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Effects of Ru addition to Pd/Al₂O₃ catalysts on methanol steam reforming reaction: A mechanistic study



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step of the MSR reaction.

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ARTICLE INFO	A B S T R A C T				
<i>Keywords:</i> Carbon monoxide Oxidation Room temperature Metallic Pd Valence state Particle size	In this study, Pd/Al ₂ O ₃ and Pd-Ru/Al ₂ O ₃ catalysts were used to investigate the mechanism of the methanol steam reforming (MSR) reaction and the factors affecting the reaction activity. First, the MSR reaction activity was evaluated using Pd/Al ₂ O ₃ and Pd-Ru/Al ₂ O ₃ catalysts. The MSR reaction activities increased with the addition of Ru. In addition, FT-IR analysis was performed to investigate the MSR reaction mechanism. The reactions with the Pd/Al ₂ O ₃ and Pd-Ru/Al ₂ O ₃ catalysts proceeded through the same mechanism. After methanol was adsorbed on the catalyst surface as methoxy and formate species, it was converted into CO through decomposition and reaction with water, and then desorbed from the catalyst surface. TEM analysis revealed that the addition of Ru to the Pd/Al ₂ O ₃ catalyst resulted in small particle sizes with highly dispersed Pd on the catalyst surface, which increased the conversion to CO. Lastly, analysis of adsorption characteristics showed that the addition of Ru enhanced the desorption rate of adsorbed CO species to promote the MSR reaction activity by weakening the adsorption intensity of CO. The desorption of CO adsorption species was the rate-determining				

1. Introduction

Currently, there is an urgent need to find eco-friendly energy resources to address the environmental pollution problems caused by the use of fossil fuels. As an ideal fuel, there is increasing interest in obtaining energy from hydrogen because water is the only waste product. However, owing to the intrinsic properties of hydrogen, it is not an ideal energy medium. According to adsorption and decomposition studies on catalyst surfaces, methanol can be considered a hydrogen carrier, as it has a high content of hydrogen and can be easily decomposed without breaking C–C bonds [1–3]. Methanol has also attracted attention as one of the most promising energy carriers owing to its high power density and eco-friendly properties [4,5]. Hydrogen can be produced directly from methanol via the following reactions: methanolysis (CH₃OH \rightarrow CO + 2H₂) and methanol steam reforming (MSR) $(CH_3OH + H_2O \rightarrow CO_2 + 3H_2)$. As methanol is one of the most common synthetic chemicals and can provide chemical information about more complex carbon compounds, understanding the reaction mechanisms and properties of methanol on the surface of catalysts has attracted considerable attention.

The methanolysis and MSR reactions are effective methods for

hydrogen production. In general, Cu-based catalysts are used to produce hydrogen from methanol because of their excellent activity and selectivity [6-9]. However, there are several problems associated with Cu-based catalysts, such as requiring a pretreatment process in the hydrogen atmosphere for several hours and coagulation at temperatures above 300 °C owing to low thermal stability [10-12]. For this reason, Pd-based catalysts have recently been investigated to replace Cu-based catalysts for the production of hydrogen from methanol [10,13-15]. Previous studies have examined the mechanisms of methanol degradation on metal surfaces and transition metal catalysts [16,17]. The MSR reaction mechanism of Pd-based catalysts was first proposed by Iwasa et al. [16], who reported that the intermediate species formed on the catalyst surface varies depending on the metallic Pd and Pd allovs present, with the reactions proceeding via different reaction pathways. In addition, Easwar et al. [17] reported that the methanol conversion rate was proportional to the H₂ chemisorption amount and that the rate-determining step (RDS) was dependent on Pd when Pd/CeO2 and Pd/ZnO catalysts were compared. In addition, the selectivity for CO₂ depended on the reaction pathway, and the reaction pathway was determined by the intermediate species adsorbed on the catalyst surface. However, there are few studies on step experiments to

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clearly determine the RDS of methanol conversion and the adsorption characteristics. In addition, various density functional theory studies on methanol decomposition mechanisms have recently been reported [18,19]. Jiang et al. [19] reported that the CH₃OH - CH₂OH - CHOH - CHO - CO pathway was the most likely dehydrogenation pathway, where the high energy barrier of CH₃OH dissociation was the RDS of the total dehydrogenation reaction. However, desorption from the catalyst surface is an important factor in the catalytic reaction and may affect the overall reaction rate.

Thus, the purpose of this study was to identify the factors affecting the RDS of the catalytic reaction mechanism and to examine the effects of Ru addition on the MSR reaction characteristics by investigating the MSR reaction mechanism on a Pd/Al_2O_3 catalyst. To achieve this, we evaluated the MSR reaction characteristics, used FT-IR analysis to understand the reaction mechanisms, and applied adsorption analysis to propose factors affecting the RDS. The results of this study revealed key factors for the MSR and methanol decomposition reactions.

