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Study of Raney Ruthenium Catalyst for Methanol Synthesis

Ruthenium (Ru) catalysts are known to dissociate the CO bond easily and to be effective for methanation or Fischer–Tropsch synthesis. However, several Ru systems yield oxygen-containing compounds (*1–4*). The reasons for these oxygenate synthesis activities have not been well discussed. Raney Ru catalysts have also been found active for methanol synthesis from CO and H_2 (*5*). Methanol can be synthesized at a temperature as low as 353 K on Raney Ru. Fine particles of Raney Ru powder catalyst can be suspended in a solution for the low-temperature methanol synthesis process in which a reduced Ni complex catalyst is supposed to be used (*6*). A new methanol process under low temperature and low pressure could save much of the energy required for the process, and new catalysts including Raney Ru should be studied in detail. The point of interest in the case of Raney Ru is why methanol is produced selectively, although Ru powder gives hydrocarbon exclusively. Here, we tried to identify the surface state of Raney Ru that is related to methanol selectivity.

Cationic species have been reported to be responsible for methanol synthesis over Pd (*7*) and Rh catalysts (*8*), although importance of morphorogy of Pd surface has been proposed (*9*). Among several extractants including acetylacetone (AcAc) used for Pd/SiO_2 catalysts (*7*), a thiourea mixture was found effective in extracting the oxidized surface Ru from the Raney Ru catalysts in this work. Extracted Ru^{n+}–thiourea complexes are blue-green in solution and may be identified as $Ru(SC(NH)NH_2)^{2+}$ and/or $Ru(SC(NH)NH_2)_3$ (*10*). These complexes can be quantitatively analyzed by spectrophotometry. Usually this method is employed to measure the amount of Ru^{n+} in solutions (*10, 11*).

Five grams of Ru powder ($\phi < 0.15$ mm, 99.9% pure, Tanaka Nobel Metal Co.) was reduced by circulating H_2 (53 kPa) for 2 h at 673 K and was evacuated for 1 h. This treatment was repeated twice (*reduced Ru powder catalyst*). A number of this sample were oxidized with various amounts of O_2 (*oxidized Ru power catalyst*), and the reacted amount of O_2 was recorded. These oxidized Ru powders were transferred into 20-ml mixed solutions (81% thiourea aqueous solution 0.18 ml, 12*N* HCl a.q. 0.83 ml, and ethanol) under Ar atmosphere. The cationic Ru was extracted with the thiourea mixture by a 20-min reflex at 363 K, and the solution was filtrated under Ar atmosphere. The amount of Ru^{n+}–thiourea complexes in the solution was measured by using a spectrophotometer (Bechmann Acta CIII). A $RuCl_3$–thiourea solution was used as a calibrated standard for the spectrophotometric measurement of the Ru^{n+}–thiourea samples at a wavelength of 650 nm. Although a 620-nm wavelength is most frequently used (*11*), we obtained maximum absorbance at 650 nm.

The relationship between the amounts of oxygen consumed for the oxidation of Ru metals and the extracted amounts of Ru^{n+}–thiourea complexes from the oxidized Ru metals is plotted in Fig. 1. There is a linear relationship, although the slope is unexpectedly low. The equations of the extraction may be formulated as follows,

$$Ru^{3+} + Hth \rightleftarrows Ru(th)^{2+} + H^+$$
$$Ru(th)^{2+} + 2Hth \rightleftarrows Ru(th)_3 + 2H^+,$$

where Hth represents thiourea (*10*). The extracted complexes may be $Ru(th)^{2+}$ and

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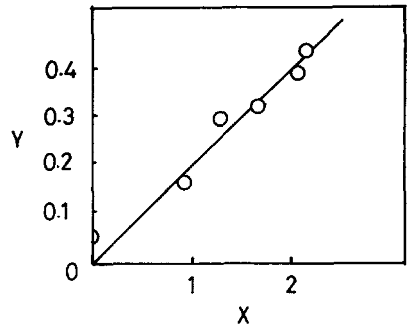

FIG. 1. Relationship between oxygen consumption index X and extracted Ru^{n+} index Y; X = (Consumed O atoms)/(Adsorbed H atoms (surface Ru number)), Y = (Extracted Ru^{n+})/(Adsorbed H atoms (surface Ru number)).

$Ru(th)_3$. If the extractable Ru^{n+} is only Ru^{3+} (or only Ru^{4+}), and if an oxygen atom accepts two electrons from a Ru^0 atom, turning thereby to Ru^{3+} (or Ru^{4+}), 28% of Ru^{3+} (or 37% of Ru^{4+}) was extracted (Fig. 1). Thus, thiourea solution is not a perfect extractant for all Ru^{n+} on the Ru metal surface. Nonetheless, this solution is the best extractant of the solutions we tried (AcAc, phenanthroline, bipyridine, and thiourea). The straight relationship between X and Y (Fig. 1) is of greatest importance. Although Ru^{3+} represents Ru^{n+} above, mixed Ru cations (Ru^{3+}, Ru^{4+}, and so forth) might be considered as Ru^{n+}. The state of Ru^{n+} on oxidized Ru powder and that on water-treated Raney Ru might be different, however, Ru^{n+}–thiourea method was chosen for the Ru^{n+} measurement of the Raney Ru catalysts.

The oxidized Ru powder was analyzed by the XPS (Shimadzu ESCA 750), however, the binding energy of the $Ru3d_{5/2}$ (280.2 eV) was near that of the Ru^0 (280.0 eV). Because the escape depth of the $Ru3d$ electron corresponds to about five layers of the Ru surface lattices, the XPS information about the surface atom may be diluted. The oxidation state of surface Ru atom was difficult to determine by an XPS measurement alone.

The most frequently used Ru–Al alloy has a composition of $Ru_{21}Al_{79}$ which is mainly composed with both Ru_4Al_{13} and $RuAl_6$ phases. The crushed alloy (0.5 g) was leached with 5 mol · l^{-1} KOH aqueous solution at 373 K for 2 h, and washed several times with decantation until the pH of the solution was decreased to 7. Five washings with decantation followed. The leached sample powder was transferred to the catalyst chamber together with the water, and evacuated for 15 h at room temperature (*Raney Ru catalyst*).

In order to change the surface states, several kinds of pretreatments, such as H_2O (2.7 kPa)–He(27 kPa) gas treatment (Table 1), were carried out. After each treatment, the water vapor was trapped with liquid nitrogen temperature. Before the reaction, BET surface area and H_2 chemisorption were measured at 77 and 273 K, respectively. The reaction was carried out using a conventional circulation system at 353 K and under an 80 kPa pressure of CO/H_2 (= $\frac{1}{3}$ molar ratio) gas mixture. Methanol and hydrocarbons with the carbon number of 1 to 9, recovered as products, were quantitatively analyzed by a gas chromatograph (Yanagimoto G3800 with FID and TCD).

The results are shown in Table 1. Raney Ru catalysts treated at the higher temperature (573 K) generally yielded higher selectivity for the methanol synthesis regardless of the treatment. The long reaction run (500 h) resulted in an activity decrease of $\frac{1}{3}$, however, did not result in any appreciable decrease in selectivity. Catalysts treated at the higher temperature gave smaller BET surface areas and less H_2 chemisorption. The number of the reduced Ru atoms on the unit catalyst surface area was calculated from the H_2 chemisorption and the BET surface area. Except for the sintered samples, the surface percentage of reduced Ru atom was decreased, depending on the treated temperature (*12*). These facts suggest either that Al and/or Al_2O_3 partially cover the catalyst surface. The XPS studies (*5*) had shown that most of the Al was reduced (Al^0) by the treatments at 373 K, but the Al was oxidized to Al^{3+} by the H_2O–He treatment at 573 K. The XPS data (*5*) also showed that the Ru

