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Hydrogenation of CO and CO_2 over Rhodium Catalysts Supported on Various Metal Oxides

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The formation of hydrocarbons in the reaction of $CO + H_2$ and $CO_2 + H_2$ was studied over rhodium catalysts supported on ZrO_2, Al_2O_3, SiO_2, and MgO. Among those catalysts, Rh on ZrO_2 was most active and Rh–MgO was least active for the above reactions. Over Rh–ZrO_2, the $CO_2 + H_2$ reaction took place even at 50°C, whereas the $CO + H_2$ reaction occurred only at a temperature higher than 130°C. The reaction of $CO_2 + H_2$ produced only methane at a temperatures up to 200°C, but a small amount of CO formed along with methane in the reverse water gas shift reaction above 200°C. In the case of the $CO + H_2$ reaction, the higher molecular weight hydrocarbons ($C_2 \sim C_4$) as well as CH_4 formed. The inverse kinetic isotope effect was observed in both reactions of $CO + H_2(D_2)$ and $CO_2 + H_2(D_2)$ over Rh–ZrO_2. However, the isotope effect was not observed in the $CO_2 + H_2(D_2)$ reaction over Rh–Al_2O_3 whose effect in the $CO + H_2$ reaction was still inverse. The activity for the $CO + H_2$ reaction over the oxidized Rh–ZrO_2 and Rh–Al_2O_3 was almost 2–10 times higher than that on the reduced catalyst. The reaction mechanisms of the above reactions are discussed.

INTRODUCTION

The synthesis of organic compounds from CO and H_2 mixtures over transition metal catalysts has been studied extensively (*1*). Although the catalytic hydrogenation of CO is a relatively simple reaction, its mechanism has been difficult to establish unambiguously. On the other hand, relatively little attention has been paid so far to the transformation of carbon in the form of CO_2 into hydrocarbons (*1–3*). Carbon dioxide can be regarded as a potentially cheap source of carbon if effective ways are discovered for the production of more valuable carbon-containing compounds. For the hydrogenation reactions of carbon oxides, transition metal catalysts are commonly used as supported type on metal oxides. This is done not only to disperse the metal component, thereby increasing the number of surface metal atoms available for catalysis, but also to stabilize these small metal crystallites after they are formed. However, once a metal is dispersed on a support, the possibility exists that metal–support interactions can occur to alter the catalytic behavior of the metal (*4–6*). In principle these changes can occur not only because of the formation of very small metal crystallites which may possess different electronic and geometric properties compared to large crystals, but also from metal–support interactions which can result in electron transfer between the metal and support. This paper reports studies of the reactions of CO and H_2, and CO_2 and H_2 to form hydrocabons and the support effect of rhodium catalyst for both reactions.

EXPERIMENTAL

Supported rhodium catalysts were prepared by impregnating ZrO_2, Al_2O_3, SiO_2, or MgO with an aqueous solution of $Rh(NO_3)_3$. After the evaporation of water, the catalysts were dried in air at 100°C for 24 hr and calcined at 500°C for 2 hr.

Zirconium oxide was prepared by the hydrolysis of $ZrOCl_2$ with aqueous ammonia, followed by calcining them at 500°C. Aluminum oxide and SiO_2 were obtained by

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calcining their hydroxides at 500°C which were prepared by the hydrolysis of $Al(NO_3)_3$ with aqueous ammonia and by the hydrolysis of ethyl orthosilicate, respectively. Magnesium oxide was obtained by heating $Mg(OH)_2$ at 500°C. The content of Rh was 2.3 wt% on the whole catalysts.