2. Experimental

2.1. Catalyst preparation

The Pd/Al₂O₃, Ru/Al₂O₃ and Pd-Ru/Al₂O₃ catalysts used in this study were prepared by the wet-impregnation method. First, using Pd (OH)₂ (Aldrich Co.) as a precursor, 1 wt% Pd (based on the weight of Al₂O₃) was dissolved in distilled water. Second, Al₂O₃ was slowly added to the Pd solution and then stirred for 1 h. The mixed solution was then evaporated using a rotary vacuum evaporator. Thereafter, the solid was dried in an oven at 103 °C for 24 h. Finally, the dried sample was calcined at 400 °C for 4 h and then reduced in 30% H₂/N₂ at 600 °C for 1 h to prepare the Pd/Al₂O₃ catalyst.

To prepare the $Pd-Ru/Al_2O_3$ catalyst, 0.9 wt% Pd and 0.1 wt% Ru (based on the weight of Al_2O_3) were dissolved in distilled water. RuNO (NO₃)₃ (Alfa Aesar Co.) was used as the Ru precursor and the subsequent process was the same as that used for the Pd/Al₂O₃ catalyst.

2.2. Catalytic activity measurement

The MSR activity tests were conducted at a steam to methanol (S/C) ratio of 2.5 and a space velocity of $10,000 \text{ h}^{-1}$ in a fixed bed reactor. The feed gas steam mixture consisted of CH₃OH, H₂O, and N₂ with a CH₃OH:H₂O:N₂ ratio of 1:2.5:4 (vol%). In addition, we injected 13.5 vol. % CH3OH in total gas. The experimental apparatus consisted of a catalytic reactor, a digital bubble flow meter, and mass flow controllers. The MSR reactor apparatus comprised a quartz tube (inner diameter: 8 mm; height: 650 mm) and a catalytic bed filled with quartz wool. The reactor was supplied with a CH₃OH/steam mixture (1:2.5, vol%) and a carrier gas, and their flow rates were controlled using a micro liquid pump (JASCO, MINICHEMI PUMP). The inlet gas supply pipe was made of stainless steel (size: 1/4') and covered with a heating band at 180 $^{\circ}$ C for preheating N₂ gas. The methanol/stem mixture supply pipe was made of stainless steel (size: 1/16') and covered with a quartz tube wound with a nichrome wire at 300 °C for vapor production. The product gases were analyzed using a gas chromatograph (6890 N Agilent Co.) equipped with 6 Å molecular sieve and Porapak-O columns and thermal conductivity detectors (TCDs).

2.3. Catalyst characterization

The specific surface areas and pore sizes of the catalysts were investigated using an ASAP 2010C analyzer (Micromeritics). The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) equation, and the average pore size was calculated using the Barrett-Joyner-Halenda (BJH) method. Each sample was analyzed in a vacuum state at 300 °C for 2 h after the gas was removed.

Field-emission transmission electron microscopy (FE-TEM) images

were recorded on a JEM-2100 F microscope (JEOL Co.) operating at 200 kV. Samples for the FE-TEM measurements were prepared by suspending ultrasonically treated catalyst powder in ethanol and placing a drop of the suspension on the Cu grid.

X-ray diffraction (XRD) analysis was performed using an X'Pert PRO MRD diffractometer (PANalytical Co.) with a Cu Ka ($\lambda = 1.5056$ Å) radiation source and the X-ray generator operating at 30 kW. XRD patterns were measured at a scanning speed of 6°/min in the 20 range of 10–90°.

The catalysts were confirmed in terms of their dispersion by CO chemisorption at 25 °C. The catalyst sample, which was activated in a 10% H_2/N_2 gas flow at 250 °C for 30 min, was cooled to 25 °C and saturated with pulses of 10% CO/N₂ gas.

The temperature-programmed reaction analyses were performed using an Autochem 2920 analyzer (Micromeritics). The temperature-programmed reduction (TPR) of H₂ was analyzed using 10% H₂/N₂ and 0.3 g of catalyst at a total flow rate of 50 cc/min. All catalysts were pretreated by injecting 5% O₂/He 50 cc/min at 300 °C and then cooling to 60 °C. After, The catalysts were then treated with 10% H₂/N₂ at 60 °C for 0.5 h. The catalyst was placed in dilute H₂, and the consumption of H₂ was monitored using a TCD in the Autochem 2920 while increasing the temperature to 800 °C at a rate of 10 °C/min.