TABLE 1

Activity and Selectivity of Raney Ru Catalysts in CO/H_2 Reaction

Catalyst code number and treatment[a]	BET surface area (m^2/g)	H_2 chemisorption (mmol/g)	Surface percent of reduced Ru[b]	Activity[c] of MeOH (μmol/h · g)	Selectivity[d] of MeOH (C%)	Ru^{n+} amount[e] (μmol/g)
1 He,H_2(373 K)	82	2.7	120	0.7	8	16
2 He,H_2(473 K)	65	1.1	64	3.1	19	139
3 He,H_2(473 K)	39	0.99	90	1.8	19	30
4 He,H_2(473 K),S	2.7	0.04	49	0.04	55	2.6
5 He,H_2(573 K)	39	0.35	34	0.5	48	n.m.[f]
6 He,H_2(573 K),S	1.0	0.02	72	0.02	61	trace
7 H_2O(473 K)	50	1.2	91	0.3	29	14
8 H_2O,H_2(473 K)	45	0.78	64	1.7	21	29
9 H_2O(573 K)	34	0.56	61	2.0	73	n.m.[f]
10 H_2O,H_2(573 K)	30	0.43	53	0.6	59	16

[a] He, He (53 kPa) treatment for 5 h; H_2, H_2 (53 kPa) treatment for 2 h twice; H_2O, H_2O (2.2 kPa)–He (27 kPa) treatment for 15 h; S, sintered by a rapid heating.

[b] Ratio of H amount adsorbed to total surface Ru number estimated from BET area.

[c] Reaction at 353 K under pressure of 80 kPa of CO/H_2 ($\frac{1}{3}$).

[d] Ratio of methanol mol to total carbon in the products.

[e] Extracted by the thiourea solution.

[f] Not measured.

was kept reduced by any treatments (280.0 eV for Ru $3d_{5/2}$), although it might reflect the outer bulk phase also.

After each reaction run of CO hydrogenation, the catalyst was transferred into 20 mL of the thiourea solution under Ar atmosphere. The amount of Ru^{n+} was analyzed. The ratio of Ru^{n+} against chemisorbed H (surface Ru) ranges from 0.3 to 6.3% (Table 1). Nontreated Raney Ru gave very low concentration of Ru^{n+} (2.6 μmol/g or 0.05% of surface Ru) before the reaction. Thus, the Ru^{n+} species seem to increase even during the CO hydrogenation reaction. Ru^{n+} is thought to be formed during the heat treatment under the existence of H_2O along with the formation of Al^{3+} (*5*).

The relationship between the activities of methanol formation and the amount of extractable Ru^{n+} are plotted in Fig. 2. The Raney Ru catalysts with greater amount of extractable Ru^{n+} give the higher activity for methanol formation. The curve is not straight probably due to several reasons such as the surface heterogeneity. Yano *et al.* (*5*) have already pointed out that the state of Al is also related to the selectivity of methanol formation on the same Raney Ru. Considering the former results (*5*) and the results we obtained, we speculate that the combination of Ru, Al^{3+}, and Ru^{n+} species

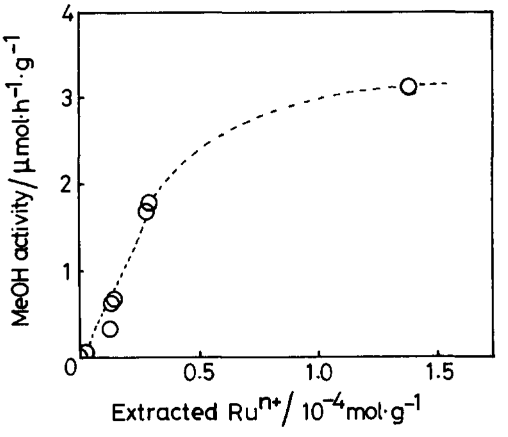

FIG. 2. Relationship between extracted Ru^{n+} and methanol formation rate at 353 K.