The reactions were carried out by using a closed recirculating system having a volume of 369 cm^3 and a flow reactor under 1 atm. The catalyst of 0.25 g was evacuated at 300°C and reduced at the same temperature for 2 hr in 80 Torr of H_2 for the recirculation reaction. A mixture of 15 Torr CO or CO_2 and 60 Torr $H_2(D_2)$ was allowed to react at various temperatures. In the flow reactor, the catalyst of 0.05 ~ 0.25 g was reduced at 300°C for 2 hr in H_2 stream. Carbon monoxide (Seitetsu Chemical Co., 99.9%) was passed through a trap maintained at −80°C to remove carbonyl compounds. The feed flow ratio (CO to H_2) was 3 : 20 and GHSV was 2760 hr^{-1} for the CO reaction. Some experiments were done under the flow ratio of 7(CO) : 20(H_2). Carbon dioxide diluted with argon (Hokusan Gas Co.) was used for the $CO_2 + H_2$ reaction. The ratio of CO_2 to H_2 was 1 : 10 and GHSV was 3600 hr^{-1} for standard experiments. The partial pressures of CO and CO_2 were changed in some experiments to obtain the partial pressure dependencies of the reaction rates. The activation energies were calculated from the results at low conversion (<12%). Products were analyzed by a gas chromatograph which was equipped with two 4 m columns of porapac R. One column was operated at room temperature for the separation of CO, CO_2, and CH_4, and another column was heated at 120°C and separated the higher hydrocarbon and water from the mixture of CO, CO_2, and CH_4. Adsorption experiments of CO or H_2 were carried out by a conventional BET apparatus. The adsorption uptake was determined as a function of pressure and the linear portion of the isotherm extrapolated to zero pressure to obtain the amount chemisorbed.

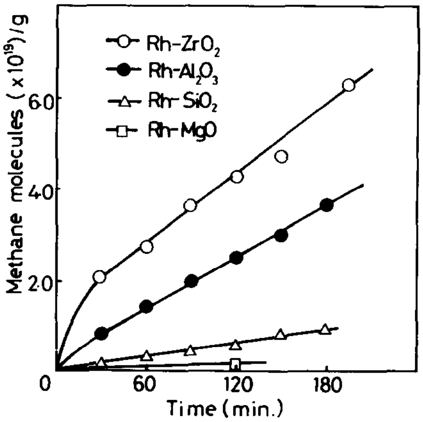

FIG. 1. Time courses of the $CO_2 + H_2$ reaction at 100°C in a recirculation system.

RESULTS

The time courses of the $CO_2 + H_2$ reaction over $Rh-ZrO_2$, $Rh-Al_2O_3$, $Rh-SiO_2$, and Rh–MgO are shown in Fig. 1. The catalytic activity was very sensitive to the support oxide used. Among those catalysts, Rh

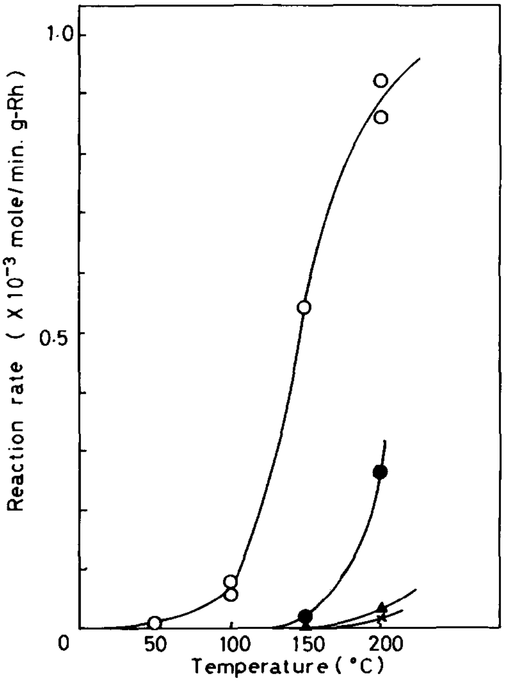

FIG. 2. Comparison of reaction rates of CO and CO_2 hydrogenation. ○, methane formation in $CO_2 + H_2$; ●, methane, ▲, C_{2+}, ×, CO_2 formation in $CO + H_2$.

supported on ZrO_2 exhibited the highest activity, while the lowest one was Rh–MgO in the reaction of $CO_2 + H_2$. The reaction product of the $CO_2 + H_2$ reaction was almost exclusively methane over the whole catalysts below 200°C, but a small amount of CO formed along with CH_4 at a temperature higher than 200°C. In a recirculation reaction, as shown in Fig. 2, the measurable reaction of $CO_2 + H_2$ took place at a temperature as low as 50°C. However, the CO + H_2 reaction occurred only above 130°C. The product of the CO + H_2 reaction was exclusively methane at 150°C as in the $CO_2 + H_2$ reaction. The rate of the CO + H_2 reaction was less than 1/20 of that of the $CO_2 + H_2$ reaction at this temperature. At higher temperatures (>200°C), the higher molecular weight hydrocarbons formed. The typical results for $CO_2 + H_2$ and CO + H_2 reactions obtained in a flow system are summarized in Table 1. Although the activ-

