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The Chemisorption of CO on Ruthenium Metals and Ruthenium–Silica Catalysts

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The chemisorption of CO on Ru-metals and supported Ru/SiO_2 catalysts was studied at 150°C. The Ru-metal made by Adams's method adsorbed a normal quantity of CO, and the results agreed with those of previous studies. The Ru-metal made by Willstätter's method and supported Ru-SiO_2 catalyst adsorbed a large quantity of CO, and the volume decreased by a repetition of the adsorption and reduction. The decrease was not caused by the residual CO of the reduction, but the sintering of Ru-metal was considered. In the case of the Ru-metal made by Willstätter's method, the volume of CO chemisorbed did not correspond to the specific surface area. In the fresh samples of supported Ru-SiO_2 catalyst, the CO/Ru values (g mol/g atom) were more than unity and the ir spectra of the sample agreed with those of $Ru_3(CO)_{12}$ and other previous studies. This suggested that there were Ru-$(CO)_2$, Ru-$(CO)_3$, etc., species in the CO chemisorption.

INTRODUCTION

The chemisorption of CO on platinum and palladium has been studied in detail, and methods for free-metal surface area determination have been reported (*1*, *2*). There have been a few studies on the chemisorption of CO on ruthenium; the kinetic study of 0.5% Ru–alumina catalysts by Low and Taylor (*3*), infrared spectroscopic studies of CO adsorbed on Ru-metals and Ru–silica by Guerra and Schulman (*4*), Guerra (*5*), and a study of the interaction of hydrogen and CO on platinum-group metals by Mckee (*6*). Although the chemisorption volumes of CO on platinum and palladium are correlated to these free-metal surfaces, in the case of ruthenium there has been no detailed study of this subject. Mckee (*6*) has reported that the volume of CO chemisorption on ruthenium metal with a surface area of 21.9 m^2/g is 2.2 ml (STP)/g, but there is a great difference from palladium with 1 cm^3 (NTP) CO equalized to 3.2 m^2 Pd by Scholten and Van Montfoort's data (*2*). We also tested the chemisorption of CO on supported ruthenium metal catalysts and obtained abnormally high volumes of CO chemisorption. It seemed likely, therefore, that a detailed study of the chemisorption of CO on ruthenium metals and catalysts should be undertaken and that the chemisorption should be compared with the surface area.

EXPERIMENTAL METHODS

Sample Preparation

Ruthenium metal powders were prepared by two methods; one was Adams and Shriner's method (*7*) for preparing platinum black, while the other was Willstätter and Waldschmidt-Leitz's method (*8*) using an HCHO aq solution to reduce H_2PtCl_6. As Adams's method has been reported in detail, by Mckee (*6*) and in other papers, we will omit its description here.

By Willstätter's method, about a 4 g portion of $RuCl_3 \cdot 3H_2O$ was dissolved in 16 ml of water, and then a 15 ml 38 wt % HCHO aq solution was added to this $RuCl_3$ solution. A 42 ml 50 wt % KOH aq solution was then slowly added drop by drop to this mixture which was cooled in an ice bath. Reaction occurred vigorously, evolving bubbles; it was completed in a few minutes at room temperature. The mixture was then heated in the water bath at 60–70°C for 30 min; this reaction went essentially to completion. The precipitate was then filtered, washed thoroughly to remove any potassium hydroxide and chloride, and dried in a desiccator at room temperature.

The ruthenium catalysts supported on silica were prepared by the cation-exchange method. The cation-exchange reaction was performed using a ruthenium-ammine complex solution and silica xerogel which had been treated with a NH_3 aq solution. The ruthenium–ammine complex was prepared by Allen *et al.* (*9*). The cation-exchanged catalyst was washed thoroughly to remove any chloride and ammonia, and dried in a desiccator at room temperature.

Apparatus and Procedure

The adsorption was carried out in a static volumetric apparatus and in a pulse-flow system. In the static method, samples weighing 0.2–0.7 g were sealed in a U-shaped tube 3–5 mm in diameter (i.d.). Hydrogen gas was passed into the U-shaped tube at 200–400°C for 3 hr and the evacuation was carried out below 1×10^{-3} Torr for 2 hr. The weights of the samples were determined from the difference between the weight before reduction and after evacuation. Before the CO adsorption, the BET surface-area determination was carried out in the usual way. The total volumes of the gas space over the samples, including the dead space in the reactor, were measured at -196 and 150°C by using He gas before each adsorption experiment. The dead volume was 2.01 cm^3. The reduction and evacuation temperatures of the samples were kept within ± 5°C by the use of an electric furnace; the CO adsorption experiment was carried out with samples kept at 150 ± 2°C by means of silicone oil bath. After every reduction, the evacuation was carried out below 10^{-3} Torr for 2 hr at the same temperature.

In the pulse-flow method, an apparatus similar to that of Gruber (*1*) was used. Samples weighing 0.1–0.2 g were reduced at 300–500°C for 2 hr. The hydrogen gas flow rate was 60 ml/min. After reduction, He gas was passed through for 1 hr at the same temperature and at a flow rate of 60 ml/min in order to replace the hydrogen gas; then its flow rate was decreased to 20 ml/min, while the temperature of sample was kept at 150°C. Under these conditions a CO slug was inserted in the carrier He gas. The CO adsorption volume, which included physical and chemical adsorptions, was determined by summing the difference in the peak area before adsorption and that after adsorption, using a correction factor obtained in the equilibrium state. After the physical and chemical adsorptions of CO, the samples were exposed to the carrier He gas at the flow rate of 60 ml/min for 2 hr at the same temperature; then the operation of CO adsorption was performed again. The CO adsorption volume was obtained by a way similar to that described above; this value showed only the physical adsorption of CO. The chemisorption of CO was calculated from the difference between this value and the former, including both adsorptions. We regarded this adsorption value, which did not decrease after treatment with the He carrier for 2 hr at the same temperature, as the chemisorption of CO in this pulse-flow system.

The infrared spectra were obtained with a Perkin-Elmer Model 125 spectrophotometer with KBr otpics by the Nujol method. The samples, which adsorbed CO in the pulse-flow system, were powdered and pasted by Nujol in an argon gas atmosphere. The pasted samples were stable in air.

Materials and Analysis

The ruthenium metal and ammine complexes were prepared from reagent-grade $RuCl_3$–$3H_2O$ (Nippon Engelhard), as has been described above. The sodium and potassium included in ruthenium metal were neglected. The silica gels, which were used as support, were prepared from the products of the Mizusawa Kagaku Kogyo

Co., Ltd., and from "Snowtex-0-40" (Nissan Chemical Industry Co., Ltd.). The purity of $RuCl_3$-$3H_2O$ and the supported quantity of the metal were determined by the colorimetry of the ruthenium–thiourea chelate (*10*) and by the gravimetric analysis of RuO_2 (*11*).

Results

The Ru Metals Made by Adams's Method

Figure 1 illustrates the adsorption of CO on a ruthenium metal made by Adams's method at 150°C. The fresh sample was previously reduced and evacuated for 2 hr at 200°C; then its weight and specific surface area were measured by the usual BET method. The adsorption equilibrium was attained within 15 min at each point (○). After the adsorption measurement, the sample was evacuated at 150°C for 2 hr, and then the adsorption of CO was determined again (●). We also assumed that the former (○) included physical and chemical adsorptions while the latter (●) included physical adsorption only. About 50% of the total CO adsorbed at 150°C could be desorbed by pumping at this temperature for 2 hr. This agreed with the results of Mckee (*6*). After the measurement of the adsorption isotherm (●), the ruthenium metal was reduced in hydrogen for 2 hr at 200°C and then evacuated at this temperature for 2 hr; the adsorption of CO was then determined again (△). The total amount of CO adsorbed (△) increased more than that of the fresh metal (○), but the amount of CO adsorbed after evacuation (▲) decreased less than the ● plots. This disagreement suggested that the metal surface was changed by reduction in hydrogen and that the reduction of the fresh sample was not enough. To confirm these phenomena, we repeated the same experiment on the same sample at the reduction temperatures of 300°C (□, ■) and 400°C (▽, ▼). The total amount of CO adsorbed in the case of 300°C (□) and the physical adsorption of CO (■) also increased more than in the preceding case, but in the case of the reduction temperature of 400°C (▽, ▼), the total adsorption and the physical adsorption of CO both decreased. We measured the specific surface area by the BET method for each reduced sample before measuring the total adsorption of CO (open symbols). These values are summarized in Table 1 in order to make it possible to compare them with those of the chemisorption of CO calculated from Fig. 1. In the case of the reduction temperature of 400°C (No. 4), v_{CO} and Sg both decreased so sintering of the metal surface was considered to occur. All values of v_{CO}/Sg except No. 1 agreed very closely with that obtained by Mckee (*6*). The value of v_{CO}/Sg of No. 1 (a fresh sample) was smaller than the others, so we considered that the reduction at 200°C for 2 hr was not enough. In subsequent experiments, the reduction was carried out at 300°C. In comparison with the pulse and statical methods, v_{CO} and CO/Ru coincided within the range of experimental error (Nos. 4, 5, 6). We thought that this was attributable to the same sample, and the sample was stabilized by the sintering of experiment No. 4.

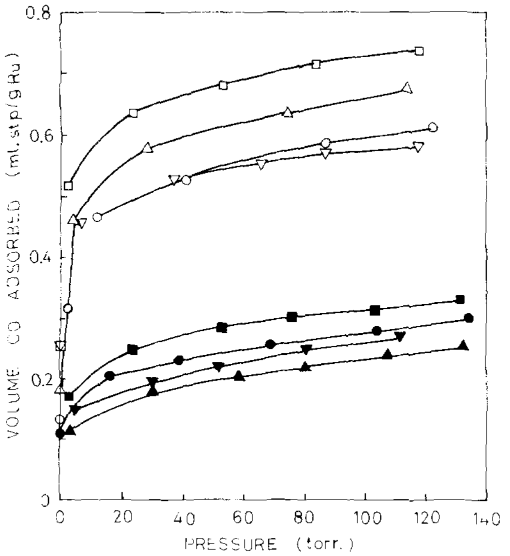

FIG. 1. Adsorption of CO on Ru-metal made by Adams's method. Adsorption carried out in this order with reduction temperature: (○) 200°C, (△) 200°C, (□) 300°C, (▽) 400°C, (open symbols) chemisorbed CO plus physisorbed CO, (closed symbols) physisorbed CO, respectively.

TABLE 1
THE ADSORPTION OF CO AND SPECIFIC SURFACE AREAS ABOUT Ru-METAL MADE BY ADAMS'S METHOD

	No.[a]	Reduction temp (°C)	Chemisorbed CO v_{CO} (ml STP/g)	Surface area Sg (m^2/g)	v_{CO}/Sg	CO/Ru (g mol/g atom) ($\times 10^{-3}$)
Static method (BET)	1	200	0.31_8	4.2_7	0.074_4	1.4_3
	2	200	0.42_8	4.3_9	0.097_7	1.9_3
	3	300	0.41_0	4.1_2	0.099_5	1.8_5
	4	400	0.32_2	3.5_0	0.092_0	1.4_5
Pulse method	5	300	0.36_3			1.6_4
	6	300	0.38_7			1.7_5
Mckee (*6*)	7	150	2.2	21.9	0.100	9.9_3

[a] Experiments were carried out No. 1, 2 . . . 6 successively.

The Ru-Metal Made by Willstätter's Method

The behavior of the Ru-metal made by Willstätter's method in Fig. 2 was similar to that of the preceding section. On the fresh sample (○, ●), the CO chemisorption was less than that of the second operation (△, ▲) in spite of the high reduction temperature (300°C). However, the values of the CO chemisorption were much larger than in the case of Adams's method, in spite of the same specific surface areas (Sg = 3–4 m^2/g). In Table 2, the CO chemisorption and the specific surface areas are summarized. The v_{CO}/Sg values are much larger than that of Table 1, but CO/Ru in the case of No. 2 is almost the same as that of Mckee (*6*). As for the pulse method, the correlation with the static method was not good because of the use of different samples, and v_{CO} decreased upon a repetition of the reduction.

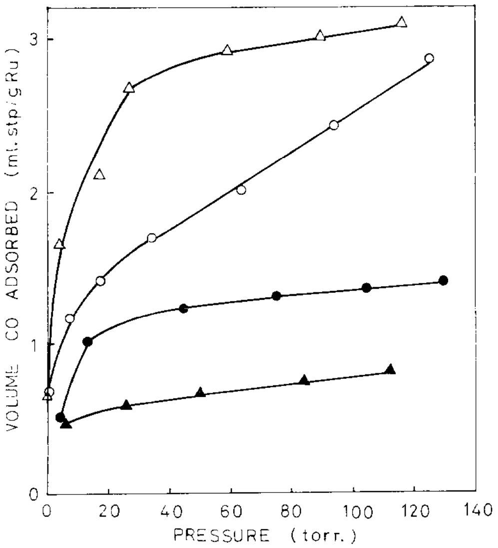

FIG. 2. Adsorption of CO on Ru-metal made by Willstätter's method: (○) fresh sample, (△) second operation; both were reduced at 300°C for 2 hr; (open symbols) chemisorbed CO plus physisorbed CO, (closed symbols) physisorbed CO, respectively.

Ru–SiO$_2$ Catalyst

Similar experiments on the adsorption of CO on the Ru–SiO_2 catalyst with a Ru-metal content of 0.0967 mg atom/g were carried out. The results are shown in Fig. 3. A fresh sample adsorbed a large quantity of CO (○, ●), and after reduction the second chemisorption decreased extremely (△, ▲). In the case of the pulse method also, there was a great difference between the fresh sample and the second operation. We cannot compare the CO chemisorption and the free-metal surface area because of the supported metal, but the CO/Ru ratio (g mol/g atom) was evaluated by means of the CO chemisorption and the Ru content. The results obtained by the pulse method on other Ru–SiO_2 catalysts are summarized in Table 3 along with the results of the above experiments. The values of CO chemisorption obtained by the pulse method did not agree with those given by the static method but were less. As for

TABLE 2
THE ADSORPTION OF CO AND SPECIFIC SURFACE AREAS ABOUT Ru-METAL MADE BY WILLSTÄTTER'S METHOD[a]

	No.	Chemisorbed CO v_{CO} (ml STP/g)	Surface area Sg (m^2/g)	v_{CO}/Sg	CO/Ru (g mol/g atom) ($\times 10^{-3}$)
Static method	1[b]	1.1_8	4.1_7	0.28_3	5.3_2
	2[b]	2.2_7	3.4_9	0.65_1	10.2_4
Pulse method	3[c]	2.0_3			9.1_6
	4[d]	1.5_4			6.9_5

[a] Reduction temp, 300°C.

[b] Experiments were carried out successively.

[c] Fresh sample.

[d] After the second reduction.

other Ru–SiO_2 catalysts with several contents of Ru and different total specific surface areas, CO chemisorption measurements by the pulse method were repeated 4 times for each. The CO/Ru values were very large, about 100 times that of Ru-metal only. v_{CO} decreased upon a repetition of adsorption and reduction for each sample.

The infrared spectra were taken with a Perkin-Elmer Model 125 by the Nujol method in order to compare the CO-chemisorbed and reduced samples. The spectra are summarized in Fig. 4. At 2100–1990

TABLE 3
THE ADSORPTION OF CO ON Ru–SiO_2 CATALYST[a]

Catalysts (Ru-content mg atom/g)	No.[b]	Chemisorbed CO v_{CO} (ml STP/g)	CO/Ru (g mol/g atom)
		Static method	
Ru–SiO_2-30-2[c] (0.0967)	1	3.1_4	1.4_4
	2	1.0_2	0.47
		Pulse method	
	1	2.5_5	1.17_6
	2	0.79_6	0.36_8
		Pulse method	
Ru–SiO_2-35-1[c] (0.367)	1	9.4_2	1.14_6
	2	4.1_2	0.50_0
	3	2.8_6	0.34_8
	4	3.1_1	0.37_8
Ru–SiO_2-35-2[c] (0.1861)	1	6.6_7	1.60_0
	2	4.3_4	1.04_0
	3	2.4_3	0.58_2
	4	2.1_6	0.51_7
Ru–SiO_2-35-3[c] (0.0932)	1	4.0_3	1.93_0
	2	2.2_7	1.09_0
	3	1.9_8	0.94_9
	4	1.7_1	0.81_8

[a] Reduction temp, 300°C.

[b] Experimental number shows that the same sample was used successively.

[c] Specific surface areas of Ru–SiO_2-30 and Ru–SiO_2-35 containing support silica gel are 91 and 242 m^2/g, respectively.

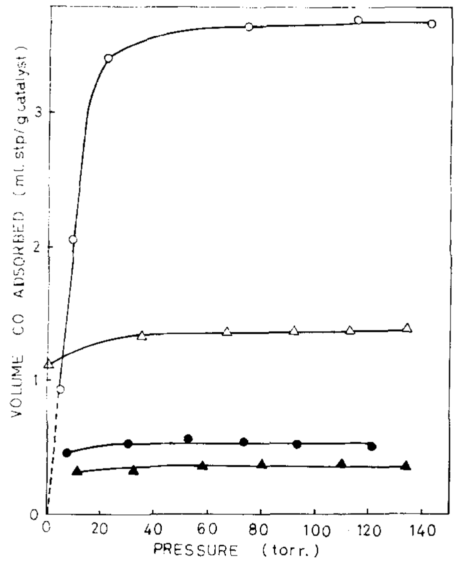

FIG. 3. Adsorption of CO on Ru-SiO_2 catalyst: (○) fresh sample, (△) second operation; both were reduced at 300°C for 2 hr; (open symbols) chemisorbed CO plus physisorbed CO, (closed symbols) physisorbed CO, respectively.

cm^{-1}, two main bands were obtained for CO-chemisorbed fresh samples. These bands became strong according to the Ru content (d, f, h). For any reduced sample, these two main bands at 2100–1900 cm^{-1} disappeared. Guerra and Schulman (4) pointed out that there were other bands at 1910–1870 cm^{-1}, but we could not distinguish these bands clearly; that of silica gel only is shown in Fig. 4. The two main bands at 2100–1990 cm^{-1} in our results agreed with the Guerra and Schulman (4) and Pichler and co-worker's results, in which two or three main bands at 2100–1990 were obtained for samples of $Ru_3(CO)_{12}$.

DISCUSSION

The CO/Ru values for two kinds of Ru-metals which were prepared in different ways, and for the Ru-SiO_2 catalyst are plotted against the pressure (Torr) in Fig. 5. The plots (□, ■) of the Ru-SiO_2 catalyst were about 100 times that of Ru-metal only; even if the CO chemisorption decreased upon the repetition of adsorption and reduction, the CO/Ru values for the

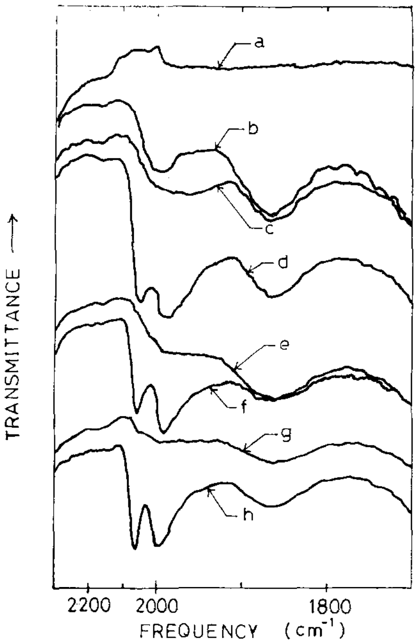

FIG. 4. Spectra of CO adsorbed by Ru-SiO_2 catalyst: (a) Nujol; (b) silica gel; (d, f, h) CO adsorbed catalsyt which Ru contents are 0.0932, 0.1861, and 0.367 mg atom/g, respectively; (c, e, g) spectra after reduction of catalysts (d, f, and h), respectively, at 300°C for 2 hr.

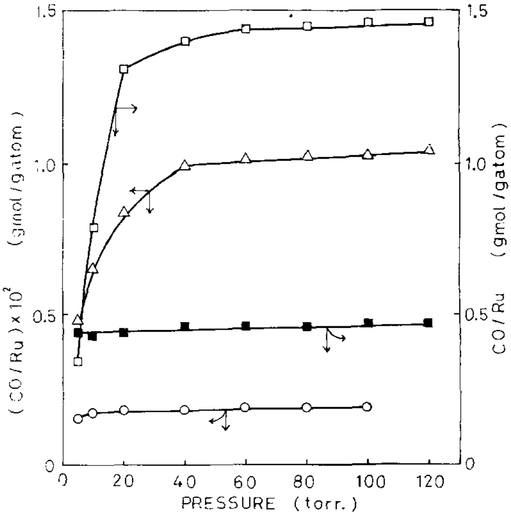

FIG. 5. Variation of CO/Ru with equilibrium CO pressure: (○) Ru-metal made by Adams's method; (△) Ru-metal made by Willstätter's method; (□) fresh Ru-SiO_2 catalyst which Ru content is 0.0967 mg atom/g; (■) after the second reduction for the same Ru-SiO_2 catalyst above.

Ru–SiO_2 catalyst were still about 50 times that of the Ru-metal only. This was observed in the case of the pulse method by comparing with Tables 2 and 3. The CO chemisorption of the pulse method tends to be smaller than that of the static method because the measurements are carried out in a flow system and because the equilibrium states of adsorption and desorption are not attained. This tendency is remarkable with samples which adsorb a large quantity of CO, such as the Ru–SiO_2 catalyst. On the contrary, Ru-metals such as the Adams's Ru-metal are stable and adsorb small amounts of CO; therefore, the agreement between the pulse and static methods is good. In Fig. 5, the chemisorption of the fresh sample of the Ru-SiO_2 catalyst (□) and that of the Ru-metal made by Willstätter's method (△) are shown to depend on the CO pressure at 0–40 Torr. This fact suggests that CO dissolves in Ru-metal and that consequently, the CO/Ru values are great in spite of the small surface area. In any event, the CO chemisorption does not correspond to the free-metal surface area. It is reasonable that the decrease in CO chemisorption upon a repetition of reduction is not caused by the residual CO after reduction, but attributable to the sintering of the Ru-metal, which is caused by the methanation reaction in reduction, because there is no band in the ir spectra after reduction; in Adams's Ru-metal, a reproducibility by reduction was reported by Mckee (*6*). In the case of the Ru–SiO_2 catalyst, the CO/Ru values of the fresh samples in Fig. 5 (□) and Table 3 are more than unity. This suggests that there are Ru–$(CO)_2$ and Ru–$(CO)_3$ species in the CO chemisorption; this suggestion is supported by the fact that the two main bands of the ir spectra at 2100–1990 cm^{-1} coincide with those of $Ru_3(CO)_{12}$. Further studies will be made regarding the detection of Ru–$(CO)_n$ in CO chemisorption on the Ru-catalyst.

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