TABLE 2

Activity and Selectivity of Ru Catalysts in CO/H_2 Reaction

Catalyst (Treatment[a])	BET surface area (m^2/g)	H_2 chemisorption ($\mu mol/g$)	Surface percent of reduced Ru	Activity[d] of			Selectivity[e] of			Ru^{n+} amount[f] ($\mu mol/g$)
				MeOH	MeCHO	Me_2O	MeOH	MeCHO	Me_2O	
				(nmol/h · g)			(C%)			
Reduced Ru powder	0.67	16	100[b]	1.5	0.5	n.d.[g]	2	1	n.d.[g]	0.3
Oxidized Ru powder (O_2)	0.67	n.m.[h]	n.m.[h]	1.4	1.1	n.d.[g]	1	1	n.d.[g]	0.4
Ru + Al_2O_3	1.5	12	(30)[c]	0.1	n.d.[g]	n.d.[g]	0.1	n.d.[g]	n.d.[g]	0.6
1 wt% Ru/Al_2O_3 (H_2–H_2O)	109	16	(0.6)[c]	n.d.[g]	n.d.[g]	26	n.d.[g]	n.d.[g]	43	1.3
1 wt% Ru/Al_2O_3 (H_2O–He)	102	28	(1.0)[c]	3.9	n.d.[g]	37	1	n.d.[g]	26	3.0

[a] O_2, O_2 (27 kPa) treatment at 373 K several times; H_2–H_2O, H_2 (60 kPa)–H_2O (2.7 kPa) treatment at 573 K for 17 h; H_2O–He, H_2O (2.6 kPa)–He (53 kPa) treatment at 573 K for 15 h.

[b] Ratio of amount of H adsorbed to assumed surface Ru number estimated from BET area.

[c] The rest part corresponds to the area of Al_2O_3 additive or support.

[d] Reaction at 353 K under pressure of 80 kPa of CO/H_2 ($\frac{1}{3}$).

[e] Ratio of methanol mol to total carbon in the products.

[f] Extracted by the thiourea solution.

[g] Not detected.

[h] Not measured.

is important for methanol formation from CO and H_2.

Methanol synthesis over the other types of Ru catalysts was studied for comparison (Table 2). A mixture of 2 g of Ru and 0.006 g of aluminium isopropoxide with a little water (in an amount sufficient to cover about 70% of the surface of the Ru powder) was reduced with H_2 (53 kPa) at 673 K several times until no hydrocarbons were detected. After the 1-h evacuation at 673 K, the mixture was treated with circulating H_2O (2.7 kPa)–He (27 kPa) gas mixture at 473 K for 15 h. The water vapor was trapped with liquid nitrogen temperature for 1 h, and was evacuated at 473 K for 1 h (*Ru + Al_2O_3 catalyst*). A 1-wt% Ru/Al_2O_3 was prepared according to Kobori *et al.* (*4*) by impregnating alumina (aluminium oxide C, Aerosil) with $RuCl_3$ in an aqueous solution. The dried Ru/Al_2O_3 catalyst (2 g) was evacuated for 1 day at room temperature, and was reduced with H_2 (53 kPa) twice for 1.5 and 2 h, respectively. After 1 h evacuation, the catalyst was treated with circulating H_2–H_2O (mixture) or H_2–He mixture at 573 K. The water vapor was trapped with liquid nitrogen temperature and evacuated at 573 K for 1 h (*1 wt% Ru/Al_2O_3 catalyst*).

Before the reaction, BET surface area (77 K) and H_2 chemisorption (273 K) of these catalysts (except the oxidized Ru powder) were measured. The reaction was also carried out at 353 K under an 80 kPa pressure of CO/H_2 ($\frac{1}{3}$). After the reaction an amount of Ru^{n+} was measured by the thiourea method. The results of the hydrogenation of CO over various Ru catalysts are shown in Table 2. The 1-wt% Ru/Al_2O_3 catalysts produced dimethyl ether (DME), the dehydration product of methanol on the acidic sites of the support. Among the two Ru/Al_2O_3 catalysts, the one treated with H_2O–He gave more DME and methanol, and has a higher amount of Ru^{n+} than the one treated with H_2–H_2O. However, one of the important results is that the activity of Raney Ru (Table 1) is much higher than that of Ru/Al_2O_3 (Table 2), comparing a sample of code number 2 in Table 1 with 1-wt% Ru/Al_2O_3 (H_2O–He) in Table 2. The ratios of the former to the latter with respect to BET area, H_2 chemisorption, activity, and Ru^{n+} amount are 0.64, 39, 76, and 46, respectively. Thus, the high activity is related to the high surface Ru number and the high Ru^{n+} concentration in Raney Ru.

The activities and selectivies for methanol formation of three Ru powder catalysts are low (Table 2). Probably Ru^{n+} in Ru powders was reduced to Ru^0 during the reaction. The bindings between Ru and Al_2O_3 seem to be weak in the Ru + Al_2O_3 catalyst and strong in the Ru/Al_2O_3 catalyst, according to the above assumption. In the case of the Ru + Al_2O_3 catalysts, the Al_2O_3 did not act as a good stabilizer of Ru^{n+} and methanol was not produced. This is because the Ru + Al_2O_3 catalysts were made by simply mixing the Al_2O_3 to Ru metal. However, for the Ru/Al_2O_3 catalysts, the Ru metal particles are well dispersed on Al_2O_3 providing the intimate Ru–Al_2O_3 interaction. Such proper interaction of alumina with Ru in the Raney Ru catalysts and the Ru/Al_2O_3 catalysts might prevent the Ru^{n+} being reduced. These results strongly suggest that the coexistence of Ru, Al^{3+}, and Ru^{n+} is required for methanol formation from CO and H_2.

It is speculated that Ru^{n+}–O^{2-}–Al^{3+} is one of the active sites for methanol formation. Ru^0 is considered to dissociate H_2. The carbon of chemisorbed CO might be bonded to Ru^{n+} and its oxygen stabilized by Al^{3+} (Ru^{n+}–O^{2-}–Al^{3+}). Another possibility is that the carbon might bond to the Ru atom and its oxygen be stabilized by Ru^{n+} (Ru–Ru^{n+}(–O^{2-}–Al^{3+})). These bindings could activate, but not dissociate, the CO bond which will be attacked by the H atoms activated over the Ru metal.

Driessen *et al.* (*7*) and van der Lee *et al.* (*8*) concluded that Pd^{n+} and Rh^{n+} are active centers of methanol synthesis, and that Mg^{2+} and La^{2+} are essential to stabilize the cationic form of Pd and Rh. Our results are similar to their conclusions. Kikuzono *et al.* (*13*) found that the activity of methanol was increased by doping Li^+ and Na^+ into supported Pd catalysts made from precursor complexes (M_2PdCl_4, M = Li, Na). Ichikawa *et al.* also suggest that the cationic species (Fe^{3+}) in RhFe ensembles stabilizes formyl species which is converted into methanol (*14*). Here, another idea might be possible that smaller ensemble of surface Ru atoms suppress CO dissociation. Well-dispersed alumina on Raney Ru might form a number of small ensembles of Ru atoms. Since we could not determine the ensemble size for each sample, we can not conclude the controversy. Importance of the morphology (surface geometry) has been pointed out (*9*).

Methanol is obtained as a main product from CO and H_2 over H_2O–He-treated Raney Ru at 353 K under the pressure of 80 kPa of CO/H_2 ($\frac{1}{3}$), although hydrocarbons are exclusively obtained over Ru powder. The activity of methanol synthesis was found to be well correlated with the amount of Ru extractable from the catalysts as Ru^{n+}–thiourea complexes. Considering the reported fact that selectivity for methanol formation was increased with an increase in the amount of Al^{3+}, it was assumed that the combination of Ru, Al^{3+}, and Ru^{n+} species were necessary for the methanol formation on the Raney Ru catalysts. Al_2O_3-supported Ru catalysts also contain Ru^{n+} and can catalyze methanol synthesis. However, the methanol activity of Raney Ru is much higher than the activity of the supported catalysts because of the high concentration of surface Ru atom per g-catalyst.

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