TABLE 1

Hydrogenation of CO and CO_2 over Rh Catalysts[a]

Catalyst	CO + H_2						$CO_2 + H_2$	
	Reaction temperature (°C)	Conversion (%)	Selectivity (wt%)				Reaction temperature (°C)	Conversion (%)
			C_1	C_2	C_3–C_4	CO_2		
Rh–ZrO_2	160	0.4	≃100	—	—	—	160	9.3
	180	1.0	≃100	—	—	—	180	23.0
	200	3.5	≃100	—	—	—	200	39.1
	200(ox)	(73.1)	(60.9)	(7.9)	(27.2)	(4.0)	220	67.0
		5.1	82.6	3.7	11.0	2.7	240	85.0
	220	13.5	86.1	2.7	10.2	1.0		
	220(ox)	(100)	(95.8)	(3.9)	(0)	(0.3)		
		27.2	77.4	3.1	18.3	1.2		
	220(ox)[b,c]	(100)	(97.2)	(2.4)	(0)	(0.4)		
	220(ox)[b,d]	(99.5)	(84.1)	(8.2)	(5.6)	(2.1)		
	290	100	61.4	11.7	12.1	14.8		
Rh–Al_2O_3	180	(0)	—	—	—	—	160	2.0
	180(ox)	(4.4)	(54.5)	(5.7)	(17.2)	(22.6)	180	4.0
		0.5	≃70	—	—	30	200	8.7
	200	0.8	95.0	0	0	5.0	220	22.0
	220	1.5	89.2	7.6	0	3.2	240	40.6
	220(ox)	(17.1)	(80.3)	(7.5)	(9.6)	(2.6)		
		3.6	73.2	7.3	14.6	4.9		
	240	5.2	92.9	5.2	0	1.9		
Rh–SiO_2	200	0.6	≃100	—	—	—	170	1.7
	220	1.0	94.0	0	0	6.0	180	2.5
	240	2.2	90.9	4.5	0	4.6	200	5.2
	260	6.1	90.2	3.3	0	6.5	240	19.0
Rh–MgO	300	0.5	≃100	—	—	—	260	0.6
	320	1.3	≃100	—	—	—	280	1.0
	340	2.8	96.4	3.6	—	—	300	2.6
							320	4.6

[a] Catalyst weight, 0.25 g; CO : H_2 = 3 : 20: CO flow, 1.34×10^{-4} mol/min.

[b] CO : H_2 = 7 : 20: CO flow, 3.125×10^{-4} mol/min. CO_2 : H_2 = 1 : 10: CO_2 flow, 0.89×10^{-4} mol/min. (ox), catalyst was preoxidized at 500°C.

[c] 1.5 min after the reaction started.

[d] 13.5 min after the reaction started. The initial activity is shown in parentheses.

TABLE 2

Activation Energies (kcal/mol)

Catalyst	Reaction	
	$CO + H_2$	$CO_2 + H_2$
$Rh\text{-}ZrO_2$	25.1	14.9
$Rh\text{-}Al_2O_3$	23.7	17.0
$Rh\text{-}SiO_2$	28.5	15.9
$Rh\text{-}MgO$	29.4	23.1

ity for the $CO + H_2$ reaction was lower than that for $CO_2 + H_2$, the order of activity was the same in both reactions: $Rh\text{-}ZrO > Rh\text{-}Al_2O_3 \geq Rh\text{-}SiO_2 \gg Rh\text{-}MgO$. In the reaction of $CO + H_2$, $C_2 \sim C_4$ products were obtained at a temperature higher than 220°C over $Rh\text{-}ZrO_2$. However, only a small amount of C_2 hydrocarbon formed at a temperature higher than 220°C in the cases of $Rh\text{-}Al_2O_3$ and $Rh\text{-}SiO_2$. