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A Kinetic Study on the Catalytic Performance of Rh/TiO_2 Reduced at Different Temperatures in the CO–H_2 Reaction

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Catalytic CO–H_2 reaction on Rh/TiO_2 reduced at 200, 400, and 500°C (Cat-200, -400, -500) for 2 h was kinetically studied at 250°C using a circulating reactor and Fourier transform–infrared (FT-IR) spectroscopy to determine how Cat-400 exhibited the highest activity. The rate equation distinguished the best catalyst with zero and first orders in CO and H_2, respectively, from other catalysts with negative order in CO. The adsorption ability of the catalyst at 200°C was comparable to that of Cat-200, and two to three times larger than that of Cat-500, although the ability of Cat-200 was much larger at room temperature. Carbon monoxide adsorbed on the catalysts reversibly as well as irreversibly. IR spectroscopy revealed that the major form of irreversibly adsorbed CO was linear on Cat-200, whereas similar amounts of linear and bridge forms were observed on Cat-400 and Cat-500. These latter forms were highly reactive against hydrogen molecules when no carbon monoxide was present in the gas phase. Based on these results, the highest activity of Cat-400 is ascribed to rhodium metal modified by properly reduced TiO_2 to show the appropriate adsorption ability of carbon monoxide which least retards the activation of hydrogen according to first-order kinetics. Typical strong metal–support interaction decreases the catalytic activity by decreasing the active sites and strengthening the CO adsorption too much.

INTRODUCTION

The roles of catalyst supports in catalytic CO–H_2 reactions have been extensively investigated in recent years in order to design better catalysts (*1*). Titania is one of the most interesting supports that is used to modify the catalytic activity and selectivity of noble metals (*2–5*) through the strong metal–support interactions (SMSI) (*1*). However, the chemical features of SMSI have not been fully understood in spite of many extensive studies (*7–10*).

Hence few attempts to prepare better catalysts of higher catalytic activity per catalyst weight based on the SMSI concept have been reported (*4, 11*) although the superiority of titania over alumina and silica as the catalyst support has been recognized (*4, 5, 11*). Kikuchi *et al.* (*12*) reported recently that Ru supported on a rutile of large surface area showed a larger activity per weight in the SMSI state than in the non-SMSI state. Vannice (*13*) claimed that maximum activity of Ni/TiO_2 was obtained by addition of a small amount of Pt which helped the reduction of nickel at 200°C where the most preferable interaction between Ni and TiO_2 was expected.

The present authors (*14*) reported that the reduction temperature and time had significant effects on the catalytic activity of Rh/TiO_2 for the CO–H_2 reaction: The highest activity was obtained by the reduction at 400°C for 2 h, which appeared to induce proper metal–support interactions. The small difference in the adsorption abilities of these catalysts against O_2 at room temperature should be noted (*14*) since the very different abilities against H_2 and CO were observed at room temperature (*6*). Such results may suggest the necessity of a more precise understanding of the chemistry of the catalysts. The kinetic, adsorption, and spectroscopic (IR) studies of CO–H_2 reaction on Rh/TiO_2 reduced at different

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temperatures were attempted in order to reveal some kinetic characteristics of their active sites in this particular catalytic reaction. Some basic guidelines for the preparation of better catalyst relying on the support can be provided.

EXPERIMENTAL

Catalyst. Rh/TiO_2 was prepared by the impregnation of $RhCl_3 \cdot 3H_2O$ on TiO_2 (Aerosil P-25, 50 m^2/g; purity >97%, the major impurities reported by the supplier are $Al_2O_3 < 0.3\%$, $HCl < 0.3\%$, $MgO < 0.08\%$, $Na_2O < 0.05\%$, CaO trace, heavy metals < 5 ppm; crystal forms: 80% anatase and 20% rutile) using a methanol solution (Rh; 4.6 wt% on TiO_2). The catalyst was reduced with hydrogen of 200 Torr *in situ* using a circulating reactor, by raising the reduction temperature from room temperature to the prescribed one, holding the temperature for 2 h, and then cooling to 200°C where the catalyst was evacuated for 1 h before the reaction. Three sets of reduction conditions were examined according to a previous paper (*14*): 200°C–2 h (Cat-200), 400°C–2 h (Cat-400), and 500°C–2 h (Cat-500). After the reduction at all temperatures no changes in crystal composition were observed.