The temperature-programmed desorption (TPD) of CO and CH₃OH was performed with 0.3 g of catalyst at total flow of 50 cc/min. All catalysts were pretreated before the TPD analysis. The catalysts were then treated with 1% CO/Ar or 1500 ppm CH₃OH/N₂ at 60 °C for 0.5 h. The absorbed CO or CH₃OH was purged with Ar for 1 h before starting the TPD analysis. During the TPD analysis, the quantities of CO (m/e = 28), CO₂ (m/e = 44), CH₄ (m/e = 16), and H₂ (m/e = 2) were continuously monitored using a quadrupole mass spectrometer (QMS 422) while the temperature was increased to 800 °C at a rate of 10 °C/min.

The temperature-programmed surface reaction (TPSR) analysis was performed with 0.3 g of catalyst using a fixed bed reactor and the QMS. Before the TPSR analysis, all the catalysts were pretreated in Ar at 300 °C for 0.5 h and then cooled to 100 °C. During injection of CH₃OH, H₂O, and N₂ at a ratio of 1:2.5:4 (vol%), the temperature was increased up to 500 °C at a rate of 10 °C/min. The generated gases were monitored using the QMS.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) analysis was performed using a Nicolet iS10 spectrometer (Thermo Fisher) equipped with a Diffuse Reflectance (DR) 400 accessory for solid reflectance analysis. A CaF_2 window was used as a plate for the DR measurements and the spectra were collected using a mercury cadmium telluride detector. The sample was preprocessed with Ar at a flow rate of 50 cc/min at 300 °C for 1 h. To collect the spectra of the catalysts, a single-beam spectrum of the preprocessed sample was measured as a background, and all analyses were performed via auto scanning at a resolution of 8 cm⁻¹.

3. Results and discussion

3.1. Catalytic activity

In this study, we investigated changes in catalyst characteristics when Ru was added to a Pd/Al₂O₃ catalyst and examined the effects of the characteristics on the MSR reaction. Accordingly, we investigated the MSR reaction activities of Pd/Al₂O₃, Ru/Al₂O₃, and Pd-Ru/Al₂O₃ catalysts at a space velocity of 10,000 h⁻¹ and an S/C of 2.5, and the results are shown in Fig. 1 (a)–(d). As shown in Fig. 1 (a), the methanol conversion rate of the catalysts decreased in the following order: Pd-Ru/Al₂O₃ > Pd/Al₂O₃ > Ru/Al₂O₃. In particular, the methanol conversion rate of Ru/Al₂O₃ at 400 °C was 65%, and this catalyst showed very low reaction activity. Thus, the MSR reaction characteristics of Ru itself were low. In contrast, as the Pd/Al₂O₃ catalyst showed an excellent methanol conversion rate of 90% or more at 325 °C or



Fig. 1. Methanol steam reforming performance of Pd/Al₂O₃, Ru/Al₂O₃, and Pd-Ru/Al₂O₃ catalysts: (a) methanol conversion of catalysts, outlet gas concentration (b) Pd/Al₂O₃, (c) Ru/Al₂O₃, and (d) Pd-Ru/Al₂O₃.

highermethanol. In addition, the Pd-Ru/Al₂O₃ catalyst, in which Ru was added to the Pd/Al₂O₃ catalyst, exhibited a higher conversion rate than the Pd/Al₂O₃ catalyst in all temperature ranges. As the Pd-Ru/Al₂O₃ catalyst showed a 5% higher methanol conversion rate than the Pd/Al₂O₃ catalyst at temperatures of 325 °C or lower, the reaction activity was increased by the addition of Ru. In other words, as the MSR reaction activity of the Ru/Al₂O₃ catalyst was very low, the Ru added to the Pd/Al₂O₃ catalyst acted as a promoter rather than an active site. Thus, the properties of the Pd active site and the reaction characteristics were changed to promote the MSR reaction rate.

Fig. 1(b)–(d) shows the concentrations of the gases produced by the MSR reaction with the Pd/Al₂O₃, Ru/Al₂O₃, and Pd-Ru/Al₂O₃ catalysts. H₂ and CO were produced as products with all catalysts, and trace amounts of CH₄ were detected at a temperature of 400 °C. As only CO and H₂ were produced, these results indicate that the decomposition reaction proceeded according to Eq. (1). In addition, the production of CO2 was not observed with the Pd/Al2O3 and Pd-Ru/Al2O3 catalysts despite the injection of water, suggesting that the water gas shift reaction (Eq. (2)) did not proceed. Finally, in comparison with the behavior at 350 °C, the concentration of H₂ and CO decreased simultaneously with the production of trace amounts of CH4 at 400 °C. Meunier et al. [19] reported that methanation occurred during the semi-hydrogenation reaction of acetylene on the Pd-Zn/CeO2 catalyst. In this study, the observed production of CH4 together with the decreased production of CO and H₂ suggested that the methanation reaction (Eq. (3)) occurred, in which produced CO was converted into CH_4 through

reaction with H₂.

$$CH_3OH \to CO + 2H_2 \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{3}$$

