JOURNAL OF CATALYSIS **110**, 159–170 (1988)

A Kinetic Study on the Effects of Support on the Catalytic Performances of Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2 in a $CO–H_2$ Reaction

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Received April 28, 1987; revised October 20, 1987

The catalytic hydrogenation of CO with hydrogen over Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 reduced at 673 K was studied kinetically and by monitoring the behavior of adsorbed CO species with *in situ* FT-IR to reveal the origins of their markedly different activities. The higher activity of Rh/TiO_2 is related to the much higher reactivity of its irreversibly adsorbed CO against hydrogen. The reactivity of 17% of irreversibly adsorbed CO on Rh/Al_2O_3 was comparable to the rate of catalytic reaction, suggesting that its very limited portion is the reactive intermediate. The reactivity of the irreversibly adsorbed species on Rh/SiO_2 was much less, indicating that the reversibly adsorbed species is the reaction intermediate. The rate of carbon deposition and its reactivity against hydrogen were much less than the rate of catalytic reaction, ruling out a major contribution to the catalytic sequence. Thus, the extent of CO activation which is strongly influenced by the supports is the basis for providing markedly different activities for these catalysts.

INTRODUCTION

Designs of better catalysts for the $CO–H_2$ reaction have been extensively investigated for years. The catalyst support is one of the most influential factors to be surveyed for this purpose. Combinations of metals of group VIII and various metal oxides, such as silica, alumina, titania, zirconia, niobia, lanthania, etc., have been investigated (*1–25*). It has been documented that Rh supported on TiO_2 exhibited the highest specific activity while the lowest activity was observed for Rh/SiO_2 among Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 catalysts (*2, 3, 8, 9, 19*). Solymosi *et al.* (*8, 9*) reported that reactivities of carbon produced on Rh were very sensitive to the kind of catalyst supports used. Murakami *et al.* (*19*) reported that the rate of dissociative adsorption of CO and the reactivity of CH_x on the catalyst surface were influenced strongly by the support. The influences of these supports on the activity of Ru were also well documented (*21*). However, little information on the comparative reactivity of adsorbed CO on these catalysts is available except for the pulse reaction (*9*) or RTD (*25*) (reductive temperature desorption) methods. It is necessary to correlate kinetically the reactivity of supposed intermediates with the rate of catalytic reaction.

The present authors have studied the $CO–H_2$ reaction over Rh/TiO_2 kinetically and spectroscopically to show that the highest catalytic activity achieved by particular reduction conditions is ascribed to the very high reactivity of adsorbed CO and the balanced adsorption of CO and H_2 on Rh modified properly by the titania support (*26–29*).

In the present paper, the authors studied the kinetics and *in situ* spectroscopic behavior to determine the significant effects of titania, alumina, and silica supports on the catalytic activity and selectivity of supported Rh in the $CO–H_2$ reaction. The observation of the reactivity of adsorbed CO with FT-IR is expected to provide valuable information on the interaction of the substrate with the catalyst during the reaction. This technique is suitable to measure the

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rapid change of respective bands in IR spectra by the aid of rapid scan (0.3 s for 400–4000 cm^{-1}) at the reaction temperature. Hence, it can provide the exact reactivity of respective adsorbed CO species, being superior to other techniques to measure the reactivity of surface substances such as flow and pulse reaction methods (*9*) or RTD (*25*) in this sense.

The adsorption of hydrogen on the catalyst which carried irreversibly adsorbed CO was also observed to evaluate the retardation role of the latter species.

EXPERIMENTAL

Catalysts

Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2 were prepared by the impregnation of $RhCl_3$ $3H_2O$ on TiO_2 (50 m^2/g, P-25, Aerosil, Inc.), Al_2O_3 (100 m^2/g, C type, Aerosil Inc.), and SiO_2 (300 m^2/g, A 300, Aerosil, Inc.), respectively, from its methanol solution (Rh, 4.6 wt% on the supports). These catalysts were reduced *in situ* with hydrogen (200 Torr) for 2 h in a temperature range of 473–773 K in a gas-circulating reactor and evacuated at 473 K for 1 h before the catalytic reaction. The reactor was equipped with a cold U tube (at 77 K) to trap water and HCl liberated during the reduction.

The amount of chlorine remaining on the catalyst after the reduction and evacuation was measured by X-ray fluorescence spectroscopy.

Reaction Procedure

The catalytic reaction was carried out at 473 and 523 K in a circulating reactor (volume 800 ml) with a fixed catalyst bed (0.2 or 0.5 g cat. diluted with 5 g SiC), through which a reactant gas mixture of CO and H_2 flowed.

Partial pressures of CO and H_2 ranged from 100 to 400 Torr and 200 to 600 Torr, respectively. During the reaction, products except for methane were trapped at 77 K. The reactant gases and methane were analyzed with a gas chromatograph (analyzing column, molecular sieve 13×, 1 m) by sampling at proper intervals. Trapped products were analyzed after the reaction with a gas chromatograph (analyzing column, Porapak Q, 1 m, for CO_2; VZ-10, 2 m, lighter hydrocarbons ($<C_7$)). No analysis was attempted for heavier hydrocarbons ($>C_7$). Reaction rates were calculated from the conversion of CO (below 10%). The product selectivity, olefin content (O.C.) and carbon balance (C.B.) are defined by Eqs. (1)–(3),

$$\text{selectivity } (C_i) = \frac{iC_i \text{ (mol)}}{\text{CO converted (mol)}} \times 100\ (\%) \qquad (1)$$

$$\text{O.C.} = \frac{\sum_{i=2}^{7} iC'_i \text{ (mol)}}{\sum_{i=2}^{7} (iC_i + iC'_i) \text{ (mol)}} \times 100\ (\%) \qquad (2)$$

$$\text{C.B.} = \frac{\sum_{i=1}^{7} (iC_i + iC'_i) + CO_2 + \text{CO remaining (mol)}}{\text{CO inlet (mol)}} \times 100\ (\%), \qquad (3)$$

where C_i and C'_i are moles of a paraffin and an olefin, both containing *i* carbon atoms, respectively. The heavier hydrocarbons ($>C_7$), which were neglected in the carbon balance calculation, may stay adsorbed on the catalyst or the reactor wall.

IR Measurements

The catalyst powders (100 mg) were molded into a disk (ϕ 20 mm) and reduced with H_2 *in situ* in an IR cell (CaF_2 window) connected to a gas-circulating line. IR spectra of adsorbed CO on these catalysts were measured at 473 K by FT-IR (FT-IR-03F, JEOL, Inc.). Reversible and irreversible adsorptions of CO were distinguished by evacuating for 1 h at an adsorption temperature of 473 K: The adsorption surviving on the catalyst after the evacuation is irreversible while the adsorption found in the presence of CO in the atmosphere is reversible.

The evacuation at the adsorption temperatures left the irreversibly adsorbed CO on the catalyst. Intensities of adsorbed CO, which was calculated as the summed area of all bands present, were proportional to the isotherms obtained by volumetric measurements with all catalysts regardless of whole or irreversible adsorption. The extinction coefficients for the summed area were 1.82×10^7 cm mol^{-1} for all catalysts within an experimental error of 10%.

Reactivity of the adsorbed CO was observed at 473 K by introducing hydrogen at 400 Torr at once to compare it to the rate of the stationary catalytic reaction. The first measurement of CO remaining on the catalyst was done 1 s after hydrogen was introduced. The composition of the gas phase was analyzed with a gas chromatograph and a quadrupole mass spectrometer (Anelva, Inc., TE-600) by occasional sampling. Only methane was produced as a product without desorption of CO. Amounts of the adsorbed CO reacted with hydrogen calculated from the decrease in the intensities of the IR bands using the adsorption coefficients above obtained agreed well the amount of methane produced.

The adsorption of CO from a reactant gas mixture (CO/H_2 = 200/400 Torr) was also monitored at 473 K by introducing the well-mixed gas on the catalyst in a manner similar to that described above.

Volumetric Measurement of Adsorption

Adsorption of CO and H_2 was measured volumetrically using 1 g of catalyst at room temperature, 473 and 523 K. Adsorption of hydrogen on Rh/SiO_2 and Rh/Al_2O_3 catalysts which carried irreversibly adsorbed CO was also observed at 473 and 373 K, respectively, where no significant reaction took place.

Measurements of the Amount and the Reactivity of Surface Carbon

Activity of the catalyst for the Boudouard reaction was observed at 473 and 523 K. The amount of surface carbon produced by the reaction was estimated from the amount of CO_2 produced during the reaction. The reactivity of the carbon produced at 523 K against H_2 (400 Torr) was measured at 473 and 523 K in the circulating reactor by analyzing the gas phase 10 s after the introduction of H_2. The amount and reactivity of irreversibly adsorbed CO estimated from IR measurement was taken into account when the reactivity of the carbon was measured.

RESULTS

Catalytic Activities of Rh Supported on Silica, Alumina, and Titania

Table 1 summarizes the initial reaction rates and selectivities over Rh supported on silica, alumina, and titania and reduced in the temperature range of 473–773 K for 2 h. Their catalytic performances at 473 and 523 K were markedly different as documented in previous literature (*2, 3, 8, 9, 19*).

Rh supported on silica gave the lowest activity and olefin content with the highest methane selectivity. A very small conversion was observed for 1 h at 473 K. The rate about doubled at 523 K. A higher reduction temperature increased the catalytic activity at 523 K to a certain extent.