Reaction procedure. The catalytic reaction was carried out at 250°C in a circulating reactor (volume 800 ml) with a fixed catalyst bed (0.2 g cat. diluted with 2 g SiC), through which a reactant gas mixture of CO and H_2 was passed. Partial pressures of CO and H_2 were 100–400 and 200–600 Torr, respectively. During the reaction, all products except methane were trapped at liquid-nitrogen temperature. The reactant gases and methane were analyzed with a gas chromatograph (Molecular Sieve 13×, 1 m) by sampling at proper intervals. After the reaction, trapped products were analyzed with a gas chromatograph (Porapak Q 1 m, for CO_2; VZ-10 2 m, for hydrocarbons ($<C_7$)). No analysis was attempted against heavier hydrocarbons ($>C_8$). Reaction rates were defined as the initial reaction rates calculated from the conversion of CO (below 10%). The product selectivity, olefin content (O.C.), and carbon balance (C.B.) are defined by (conversions of CO fixed at about 30%),

selectivity (C_i)

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

O.C.

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

C.B.

$$= \frac{\sum_{i=1}^{7} (iC_i + iC_i') + CO_2 \text{ (mol)} + CO_{\text{remaining}} \text{ (mol)}}{CO_{\text{inlet}} \text{ (mol)}} \times 100\ (\%) \qquad (3)$$

and C_i, C_i', and $CO_{\text{remaining}}$ are the moles of paraffin and olefin containing *i* carbon atoms and unreacted CO, respectively. The value of carbon off-balance was assumed to correspond to heavier hydrocarbons (C_8–C_{20}) present on the catalyst or as liquids on the reactor wall. Such hydrocarbons were recovered from time to time by washing the catalyst and the reactor wall with THF after the reaction.

Adsorption and IR measurements. Adsorption of CO and H_2 on the catalyst was measured volumetrically at 200°C under conditions similar to those of the catalytic reaction. IR spectra of irreversively adsorbed CO on the catalyst were measured by FT-IR (FT-IR-03F, JEOL Inc.). The catalyst (100 mg) was molded into a disk (ϕ-20 mm) and reduced *in situ* in a IR cell (CaF_2 window) connected to the circulating glass line similar to the catalytic reactor. CO (200 Torr) was adsorbed at room temperature and 200°C. After the evacuation for 1 h at the adsorption temperatures, the IR spectrum was recorded at room temperature.

TABLE 1

Effects of CO Pressure on the Catalytic Activity of Rh/TiO_2[a] for CO–H_2 Reaction

Catalyst	Rate[b]	CO pressure (Torr)	Selectivity (C.E. %)					
			Cl	C2–C4	C5–C7	CO_2	O.C.[c] (%)	C.B.[d] (%)
Cat-200	1320	100	47	41	11	1	39	100
	1180	200	30	47	18	3	66	99
	950	400	31	45	17	2	28	98
Cat-400	1360	100	64	18	17	1	24	100
	1360	200	38	32	15	2	63	95
	1460	400	28	41	20	4	74	97
Cat-500	1290	100	58	30	11	2	26	100
	990	200	30	33	17	3	55	93
	770	400	25	35	17	2	81	90

[a] Catalyst = 0.2 g, H_2 = 400 Torr, reaction temperature = 250°C.

[b] mmol CO/g Rh · h.

[c] Olefin content.

[d] Carbon balance.

RESULTS

Kinetic Study

The effects of the partial pressures of CO and H_2 on the reaction at 250°C on three catalysts, Cat-200, -400, and -500, are summarized in Tables 1 and 2. Cat-400 provided the highest activities at 250°C under the present reaction conditions as reported in a previous paper (*14*) where the reaction temperature was 200°C. Although higher H_2 pressure increased the rates on all catalysts, the extent of their increase was highest with Cat-500 and smallest with Cat-200. In contrast to H_2, higher CO pressure decreased significantly the rates on both Cat-200 and Cat-500, whereas it increased the rate on Cat-400 very slightly. Logarithmic

TABLE 2

Effects of H_2 Pressure on the Catalytic Activity of Rh/TiO_2[a] for CO–H_2

Catalyst	Rate[b]	H_2 pressure (Torr)	Selectivity (C.E. %)					
			Cl	C2–C4	C5–C7	CO_2	O.C.[c] (%)	C.B.[d] (%)
Cat-200	760	200	23	34	15	4	81	95
	1180	400	30	47	18	3	66	99
	1530	600	39	41	15	5	56	100
Cat-400	760	200	15	23	17	11	76	86
	1360	400	38	32	15	2	63	95
	2170	600	38	45	16	1	34	100
Cat-500	410	200	17	27	24	7	84	92
	990	400	30	33	17	3	55	93
	1800	600	43	36	19	2	35	100

[a] Catalyst = 0.2 g, CO = 200 Torr, reaction temperature = 250°C.

[b] mmol CO/g Rh · h.

[c] Olefin content.

[d] Carbon balance.

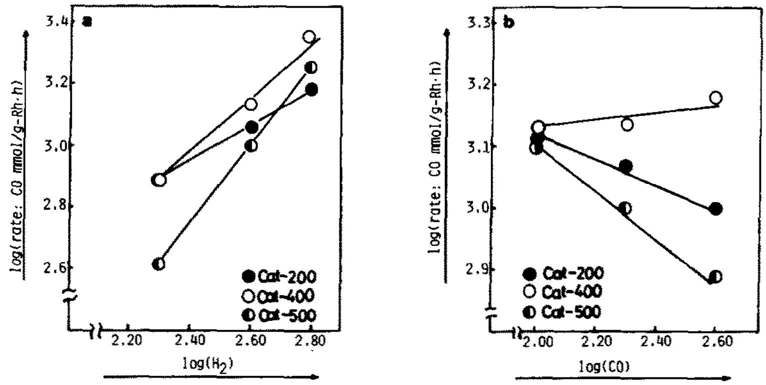

FIG. 1. Dependence of reaction rates over three catalysts on the partial pressure of H_2 (a) and CO (b). Reaction conditions: (a) P_{CO} = 200 Torr; P_{H_2} = 200, 400, 600 Torr; reaction temperature = 250°C. (b) P_{H_2} = 400 Torr; P_{CO} = 100, 200, 400 Torr; reaction temperature = 250°C. For further details, see Tables 1 and 2.

plots of these rates vs partial pressures on CO and H_2 exhibited respective linear correlations with all catalysts, as shown in Fig. 1, that define the following rate equations and apparent rate constants at 250°C.

Cat-200

$$r = k_{200} P_{CO}^{-0.2} P_{H_2}^{0.6}$$

$$(k_{200} = 93.4 \text{ mmol/g Rh} \cdot \text{h} \cdot \text{Torr}^2)$$

Cat-400

$$r = k_{400} P_{CO}^{0.0} P_{H_2}^{0.9}$$

$$(k_{400} = 6.18 \text{ mmol/g Rh} \cdot \text{h} \cdot \text{Torr}^2)$$

Cat-500

$$r = k_{500} P_{CO}^{-0.4} P_{H_2}^{1.3}$$

$$(k_{500} = 3.42 \text{ mmol/g Rh} \cdot \text{h} \cdot \text{Torr}^2).$$

The apparent rate constant of Cat-400 was much smaller than that of Cat-200, indicating that its highest activity under the present conditions is due to larger reaction orders in both CO and H_2.

Partial pressures of CO and H_2 also influenced the product distribution, although the differences among the catalysts used were rather small (Tables 1 and 2). Generally speaking, the increase of CO pressure decreased the selectivity of methane and carbon balance, but increased the selectivities for C_2–C_7 hydrocarbons and olefin content. Such effects of CO pressure were larger with Cat-400 and Cat-500 than with Cat-200.

The effects of H_2 pressure were generally more likely to increase the selectivity of methane as well as C_2–C_4 hydrocarbons and carbon balance by reducing the olefin content. Cat-200 was again the least influenced. Cat-200 exhibited the lowest selectivity of methane and the highest olefin content and carbon balance. The higher carbon balance suggests less formation of long chain hydrocarbons ($>C_8$) under the present conditions. In a particular run on Cat-400 (H_2 = 200 Torr), 10% of the long chain hydrocarbons were recovered by washing so as to improve the balance from 86 to 96%.

Adsorption

The adsorption isotherms of CO on Cat-400 at 200°C are illustrated in Fig. 2. The adsorption of CO was rapid for the initial few minutes and then slowed to the point of almost leveling off. In the first run (Fig. 2a), the adsorption increased with increasing pressure until 100 Torr over all catalysts. Cat-400 exhibited the largest amounts of adsorption. The adsorption was much lower in the second run after the evacuation at 200°C (Fig. 2b). It was saturated on both Cat-200 and Cat-400 at 100 Torr, whereas it

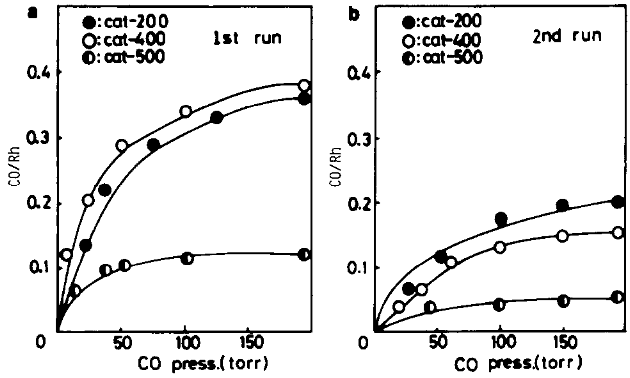

FIG. 2. Adsorption abilities of Rh/TiO_2 catalysts against CO.

was saturated at a pressure as low as 30 Torr on Cat-500. Based on the two isotherms, the amounts of reversible and irreversible adsorption were connected to those observed in the second run and the difference between the first and second runs, respectively, at 200 Torr.

Adsorption of H_2 saturated at about 200 Torr and was completely reversible at this temperature over all catalysts. Whole adsorption amounts of H_2 were calculated by extrapolation of the high-pressure linear part of the isotherm to zero pressure according to the literature (*6*).

The amounts of adsorption (H/Rh and CO/Rh) are summarized in Table 3. The amounts of adsorption at room temperature are also included in Table 3 for comparison as reported in the literature (*4*, *6*). First, it should be noted that relative adsorption abilities of the catalysts were very different at room temperature and 200°C. Cat-200, which was not in the SMSI state, adsorbed the largest amounts of CO and H_2 among the catalysts at room temperature. Cat-400, which adsorbed half of the amounts CO and H_2 adsorbed on Cat-200 at room temperature as reported, adsorbed similar amounts at 200°C. Cat-500 adsorbed much more at 200°C than at room temperature; the amounts of CO and H_2 adsorbed at 200°C were roughly one-half and one-third, respectively, those of Cat-200.

The adsorption equilibrium constants of

TABLE 3

Adsorption Abilities of the Catalysts against H_2 and CO

	H_2			CO		
	Amount (H/Rh)[a]		K_H[b] (200°C)	Amount (CO/Rh)[c]		K_{CO}[d] (200°C)
	RT	200°C		RT	200°C(rev./irrev.)	
Cat-200	0.54	0.17	1.3	0.52	0.31(0.14/0.17)	0.4
Cat-400	0.23	0.16	0.9	0.32	0.33(0.12/0.21)	0.3
Cat-500	0.05	0.13	0.6	0.08	0.12(0.03/0.09)	20

[a] Extrapolation of linear parts of isotherm to zero pressure.

[b] Equilibrium constant of hydrogen.

[c] P_{CO} equilibrium = 200 Torr.

[d] Equilibrium constant for reversibly adsorbed CO.

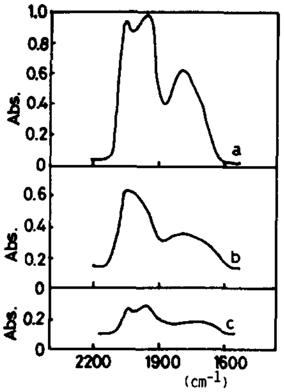

FIG. 3. IR spectra of CO irreversibly adsorbed at room temperature. (a) Cat-200, (b) Cat-400, (c) Cat-500.

the respective reversible adsorptions on the catalysts are summarized also in Table 3; the following Langmuir isotherm equation is used for the calculation:

$$\theta = \frac{KP}{1 + KP}. \tag{4}$$

The constant for H_2 was decreased by the higher reduction temperature, Cat-200 > Cat-400 > Cat-500. On the other hand, the equilibrium constant of CO on Cat-500 was much larger than those on Cat-200 and Cat-400. The constant for CO was much larger than that for H_2 on Cat-500, whereas those of CO were smaller than those of H_2 on the latter two catalysts. Reversibly adsorbed CO on Cat-500 may retard the adsorption of H_2.

The ratio of reversible/irreversible adsorption of CO as defined above was largest on Cat-200 and decreased with higher reduction temperature of the catalysts.

IR Spectra of Adsorbed CO

IR spectra of irreversibly adsorbed CO on three catalysts at room temperature and 200°C are illustrated in Figs. 3 and 4, respectively, where the background was subtracted. At room temperature, similar amounts of linear (2106–2000 cm^{-1}) and bridge forms (~1900 cm^{-1}, broad) of adsorbed CO were observed on all catalysts. The relative intensities of the CO band on these catalysts were consistent with the amounts adsorbed on them (see Table 3).

The major species of irreversible adsorption were different at 200°C on the catalysts. The linear form (2044 cm^{-1}) was dominant on Cat-200 with a very minor bridge form (a very weak band around 1900 cm^{-1}; linear/bridge rate: 9/1). In contrast, both linear and bridge forms were found on Cat-400 and Cat-500 (linear/bridge rate: 6/4).

The irreversibly adsorbed CO species on Cat-400 were hydrogenated completely within 1 min by the introduction of H_2 of 1 Torr at 200°C. The conversion rate of irreversibly adsorbed CO was much larger than that in the catalytic reaction under simulated pressures of CO (200 Torr) and H_2 (1 Torr). Higher reactivities of CO under similar conditions were observable on other catalysts. Retardation of CO is suspected in the catalytic reaction at very low hydrogen pressure.

DISCUSSION

The reduction condition of 400°C for 2 h to the Rh/TiO$_2$ catalyst was found to provide the highest catalytic activity for the hydrogenation of carbon monoxide through

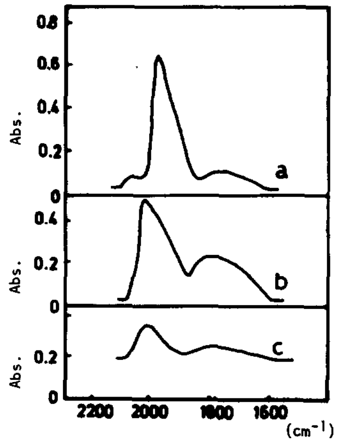

FIG. 4. IR spectra of CO irreversibly adsorbed at 200°C. (a) Cat-200, (b) Cat-400, (c) Cat-500.

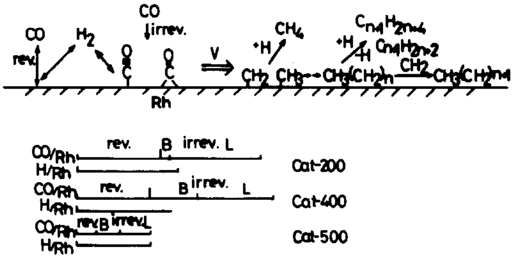

FIG. 5. Reaction scheme.

modification of the kinetics of the reaction. Based on the rate equation, the retardation influence on Cat-400 is not the key to its highest activity in spite of its rather small rate constant, indicating that the nature of its active sites is influenced strongly by the reduction conditions.

According to the reaction scheme illustrated in Fig. 5, the rate of the present catalytic reaction, i.e., that of CO consumption, is in principle a function of the number of active sites and the abilities for adsorption and activation against both hydrogen and carbon monoxide. The reaction of irreversibly adsorbed carbon monoxide with reversibly adsorbed hydrogen appears to be the rate-determining step for CO consumption because the rate of adsorption was very rapid in comparison with the catalytic reaction. The number of active sites can be counted by the adsorption of carbon monoxide and hydrogen under the reaction conditions. According to the literature (*4*, *11*, *13*), the number of active sites has been estimated from the extent of the adsorption of hydrogen at room temperature, suggesting a significant decrease in the SMSI state. However, the present study indicated definitely that Cat-200 and Cat-400 have a similar number of active sites at the reaction temperature in spite of the large difference at room temperature.

Half of the active sites on Cat-200 find it difficult to remain on the surface under the reaction conditions. In contrast, Cat-400 retained the same amounts of reactants at room and reaction temperatures. The number of active sites on Cat-500 is one-half those of Cat-200 and Cat-400, as the results of SMSI completion often postulate, although more adsorption takes place on this catalyst at the reaction temperature. Because it adsorbs the least Cat-500 has the lowest activity.

In order to count the exact number of working sites under the reaction conditions, the inhibition of carbon monoxide against hydrogen adsorption should be taken into account as the negative reaction order in carbon monoxide suggests, since the former reactant adsorbs more strongly on some catalysts. The amounts of adsorbed CO and H_2 and their forms are illustrated in Fig. 5. Reversibly adsorbed carbon monoxide may play major inhibition roles because irreversibly adsorbed carbon monoxide is the reaction partner. The very high reactivity of irreversibly adsorbed carbon monoxide also suggests the retardation effect of reversibly adsorbed CO. The largest equilibrium constant of CO adsorption on Cat-500 may most inhibit the adsorption of hydrogen, providing the smallest reaction order in CO and the highest one in H_2.

The difference in the equilibrium constants of CO adsorption of Cat-400 and Cat-200 was too small to explain the different values of their reaction orders. The marked difference is the ratio of linear/bridged forms for irreversibly adsorbed species as summarized in Fig. 5. The linear form dominates on Cat-200, whereas both forms are equally present on Cat-400. According to Norton *et al.* (*15*), the linear form adsorbs more strongly on the Pt(111) plane. The bridged form can give up the active site for the high pressure of hydrogen. As a consequence, no inhibition of carbon monoxide (zero order) and first order in hydrogen are induced on Cat-400. In contrast, hydrogen of higher pressure cannot replace the linear form on Cat-200, giving the order of 0.6 through its dissociative adsorption. More detailed spectroscopic studies at rapid scan are required to ascertain this hypothesis. Such FT-IR technique at rapid scan can also distinguish the reactivities of irreversibly adsorbed CO on the catalysts which reacted within 1 min.

Some differences in the product distribution on the present catalysts should also reflect the adsorption and reactivities of hydrogen and carbon monoxide as discussed above. However, as the Pettit mechanism suggests (*16*), the situation is too complex to be discussed at the present stage since the hydrogenation of carbon monoxide and methylene intermediates, the chain growth of methylene intermediates, and the desorption and readsorption of olefins at least take place competitively to define the selectivity.

The catalytic performance described above reflects without doubt the nature of the rhodium modified by the supporting titania as widely discussed in terms of the SMSI mechanism (*4, 5, 8–10*). Although the structural details of rhodium on titania are not in the scope of the present article, the fact that the proper reduction of Rh/TiO_2 provided the highest activity by modifying its ability to adsorb carbon monoxide and hydrogen suggests the importance of electronic interaction between rhodium and titania in defining the catalytic nature of rhodium. It is well known that as a support for rhodium, titania is superior to silica or alumina (*4, 5, 11, 17*). The concept of such chemical modification can provide a guideline for preparing better catalysts by defining kinetically what factors of the support bring about better catalyst performance.

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