3.2. Characterization of Pd/Al2O3 and Pd-Ru/Al2O3 catalysts

FE-TEM images of the Pd/Al₂O₃ and Pd-Ru/Al₂O₃ catalysts are shown in Fig. 2. The addition of Ru to the Pd/Al₂O₃ catalyst affected the particle size. In the case of the Pd/Al₂O₃ catalyst, the average particle size of the active particles was 5.5 nm. In contrast, the average particle size of the active particles in the Pd-Ru/Al₂O₃ catalyst was 3.1 nm. The active particle size of the catalyst with added Ru was smaller than that of the Pd/Al₂O₃ catalyst. Huang et al. [20] compared two catalysts by depositing Pd and PdRu on a mesoporous silica support and found that the dispersion of Pd was increased by the formation of a Pd-Ru alloy when Ru was added to Pd. Ma et al. [21] compared the catalysts obtained by depositing Pd and PdRu on a carbon support. The active particle diameter of Pd (3.4 nm) decreased to 2.8 nm when Ru was added. In general, Pd is known to aggregate easily with heat treatment. El Hawa et al. [22] reported that the formation of a Pd-Ru alloy could improve the thermal stability of Pd. In this study, a Pd-Ru alloy was formed when Ru was added and the thermal stability was increased to suppress the aggregation of Pd and decrease the particle size of Pd.



Fig. 2. TEM images of (a) $1\% Pd/Al_2O_3$ and (b) $0.9\% Pd\text{-}0.1\% Ru/Al_2O_3$ catalysts.

Table 1 shows the average particle sizes determined from the TEM images and the basic physical properties of the catalysts. The surface areas of the Pd/Al₂O₃ and Pd-Ru/Al₂O₃ catalysts calculated by BET analysis were 139 and $132 \text{ m}^2/\text{g}$, respectively. Thus, the surface areas of these catalysts were similar, and there was no significant variation in the pore sizes and pore volumes.

Fig. 3 shows XRD patterns of the Pd/Al₂O₃, Pd-Ru/Al₂O₃, and Al₂O₃ catalysts. For all three samples, strong peaks were observed at 20°, 32°, 38°, 46°, and 66.8°, which correspond to r-Al₂O₃, the support. In contrast, for the Pd/Al₂O₃ and Pd-Ru/Al₂O₃ catalysts, peaks were also

observed at 40°, 47°, and 68°, corresponding to metallic Pd [23,24]. The intensities of the peaks attributed to metallic Pd were larger for the Pd/ Al_2O_3 catalyst than the Pd-Ru/ Al_2O_3 catalyst. These differences were caused by the formation of a Pd-Ru alloy when Ru was added to the Pd/ Al_2O_3 catalyst. These results were consistent with the results of the TEM analysis.

A H₂-TPR analysis was performed to evaluate the reducibility of the catalyst, and the results are shown in Fig. 4. In the case of the Pd/Al₂O₃ catalyst, a decrease peak occurred owing to desorption of H₂ adsorbed on the surface of the catalyst at temperatures of 50–100 °C. Further, H₂

Table 1

The physical properties of Po	/Al ₂ O ₃ and Pd-	•Ru/Al ₂ O ₃ cataly	ysts
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Catalyst	Chemical composition ^a		Active particle size (nm)		Metal dispersion (%) ^c	S_{BET} (m^2/g)	Total pore volume	Mean pore size
	Pd (%)	Ru (%)				(/ 8)	(cm / g)	()
1%Pd/Al ₂ O ₃ 0.9%Pd-0.1%Ru/Al ₂ O ₃	1.01 0.89	- 0.09	5.2 ^b 3.5 ^b	7.8 [°] 5.7 [°]	14.4 19.3	139 132	0.068 0.065	1.98 1.98

^a Determined by ICP-OES analysis; other values are nominal values.

^b Determined by TEM analysis.

^c Determined by CP chemisorption analysis.



Fig. 3. XRD patterns of $Al_2O_3,\,1\% Pd/Al_2O_3,$ and $0.9\% Pd-0.1\% Ru/Al_2O_3$ catalysts.



Fig. 4. Temperature-programed reduction of H_2 over 1%Pd/Al₂O₃ and 0.9%Pd-0.1%Ru/Al₂O₃ catalysts.

consumption peaks were observed at temperatures in the range of 100–200 °C and 400–600 °C. In contrast, in the case of the Pd-Ru/Al₂O₃ catalyst, decrease peaks, which were smaller than those observed for Pd/Al₂O₃, were observed in the temperature range of 50–100 °C and a H₂ consumption peak, which was larger than that observed for Pd/Al₂O₃, was observed in the temperature range of 100–200 °C. In addition, in the range of 350–600 °C, H₂ consumption peaks were observed at 450 and 500 °C, similar to those observed for Pd/Al₂O₃. The hydrogen consumption peak at 450 °C and 500 °C is the peak due to spill over from Pd and Pd-Ru to the support material. Zheng at al. [25] reported H₂ consumption peaks at high temperatures (> 300 °C) were observed for Pd/Al₂O₃ catalysts, and were either assigned to the

hydrogen consumption by a spillover from Pd to the support material. Also, they reported that high-temperature H_2 consumption is due to interactions between well-dispersed PdOx species. As a result of the preceding CO-Chemisorption and TEM analyzes when Ru is added, active metal is highly dispersed. For this reason, a larger amount of water consumption has occurred by spillover in the Pd-Ru catalyst.

