchange reaction on Rh(C)/AC (reaction temperature = 413 K, CH₄ conversion 10.1%) and on Rh(C)/AC treated with CO at 473 K (433 K, 7.1%).



Fig. 9 Effects of Rh-loading on the rate for exchange reaction between CH₄ and D₂ at 433 K (\bigcirc , on Rh(C)/AC; \triangle , on Rh(N)/AC).



Fig. 10 Comparison of catalytic behavior of Rh(N)/AC(2.0 wt.%) (Δ) with Rh(N)/AC(4.0 wt.%) (\blacktriangle) for the exchange reaction between CH₄ and D_2

Rh(N) with 2.0 wt.% Rh (90 kJ mol⁻¹), suggesting the presence of highly dispersed Rh species. The CO chemisorption and XPS results on Rh(N)/AC indicate the presence of highly dispersed Rh species in the pore of active-carbon support at the high Rh-loading (see Fig. 2). In addition, the decrease in the amount of CO chemisorbed was induced by the treatment of Rh(N)/AC(4 wt.%) with CO as shown in Fig. 2, which was due to the conversion of the dispersed Rh species into metal particles. The product distribution of methane on Rh(N)/AC(4 wt.%) is compared with that on Rh(N)/AC(2 wt.%) in Fig. 11. The content of CD_4 for the former was found to be less than that for the latter, indicating the higher ratio of highly dispersed Rh species against relatively large particles of Rh. Thus, the remarkable increase in the activity (r) for H/Dexchange reaction between CH_4 and D_2 on Rh(N)/AC corresponded well to the formation of the highly dispersed Rh species in the pores.

In conclusion, the dispersion profile of Rh species on Rh(C)/AC with respect to the change in Rh-loading was found to be very different from that on Rh(N)/AC by means of CO adsorption and XPS techniques. On the former, Rh species are mainly present in a highly dispersed form throughout the



Fig. 11 Product distribution in methane formed during the exchange reaction on Rh(N)/AC(2.0 wt.%) (reaction temperature = 443 K, CH_4 conversion = 10.1% and on Rh(N)/AC(4.0 wt.%) (443 K, 23.1%).

pores of active-carbon support. On the latter, however, the predominant Rh species were found to be relatively large metal particles of Rh in the region of low Rh-loading, whereas the amount of Rh species in a highly dispersed form increased with an increase in Rh-loading. The catalytic behavior in the exchange reaction between CH₄ and D₂ reflected well the difference in Rh-dispersion on the catalyst. The catalyst containing the higher concentration of the dispersed phase showed the higher apparent activation energy and the higher value for the ratio of CH_3D/CD_4 formed.

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