Rh on alumina showed an intermediate activity and selectivity for C_2–C_4 at both temperatures. The olefin content was comparable to that of Rh on titania, although the selectivity for hydrocarbons other than methane was much lower. The catalytic activity increased significantly with increasing reduction temperature although the selectivity was essentially unchanged.

Rh on titania showed the highest activity and lowest selectivity for methane with marked production of C_2–C_7 hydrocarbons as previously reported (*26, 27*). The reduction a 673 K provided the highest activity (*26*).

The Boudouard reaction was slow at 523 K and negligibly slow at 473 K on all catalysts when only CO was introduced on the catalyst. The rates of the reaction at 523 K were 10, 3, and 0.1 mmol CO/g Rh · h, re-

TABLE 1

Effects of Support and Reaction Temperature on the Catalytic Activity and the Product Distribution of Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2 for $CO–H_2$ Reaction[a]

Support	Redn. temp. (°C)	Rate[b] at react. temp. (K)		Selectivity (%)				O.C.[c]	C.B.[d]	Remarks
		473	523	C_1	C_2 ~ C_4	C_5 ~ C_7	CO_2			
SiO_2	200		30	56	16	1	Trace	5	91	Present work
	400	20	40(0.1)[e]	48	10	1	Trace	5	87	
	500		50	33	15	Trace	Trace	4	81	
Al_2O_3	200		230	33	15	3	Trace	56	90	Present work
	400	40	270(3)[e]	46	23	5	Trace	57	88	
	450		330	41	27	5	Trace	67	91	
	500		550	41	19	6	Trace	50	90	
TiO_2	200		1200	30	47	18	3	66	99	Previous work
	400	180	1350(10)[e]	38	32	15	2	60	97	
	500		1000	30	33	17	3	57	96	

[a] Rh/TiO_2, Rh/Al_2O_3; 0.2 g; Rh/SiO_2, 0.4 g; $CO/H_2 = 200/400$ Torr.

[b] mmol CO/g Rh · h.

[c] Olefin content.

[d] Carbon balance.

[e] Rate of Boundouard reaction, CO = 200 Torr, at 523 K.

spectively, on Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2. Although this activity order of the catalysts was same as that for the $CO–H_2$ reaction, the rates of the former reaction were much smaller than those of the latter reaction on the same catalyst. During the reaction only very small amounts of surface carbon were detected after the evacuation of the gas phase.

Reaction Kinetics

Rate equations for the CO hydrogenation reaction on Rh catalysts at 523 K are summarized by Eqs. (4)–(6):

$$Rh/SiO_2:\ r = k_{Si}P_{CO}^{0.1}P_{H_2}^{0.6}$$
$$(k_{Si} = 0.72 \text{ mmol CO/g Rh} \cdot \text{h Torr}^{0.7}) \quad (4)$$

$$Rh/Al_2O_3:\ r = k_{Al}P_{CO}^{-0.2}P_{H_2}^{1.5}$$
$$(k_{Al} = 0.10 \text{ mmol CO/g Rh} \cdot \text{h Torr}^{1.3}) \quad (5)$$

$$Rh/TiO_2:\ r = k_{Ti}P_{CO}^{0.0}P_{H_2}^{0.9}$$
$$(k_{Ti} = 6.81 \text{ mmol CO/g Rh} \cdot \text{h Torr}^{0.9}). \quad (6)$$

The apparent rate constants are also given with the equations. Activation energy was 23 ± 1 kcal/mol between 473 and 523 K for all catalysts.

The reaction orders were quite variable depending upon the supports. Rh/SiO_2 showed half-order dependence on hydrogen, and the highest order on Rh/Al_2O_3 was as large as 1.5 while Rh/TiO_2 showed first order. Rh/Al_2O_3 showed a negative order in CO whereas the other catalysts were essentially zero order in CO. A retardation role of adsorbed CO is suggested on the former catalyst. It should be also noted that the smallest rate constant was observed on Rh/Al_2O_3.

The reaction orders in both H_2 and CO for Rh/TiO_2 were moderate and the rate constant was largest. These kinetic parameters may provide the largest activity under the present conditions.

Adsorption Ability

Adsorbed amounts of hydrogen at 473 and 523 K and of carbon monoxide at 473 K on Rh catalysts are summarized in Table 2,

TABLE 2

Adsorption of H_2 and CO on Rh Catalysts[a]

Catalyst	H/Rh			CO/Rh (473 K)		Dispersion[e] (%)	Remarks
	RT	473 K	523 K	Total[b]	(rev[c]/irrev[d])		
Rh/SiO_2	0.28	0.12	0.07	0.26	(0.04/0.22)	28	Present work
Rh/Al_2O_3	0.18	0.15	—	0.24	(0.13/0.11)	18	Present work
Rh/TiO_2	0.23	0.16	0.14	0.33	(0.12/0.21)	43	Previous work (*28*)

[a] Reduction condition, 673 K; 2 h.
[b] Equilibrium pressure of CO, 200 Torr.
[c] Equilibrium pressure of CO, 200 Torr, after evacuation at 473 K for 1 h.
[d] The difference between total and reversible adsorption.
[e] Estimated based on the adsorption amount of H_2 at room temperature.

where the adsorption of hydrogen at room temperature and the extent of metal dispersion calculated from the adsorption are included for comparison. Although the amount of hydrogen adsorption was in the order of $SiO_2 > TiO_2 > Al_2O_3$ at room temperature, the order changed to $TiO_2 > Al_2O_3 > SiO_2$ at elevated temperatures. A large decrease in the adsorbed amount on Rh/SiO_2 was noted as the temperature rose to 473 and 523 K, while Rh/Al_2O_3 showed a smaller decrease. Rh/TiO_2 showed a moderate decrease at higher temperatures. For all catalysts, the amounts of adsorbed hydrogen after the reaction were unchanged from those before the reaction within an experimental error (±3%).

Such results suggest that the dispersion of Rh metal estimated from the hydrogen adsorption at room temperature cannot be the most important parameter for the catalytic activity as reported previously (*26*). Furthermore, it must be noted that the adsorption at room temperature cannot always reflect the dispersion of Rh metal because of the catalyst–support interactions as reported previously (*26, 27*).

The adsorption ability of the catalyst for CO was in the order of $TiO_2 > SiO_2 \simeq Al_2O_3$ at 473 K. The adsorbed CO was divided into two categories, one desorbed (rev) under vacuum for 1 h at the adsorption temperature and the other stayed (irrev) on the catalyst. The ratios of rev/irrev were 0.04/0.22, 0.13/0.11, and 0.12/0.21, respectively, on Rh/SiO_2, Rh/Al_2O_3, and Rh/TiO_2. Thus, the catalysts showed rather contrasting abilities for the adsorption of CO, strongly depending upon the supports. It is noted that Rh/SiO_2 and Rh/TiO_2 carried similar amounts of irreversibly adsorbed CO while Rh/Al_2O_3 adsorbed half of that on the two former catalysts. It should be noted that Rh/SiO_2 adsorbed reversibly a very small amount of CO in comparison to two other catalysts. The difference in the adsorption ability does not fully explain the marked difference in the catalytic activity as often postulated (*5, 8, 9*).

IR Measurement of Adsorbed CO

IR spectra of adsorbed CO on the catalyst at 473 K are illustrated in Fig. 1, where the spectra in the presence of CO (200 Torr) (1a) and those after the evacuation (1b) are compared. The former conditions provided adsorption bands at ~1900, 2060, a pair of 2100 and 2030, and 2170 cm^{-1}, which have been ascribed to bridging (*30*), linear (*30*), twin (*30*), and physisorbed CO (*28, 30*) species, respectively. The last identification, distinguished from the species in the gas phase, is based on the observation that the intensity of the band decreased by the introduction of hydrogen even when CO pressure was kept constant (*28*).

Their intensities varied considerably, depending on the nature of the support. The

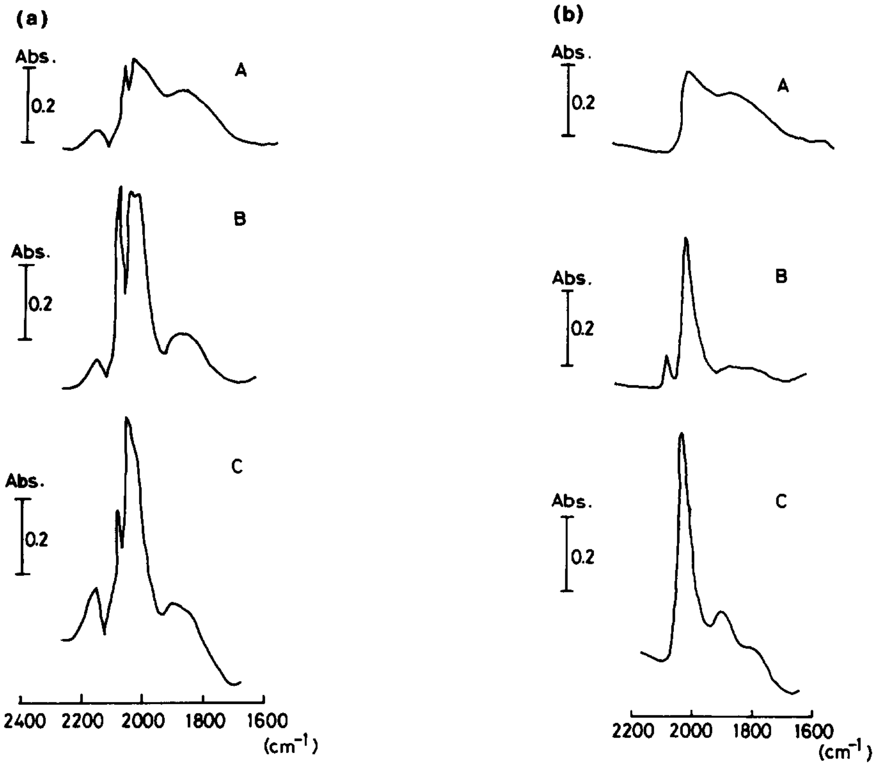

FIG. 1. (a) IR spectra of adsorbed CO at 473 K. (A) Rh/SiO_2; (B) Rh/Al_2O_3; (C) Rh/TiO_2. P_{CO} = 200 Torr. (b) IR spectra of irreversibly adsorbed CO at 473 K. (A) Rh/SiO_2; (B) Rh/Al_2O_3; (C) Rh/TiO_2.

adsorbed CO species at 473 K were quantified and illustrated in the units of CO molecule/Rh atom in Fig. 2. The total amount of adsorption was quite consistent with that measured volumetrically. Extinction coefficients for every form of adsorbed CO were reported to be neither equal nor constant on supported Pt (*31*). However, since several key assumptions were not proven, the intensity ratios of each peak area of adsorbed species, as the first approximation, are shown in Figs. 2–4 on the basis of that described under Experimental. The linear species were dominant on both Rh/Al_2O_3 and Rh/TiO_2; however, more bridging species were present on Rh/SiO_2. Very minor amounts of physisorbed species were observed on all catalysts when gas phase CO was present. Physisorbed and twin CO disappeared completely after evacuation except for the twin CO on Rh/Al_2O_3, a small amount of which remained after evacuation (Fig. 1b, B), where considerable amounts of linear and bridging species remained on the catalysts (Figs. 1b and 2), indicating that both reversibly and irreversibly adsorbed CO are included in the bands at 2060 and ~1900 cm^{-1}.

Rh/SiO_2 kept its major amounts of linear and bridging forms of adsorbed CO after the

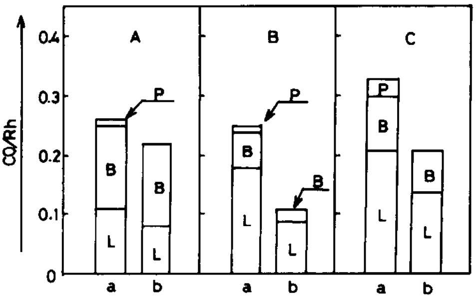

FIG. 2. Intensities of IR spectra of CO adsorbed on Rh catalysts at 473 K. (A) Rh/SiO_2; (B) Rh/Al_2O_3; (C) Rh/TiO_2. (a) CO, 200 Torr; (b) after evacuation at 473 K for 1 h.

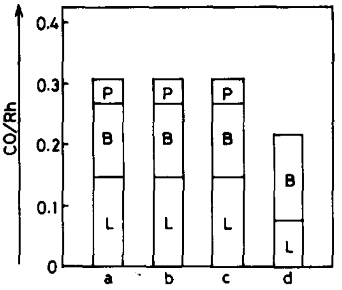

FIG. 3. Quantities of adsorbed CO species on Rh/SiO_2 in competitive adsorption with H_2 at 473 K (CO/H_2, 200/400 (Torr)). (a) 10 s; (b) 3–30 min; (c) 1 h; (d) after evacuation at 473 K for 1 h.

evacuation, whereas Rh/Al_2O_3 lost half of the adsorbed species, indicating again that irreversibly adsorbed CO was dominant on Rh/SiO_2. Rh/TiO_2 liberated 30% of the adsorbed species during evacuation. The ratios of linear and bridging forms were almost unchanged after the evacuation.

Competitive Adsorption of CO and H_2

The quantities of chemically and physically adsorbed CO observed by IR on Rh/SiO_2 and Rh/Al_2O_3 under competitive conditions with H_2 (pressures of CO and H_2 were 200 and 400 Torr, respectively) at 473 K are illustrated in Figs. 3 and 4. The total adsorption amount and the compositions of adsorbed species in the time course were markedly different due to the supports.

The copresence of hydrogen brought about no change at all in the positions of bands ascribed to adsorbed CO species in the absence of hydrogen, but changed their intensity significantly. On Rh/SiO_2, the total amount of adsorbed CO was constant regardless of the adsorption time after the introduction of the mixed gas. Comparison with the adsorption of CO only showed that the total amount increased due to a marked increase in physisorption with a slight decrease in chemically adsorbed CO. After 1 h of adsorption, evacuation for 1 h at 473 K left the same amount of irreversibly adsorbed CO and the same linear/bridging ratio to those obtained in the adsorption of CO alone. Throughout the competitive adsorption, no band due to hydrocarbons was observed.

Rh/Al_2O_3 adsorbed a small amount of CO after 10 s, and the adsorption increased 3 min to become constant for 1 h, suggesting that adsorption of H_2 was faster than that of CO at the very early stage and following replacement of adsorbed hydrogen with CO. The total amount of adsorbed CO after 3 min was same as that obtained by adsorption of CO alone; however, the bridging species peak intensity increased to twice that for CO adsorbed alone at the sacrifice of linear species. No hydrocarbon species were observed throughout the adsorption. After 1 h of competitive adsorption, the amount of irreversibly adsorbed CO on Rh/Al_2O_3 was roughly twice as large as that of CO adsorbed alone, being due to the marked increase in bridging species.

In contrast to these catalysts, as reported previously (*28*), the same adsorption of CO as that during its adsorption alone was observed on Rh/TiO_2 during an initial minute, and the adsorption amount of CO then decreased gradually to reach that of the stationary state after 6 min, when some bands ascribed to hydrocarbon intermediates appeared in the spectra.

Reactivity of Irreversibly Adsorbed CO with H_2

The time courses of conversion of irreversibly adsorbed CO with H_2 on three catalysts and their conversion rates are sum-

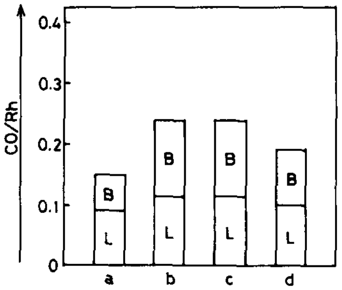

FIG. 4. Quantities of adsorbed CO species on Rh/Al_2O_3 in competitive adsorption with H_2 at 473 K (CO/H_2, 200/400 (Torr)). (a) 10 s; (b) 3–30 min; (c) 1 h; (d) after evacuation at 473 K for 1 h.

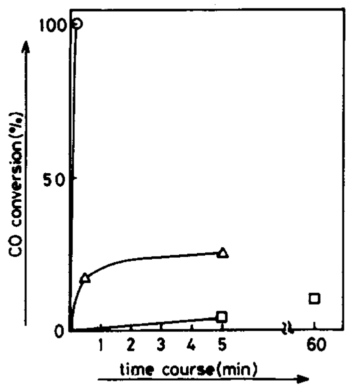

FIG. 5. Reactivity of irreversibly adsorbed CO with H_2 at 473 K. (□) Rh/SiO_2; (△) Rh/Al_2O_3; (○) Rh/TiO_2.

marized in Fig. 5 and Table 3, respectively. The reaction of all irreversibly adsorbed CO on Rh/TiO_2 with H_2 (400 Torr) was completed to give methane within 1 s at 473 K as reported previously (*28, 29*). A good material balance was obtained. No carbon was found on the catalyst, although hydrogen has been reported to accelerate the formation of surface carbon from CO over Rh (*7*), Pd, and Ru catalysts (*24, 32, 33*). The rate of the reaction at 473 K was estimated to be larger than 5×10^3 mmol CO/g Rh · h. The very high reactivity of CO species on Rh/TiO_2 should be noted. The rate of this conversion was much larger than that of the catalytic reaction at the same temperature on the same catalyst.

The conversion of irreversibly adsorbed CO on Rh/Al_2O_3 with H_2 was much slower at 473 K. Although no change was observed after 1 s, conversions of 17 and 26% for adsorbed CO (linear, twin, and bridging species) were obtained after 25 s and 5 min, respectively, the rest (74% of the adsorbed species) took ca. 1 h for their complete conversion. Thus, all adsorbed CO was converted into methane. From the conversion (17%) within 25 s, the rate was calculated to be 3×10 mmol CO/g Rh · h as shown in Table 3. Such a rate of the reactive portion at 473 K is comparable to that of the catalytic reaction on the same catalyst under stationary conditions. A very limited portion of this species is suggested to be the major reaction intermediate.

The conversion of irreversibly adsorbed CO on Rh/SiO_2 was much slower. Only 4% conversion of the adsorbed CO, mainly the bridging species, took 5 min, and another 10% was converted after 1 h. The rate was estimated to be 1 mmol CO/g Rh · h from the initial conversion within 5 min. Such a rate was much smaller than that of the catalytic reaction on the same catalyst at the same temperature. Therefore, the irreversibly adsorbed species may be excluded as the reactive intermediate on Rh/SiO_2.

The reactivities of irreversibly adsorbed species after competitive adsorption were found to be almost the same as those of CO adsorption alone on Rh/Al_2O_3 and Rh/SiO_2, whereas the former rate was smaller than the latter rate on Rh/TiO_2 mainly due to adsorbed hydrocarbon products (*28*).

Reactivity of Surface Carbon

The reactivity of surface carbon produced through the Boudouard reaction at 523 K was measured because the Boudouard reaction was very slow at 473 K. On Rh/TiO_2, the Boudouard reaction for 1 h produced surface carbon to the extent of C/Rh = 0.08. The carbon reacted with H_2 to be converted completely into CH_4 within 10 s at 523 K, the conversion rate being thus calculated to be 1×10^{-1} atom C/g Rh · h which was much smaller than the conversion rate of the irreversibly adsorbed CO at 473 K and that of the catalytic reac-

TABLE 3

Reactivity of Irreversibly Adsorbed CO with H_2 at 473 K

Catalyst	Rate[a]
Rh/SiO_2	1
Rh/Al_2O_3	4×10
Rh/TiO_2	5×10^3

[a] Rate; mmol CO/g Rh · h.

tion at 523 K. Although Rh/Al_2O_3 carried a surface carbon ratio of C/Rh = 0.13 after 1 h of the Boudouard reaction, the carbon did not react with H_2 within 10 s at 523 K and its complete conversion required more than 1 h. The amount of surface carbon produced from CO on Rh/SiO_2 was so small, C/Rh < 0.02, that even after 3 h its reactivity could not be measured. The surface carbon produced at 523 K did not exhibit any reactivity over all catalysts with H_2 at 473 K even after 20 h.

Adsorption of Hydrogen on the Catalysts Carrying Irreversibly Adsorbed CO

Table 4 summarizes the hydrogen adsorption abilities of Rh/Al_2O_3 and Rh/SiO_2, both of which carried irreversibly adsorbed CO (adsorbed at 473 K) on their surfaces. Rh/Al_2O_3 under such a state (CO/Rh = 0.11) adsorbed hydrogen to a H/Rh ratio of 0.2 at 373 K. This level of adsorption was similar to that on the same catalyst without irreversibly adsorbed CO, indicating little retardation of the irreversibly adsorbed CO species on the adsorption of hydrogen.

The Rh/SiO_2 carrying irreversibly adsorbed CO (CO/Rh = 0.22) adsorbed hydrogen to a ratio of H/Rh = 0.04 at 473 K. This level of adsorption was much less than that on the same catalyst without this CO species (H/Rh = 0.12). This amount is comparable to that of reversibly adsorbed CO. The irreversibly adsorbed CO may occupy sites for hydrogen adsorption on Rh/SiO_2.

Because of the high reactivity of the adsorbed CO with H_2 on Rh/TiO_2, the reaction took place even at 373 K so that the effects of irreversibly adsorbed CO on the adsorption of H_2 could not be measured above 373 K.

TABLE 4

Ability of Catalysts Carrying Irreversibly Adsorbed CO to Adsorb H_2[a]

Catalyst	H_2 adsorption temperature (K)	Irreversibly adsorbed CO[b] (CO/Rh)	H/Rh	
			With CO irrev	Without CO irrev
Rh/SiO_2	473	0.22	0.04	0.12
Rh/Al_2O_3	373	0.11	0.20	0.22

[a] Equilibrium pressure of H_2, 400 Torr.

[b] Irreversibly adsorbed CO at 473 K.

Chlorine on the Catalysts after Reduction and Evacuation

Chlorine derived from $RhCl_3$ may remain on the catalysts after the reduction and evacuation at elevated temperatures, thereby influencing the catalytic activity. The amounts of remaining chlorine were found to be 0.36, 0.35, and 0.34 (Cl/Rh atomic ratio) on Rh/TiO_2, Rh/Al_2O_3, and Rh/SiO_2, respectively. It should be noted that such a considerable amount remained on all catalysts.

DISCUSSION

The present study confirmed the strong influence of the supports on the catalytic activity of Rh for the $CO–H_2$ reaction as widely recognized with metal catalysts (*2–4, 8, 19*). The catalytic activities of Rh on TiO_2, Al_2O_3, and SiO_2 varied by two orders of magnitude at both 473 and 523 K. The highest activity of the TiO_2-supported catalyst under the conditions of the present study reflects kinetically the largest apparent rate constant, and zero and first orders in CO and H_2, respectively. Such reaction orders suggest no or only small retardation by CO and a favorable influence of hydrogen pressure on the catalyst. In contrast, retardation by CO on the Al_2O_3-supported catalyst and less influence of hydrogen pressure on the SiO_2-supported catalyst, in addition to very small rate constants on both catalysts, may partly explain their inferior activities in a kinetic sense.

The adsorption of reactants at room temperature has been compared to the catalytic activity in SMSI studies (*4–6*). However, the present study revealed that several adsorbed CO species are present on the catalysts and that these amounts varied, depending on the support, under the reaction conditions. The difference in dispersions calculated from the H_2 adsorption at room temperature was much smaller than the difference in the catalytic activities, as shown Table 2, suggesting that dispersion of Rh thus calculated is not the main factor for the activity. Hence, such a simple adsorption characterization may never be an adequate measure to evaluate the catalytic activity.