According to the H₂-TPR analysis, the H₂ desorption peaks occurring at 50-100 °C occur owing to the desorption of H₂ adsorbed on Pd during the pretreatment process. Baylet et al. [26] observed the consumption and emission of H₂ during the H₂-TPR analysis of a Pd/Al₂O₃ catalyst by heating and cooling twice in the range of 0-80 °C. They reported that the emission of H₂ occurred during heating at 68 °C and absorption of H₂ occurred during cooling. Pd absorbed H₂ at low temperatures to form a PdH phase (H₂ + 2Pd \leftrightarrow 2PdH). The Pd-Ru/ Al₂O₃ catalyst showed H₂ desorption peaks smaller than those of the Pd/Al₂O₃ catalyst because the number of Pd sites that could absorb H₂ was decreased by the formation of the Ru-Pd alloy. These findings were consistent with the TEM and XRD results. In addition, the increase in the H₂ consumption peaks in the temperature ranges of 100-200 °C and 350-600 °C and the shift to low temperatures were caused by an increase in reducibility owing to increased H₂ consumption and the formation of the Pd-Ru alloy occurring at the RuO site obtained by addition of Ru.

3.3. Mechanistic study of the MSR reaction using Pd/Al2O3 and Pd-Ru/Al2O3 catalysts

Understanding the characteristics of reactions on catalyst surfaces through mechanistic studies is important for identifying factors that affect the RDS and promote the reaction activity. In this study, DRIFT analysis was performed using FT-IR to investigate the characteristics of the reactions on the surfaces of the Pd/Al_2O_3 and $Pd-Ru/Al_2O_3$ catalysts.

All DRIFT analyses were performed after impurities were removed from the catalyst surfaces by injecting Ar at 400 °C for 30 min before the experiments. First, to investigate the adsorption characteristics of methanol on the catalyst surfaces, changes in the surface of the Pd/Al₂O₃ catalyst were observed by injecting methanol at a temperature of 300 °C for 20 min. Adsorption peaks caused by the injection of methanol have been reported in many papers [14,17,27,28]. Ranganathan et al. [17] performed an FT-IR analysis of Pd/ZnO and Pd/CeO₂ catalysts and reported that C–H peaks were observed at 2934, 2843, and 2818 cm⁻¹ upon the injection of methanol. Haghofer et al. [14] performed an FT-IR analysis to investigate the MSR characteristics of a Pd/Ga₂O₃ catalyst. As the MSR reaction proceeded, a linear CO bond was observed to be absorbed on Pd (2056 cm⁻¹). Adsorbed CO species in a bridgebonded form (1968 cm⁻¹) and a hollow/bridge-bonded form (1920 cm⁻¹) were also observed.

As shown in Fig. 5, peaks were observed at 2944, 2906, 2843, 2820, 2053, 1920, 1600, 1390, and 1374 cm^{-1} upon injection of methanol. The peaks at 2944 and 2843 cm⁻¹, corresponding to C–H stretching (bridged), were caused by the adsorption of methoxy species and the peak at 2906 cm⁻¹ was caused by the adsorption of formate species. The peak at 2820 cm⁻¹ was also caused by the adsorption of methoxy species [17]. The peaks observed at 2053 and 1920 cm⁻¹ corresponded to CO adsorption species linearly adsorbed on the surface of Pd (2053 cm⁻¹) and CO adsorption species in the hollow/bridge-bonded form (1920 cm⁻¹) [29]. Finally, the adsorption peaks at 1600, 1390, and 1374 cm⁻¹ were caused by formate species adsorbed in various forms on the catalyst surface. Thus, CO adsorption species, methoxy species in the form of C–H, and formate species were adsorbed on the surface of the catalyst upon injection of methanol.

When the adsorption characteristics of the catalyst surface were examined over time, formate species (peaks at 1600, 1390, and 1374 cm^{-1}) were formed in the first 2 min after the injection of methanol. In comparison, relatively few methoxy species (peaks at 2944,



Fig. 5. Dynamic changes in the in situ FT-IR spectra for methanol adsorption on Pd/Al_2O_3 at 300 °C as a function of time (inlet gas: 1500 ppm methanol mixed with N_2). [MeOH ads: (a) 1 min, (b) 2 min, (c) 3 min, (d) 4 min, (e) 6 min, (f) 10 min, (g) 15 min, (h) 20 min].



Fig. 6. Dynamic changes in the in situ FT-IR spectra for Ar purging after methanol adsorption on Pd/Al_2O_3 at 300 °C as a function of time (inlet gas: Ar). [MeOH ads: (a) 20 min, Ar des: (b) 1 min, (c) 2 min, (d) 3 min, (e) 5 min, (f) 10 min, (g) 15 min, (h) 20 min].

2843, and 2820 cm^{-1}) and CO absorption species (peak at 1920 cm^{-1}) were formed. Subsequently, peaks at 2053 and 1920 cm⁻¹ corresponding to CO absorption species were formed from 4 min after the injection of methanol. In addition, the growth of methoxy species was observed over time after 4 min, but no changes in the peaks of CO absorption species and formate were observed. Fig. 6 shows the changes in the catalyst surface 30 min after the injection of methanol gas was stopped, with Ar injected 20 min after the injection of methanol. It was found that the peaks corresponding to the methoxy species at 2944, 2843, and 2820 cm^{-1} disappeared rapidly within 1 min of injecting Ar. In addition, the peaks corresponding to CO absorption species at 2053 and 1920 cm⁻¹ disappeared completely within 3 min of injecting Ar, indicating that this species was desorbed from the surface of the catalyst. In contrast, the peaks at 2906, 1600, 1390, and 1374 cm^{-1} corresponding to the formate species did not change, even after Ar was injected, which showed that the formate species was not desorbed from the catalyst surface.



Fig. 7. Dynamic changes in the in situ FT-IR spectra for H_2O purging after methanol adsorption on Pd/Al_2O_3 at 300 °C as a function of time (inlet gas: 3% H_2O mixed with Ar). [MeOH ads: (a) 20 min, H_2O des: (b) 1 min, (c) 2 min, (d) 3 min, (e) 5 min, (f) 10 min, (g) 15 min, (h) 20 min].

According to the results in Fig. 6, the methoxy species peak disappeared and then the CO adsorption species peak disappeared, which indicated that the methoxy species was converted into an adsorbed CO species that was then desorbed. In addition, as the peaks corresponding to the formate species did not change, even following injection of Ar, the mechanism for the methanol decomposition reaction was identified to involve methanol adsorbed on the catalyst surface as the methoxy species and only the methoxy species was converted into the CO adsorption species. Finally, the CO adsorption species was desorbed from the surface of the catalyst. According to the results shown in Fig. 5, the peaks corresponding CO, which was the final stage of the reaction on the catalyst surface, increased after 3 min and then did not change further. In contrast, the peaks corresponding to the methoxy species continued to increase up to 20 min. As the desorption rate of CO was slower than the conversion rate of methoxy species to CO, the methoxy species was not converted into CO and thus was accumulated on the catalyst surface.

Fig. 7 shows the changes in the catalyst surface caused by injecting H_2O 20 min after methanol was injected and absorbed on the catalyst surface. As a result, the peaks corresponding to the methoxy species at 2944, 2843, and 2820 cm⁻¹ tended to decrease rapidly after water was injected. In contrast, the peaks corresponding to the formate species at 2906, 1600, 1390, and 1374 cm^{-1} decreased sharply within 1 min of the injection of water and then gradually decreased over 10 min. In addition, the peaks corresponding to CO at 2053 and 1920 cm⁻¹ decreased sharply within 1 min of the injection of water and then gradually decreased over 10 min. Finally, the growth of a peak at 1640 cm⁻¹ was observed 10 min after the injection of water. This peak corresponded to water and was thought to appear due to the injection of water [30,31].

According to the results shown in Fig. 6, the methoxy and CO absorption species were all desorbed within 3 min of injecting Ar and were no longer observed on the catalyst surface. In contrast, the results in Fig. 7 showed that the methoxy species was rapidly desorbed, but the CO absorption peak was observed up to 10 min after the injection of water. According to the results in Fig. 6, there was no change in the peaks corresponding to the formate species following the injection of Ar. However, the results in Fig. 7 shows that the peaks corresponding to the formate species gradually decreased when water was injected. In other words, the formate species reacted with the injected water to be converted into CO, which was absorbed on the catalyst and then desorbed. In addition, it was found that the peak at $1640 \, {\rm cm}^{-1}$



Fig. 8. Dynamic changes in the in situ FT-IR spectra for the methanol surface reaction on Pd/Al_2O_3 and $Pd-Ru/Al_2O_3$ at 300 °C as a function of time (inlet gas: 1500 ppm methanol, H₂O mixed with N₂).

corresponding to water was observed after 10 min because water was adsorbed on the catalyst surface once all formate species that could react were consumed. Thus, the formate species was found to react with water. The FT-IR analysis revealed that methoxy and formate species were formed as methanol intermediates and were converted into adsorbed CO species, which were then desorbed from the catalyst surface. It was also found that the rate of CO desorption from the catalyst surface was slower than the rate of conversion from the intermediate species to CO. These results confirmed that the RDS of the entire reaction was the desorption of CO.

Fig. 8 shows the changes in the catalyst surface under various conditions, such as 20 min after the injection of methanol, 20 min after desorption under Ar, and 20 min after injection of H₂O for the Pd/Al₂O₃ and Pd-Ru/Al₂O₃ catalysts. The Pd-Ru/Al₂O₃ catalyst, which showed excellent reaction activity, exhibited the same overall reaction pathway as the Pd/Al₂O₃ catalyst. However, a difference between the Pd/Al₂O₃ catalyst and the Pd-Ru/Al₂O₃ catalyst was observed when methanol was injected for 20 min. In the case of the Pd-Ru/Al₂O₃ catalyst, the peaks at 2053 and 1920 cm⁻¹ corresponding to the adsorption of CO were larger than those for the Pd/Al₂O₃ catalyst, whereas the peaks at 2906, 2843, and 2820 cm^{-1} corresponding to the intermediate methoxy species were smaller than those for Pd/Al₂O₃ catalyst. These results indicated that the Pd particle size decreased with the addition of Ru, as confirmed through FE-TEM analysis, and the number of Pd sites of for conversion to and adsorption of CO increased. Thus, increased adsorption of CO occurred on the surface of catalyst with added Ru. In addition, the decrease in the methoxy species peaks may be caused by two phenomena. First, the increase in the number of sites for conversion to CO increased the conversion of methoxy species to CO, resulting in a decrease in the methoxy species peaks. Second, the decrease could be caused by an increase in the desorption rate of the CO adsorption species from the catalyst surface, which was identified as the RDS of the entire catalytic reaction. Fig. 6 shows that an increase in the methoxy species peaks was caused by the slow desorption of CO adsorption species in the final stage of the reaction. In other words, if the desorption rate of the CO adsorption species increased, the size of the methoxy species peaks could be decreased. In this study, TPD analyses were conducted to investigate how the addition of Ru affected the amount and intensity of CO adsorption, as described in the next section.



Fig. 9. Temperature-programed desorption of CO over 1%Pd/Al₂O₃ and 0.9% Pd-0.1%Ru/Al₂O₃ catalysts.

3.4. TPD and TPSR analyses

A CO-TPD analysis were performed to identify the effect of Ru addition on the adsorption characteristics of CO, and the results are shown in Fig. 9. The Pd/Al₂O₃ catalyst showed CO desorption peaks at 100 and 285 °C, whereas the Pd-Ru/Al₂O₃ catalyst with added Ru showed CO desorption peaks at 100, 220, and 260 °C. The CO peak at 100 °C corresponded to the desorption of linearly-bonded CO species adsorbed at Pd and Pd-Ru sites, whereas the CO peaks at 220, 260, and 285 °C corresponded to the desorption of Bridged CO species [32,33]. The results in Fig. 9 shows that the CO adsorption amount of the Pd-Ru/ Al₂O₃ catalyst with added Ru was greater than that of the Pd/Al₂O₃ catalyst, and that the CO desorption peak area of the Pd-Ru/Al2O3 catalyst was 1.29 times larger than that of the Pd/Al₂O₃ catalyst. The amount of CO adsorbed on the Pd-Ru/Al₂O₃ catalyst was greater than that on the Pd/Al₂O₃ catalyst. As revealed in the TEM images, such an increase was caused by the decrease in the Pd particle size caused by the formation of a Pd-Ru alloy and the increase in the number of CO adsorption sites caused by the high dispersion of Pd on the catalyst surface. In addition, the CO-TPD results revealed that CO desorption peaks of the Pd-Ru/Al₂O₃ catalyst with added Ru were observed at lower temperatures than those of the Pd/Al₂O₃ catalyst. Hartmann et al. [34] reported that the CO adsorption intensity on Pd in which a PdRu surface alloy was formed was weakened by approximately 30-40% compared with the CO adsorption intensity of CO on the bare Pd surface. In addition, Liu et al. [35] reported that a PdRu/C catalyst exhibited excellent activity for the formic acid electro-oxidation test because the adsorption intensity of CO was decreased. In this study, as a Pd-Ru alloy was formed by the addition of Ru, the desorption peak of CO on the Pd-Ru/Al₂O₃ catalyst was observed at a lower temperature than that on the Pd/Al₂O₃ catalyst, indicating that the CO adsorption intensity was weakened. As indicated by the FT-IR results, the RDS of the entire reaction was the desorption of CO adsorption species. Fig. 1



Fig. 10. Temperature-programed desorption of methanol over $1\% Pd/Al_2O_3$ and $0.9\% Pd-0.1\% Ru/Al_2O_3$ catalysts.

shows increases in the reaction activities with the addition of Ru. Such increases were caused by the decrease in CO adsorption intensity owing to the formation of the Pd-Ru alloy and the increase in CO adsorption sites. These phenomena were confirmed by the results of the methanol-TPD analysis shown in Fig. 10. The methanol-TPD analysis revealed the formation of H₂ (m/e = 2), CO (m/e = 28), CH₄ (m/e = 16), and CO₂ (m/e = 44). First, a CO₂ peak was observed in the temperature range of 100–250 °C and this peak was larger for the Pd-Ru/Al₂O₃ catalyst than for the Pd/Al₂O₃ catalyst at low temperatures. In addition, a CO₂ peak was observed in the temperatults were highly consistent with the hydrogen consumption peaks caused by oxygen species present in the catalyst observed in the H₂-TPR analysis (Fig. 4). In other words, it was found that the CO₂ peak was generated by the oxidation reaction between oxygen in the catalyst and methanol or intermediate species absorbed on the catalyst surface.

In terms of the H₂ and CO results, in the case of the Pd-Ru/Al₂O₃ catalyst, the H₂ and CO desorption peaks were observed at 218 °C. In the case of the Pd/Al₂O₃ catalyst, the H₂ and CO desorption peaks were observed at 280 °C. In addition, it was found that the CO desorption peak temperature observed in the CO-TPD analysis was similar to the desorption peak temperatures of H₂ and CO observed in the methanol-TPD analysis for both catalysts. As shown in Fig. 10, H₂ was generated in the process of converting the methoxy species into CO. In other words, as the CO adsorption species was desorbed from the catalyst surface, the adsorbed methoxy species was converted into CO, H_2 then it is concluded that desorbed from the catalyst surface. The MSR reaction was thought to proceed from the moment when the CO adsorption species adsorbed on the catalyst surface was desorbed. The formation of the Pd-Ru alloy with the addition of Ru weakened the adsorption intensity of the CO adsorption species, thus promoting the MSR reaction activity.

Lastly, Fig. 11 shows the results of the TPSR analysis. The TPSR analysis revealed that the MSR reaction proceeded from 180 °C because H_2 and CO were generated at 180 °C with the Pd-Ru/Al₂O₃ catalyst. However, as the Pd/Al₂O₃ catalyst only generated H_2 and CO from



Fig. 11. Temperature-programed methanol steam reforming over 1%Pd/Al₂O₃ and 0.9%Pd-0.1%Ru/Al₂O₃ catalysts.



Fig. 12. Reaction scheme of the methanol steam reforming over Pd-based catalysts.

220 °C, it was found that the MSR reaction proceeded at a higher temperature. As shown by the results of the methanol-TPD analysis (Fig. 10), the Pd-Ru/Al₂O₃ catalyst generated H₂ and CO from 150 °C, indicating that the MSR reaction proceeded from when the desorption of the CO adsorption species began. According to the results of the methanol-TPD and TPSR analyses, in the case of the Pd/Al₂O₃ catalyst, the generation of H₂ was observed from the same temperature. Fig. 12 shows a reaction scheme based on the results obtained in this study. In the MSR reaction, injected methanol was adsorbed on the catalyst surface as methoxy and formate species, and then converted through decomposition and reaction with H₂O into CO adsorption species, which were subsequently desorbed from the catalyst surface. In addition, the RDS of the entire reaction was found to be the desorption of CO adsorption species.

4. Conclusions

In this study, the MSR reaction activities of Pd/Al₂O₃ and Pd-Ru/ Al₂O₃ catalysts were evaluated. The MSR reaction activity was increased by the addition of Ru. FT-IR analysis revealed that methanol was adsorbed on the surfaces of the Pd/Al2O3 and Pd-Ru/Al2O3 catalysts as methoxy and formate species and then converted through decomposition and reaction with water into CO, which was desorbed from the catalyst surface. It was found that the RDS of the entire reaction was the desorption of the CO adsorption species. In addition, the TEM analysis showed that the addition of Ru to the Pd/Al₂O₃ catalyst resulted in smaller Pd particle sizes owing to the formation of a Pd-Ru alloy, which was highly dispersed on the surface of the catalyst. Thus, the CO adsorption amount was increased. The TPD analyses revealed that the formation of the Pd-Ru alloy increased the desorption rate of CO adsorption species. As the RDS of the MSR reaction was the desorption of CO, the decrease in the CO adsorption intensity caused by the formation of the Pd-Ru alloy enhanced the MSR reaction activity.

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