The amounts of both adsorbed CO and hydrogen on the catalysts, even at reaction temperatures, are rather similar when they are compared to the catalytic activities which are very different.

The Boudouard reaction is very slow and the reactivity of the surface carbon with H_2 is lower compared to that of the irreversibly adsorbed CO on the present catalysts at 473 K of this study. The formation of carbon from adsorbed CO is reportedly accelerated by hydrogen on some catalysts (*24, 32, 33*). However, it is again much slower than the catalytic reaction on the present Rh catalysts. These facts seem to argue against the carbon deposition or the reaction of a major deposited carbon species with hydrogen as important steps in the catalytic reaction at least at its initial stage at 473 K. The above discussion is also true at 523 K on Rh/Al_2O_3 and Rh/SiO_2. Although it is not easy to define the correct reactivity of surface carbon within a very short reaction time at 523 K on Rh/TiO_2, it appears smaller than that of irreversibly adsorbed CO. The Boudouard reaction is also slower than the catalytic reaction at the same temperature. Thus the surface carbon can be ruled out again as major reactive species, although Solymosi *et al.* (*8, 9*) related the reactivity of deposited carbon to the catalytic activity of Rh. A trivial assumption that a very minor portion of surface carbon produced from adsorbed CO reacts with hydrogen is never ruled out.

The reactivities of adsorbed CO and hydrogen may be of value for discussion to explain the activities of the present catalysts. Kinetic parameters such as rate constants and reaction orders reflect generally numbers of active sites, ratios of activated species of CO and H_2, and their extent of activation. First, the reactivity of irreversibly adsorbed CO on the TiO_2-supported catalyst, which is much higher than the rate of stationary catalytic reaction, indicates that they are active intermediates, as discussed in a previous paper (*30*). The species may be highly activated to provide the largest rate constant. Balanced adsorption abilities for both hydrogen and CO are another important factor in giving the largest catalytic activity with a small retardation by adsorbed CO species.

In contrast, the lower reactivity of irreversibly adsorbed species on Rh/SiO_2 rules out that they are active intermediates. Hence, the catalysis may be assumed to proceed through the reaction between some portions of the reversibly adsorbed CO and H_2, and the activation of the former species may be rather limited to give a smaller rate constant. The amount of reversibly adsorbed CO, especially the chemically adsorbed one, on the SiO_2-supported catalyst under reaction conditions is very limited (0.05 CO/Rh). Such a rather limited amount of reversibly adsorbed CO on the catalyst may cause the positive reaction order in CO. The dissociative adsorption of H_2 is assumed to be in equilibrium with gaseous H_2 to exhibit the reaction order of one-half in H_2. Irreversibly adsorbed CO, which reduces the amount of active sites left for reactive CO and H_2 species, may be saturated at lower CO pressure and be indifferent to the reaction order.

A very limited portion of the irreversibly adsorbed CO on Rh/Al_2O_3 is more reactive than that on Rh/SiO_2 and is comparable to the rate of stationary catalytic reaction. Hence, this portion may be the major active species. A very small amount of reactive CO species may be a reason for the smallest rate constant. Since the irreversibly adsorbed CO does not retard the adsorption of H_2, the competitive adsorption of reversibly adsorbed CO and H_2 may strongly influence the reaction orders and rate constant. The very preferential adsorption of CO may provide a negative order in CO and a larger order than unity in H_2.

According to the above discussion, the reactivity of active CO species is concluded to be most influential on the catalytic activity, although the reactivity of hydrogen, which is difficult to be estimated separately, may also be influential.

The present authors have no experimental basis on which to discuss the reaction steps between adsorbed CO and hydrocarbons. Some reactive CH_x species may be produced as intermediates (*16, 33*).

So far, the reactivity of CO species on the catalysts is not correlated to their structural parameters. The similar absorption positions in the IR spectra, regardless of the different catalytic activities obtained in the present study, suggest that their reactivities are rather indifferent to the strength of their C–O bond as detected by IR spectroscopy. The hydrogenation susceptibility of their carbon atoms is of value for further study.

The reactivity of adsorbed CO and the competitive adsorption of CO and H_2 to share the active sites, both of which are very influential on the catalytic activity and selectivity, should depend very much on the electronic state of Rh supported on these oxide supports. The electronic interaction between Rh and oxide is, thus, suggested to define the catalytic activity. The chemical natures of the support adjacent to the supported Rh particles after the catalyst reduction are one of the major factors for the catalyst performance (*31*). It is also possible for the support to participate directly in activation of reactants (*11, 12, 22, 23, 31*).

A considerable amount of chlorine (Cl/Rh = 0.35) was found remaining on all catalysts after the reduction at 673 K and evacuation at 473 K. The liberation of chlorine may further activate the metal and/or the support for their interaction. Definite discussion of interaction of this kind is beyond the scope of the present paper, although it may lead to a higher activity of the present catalysts.

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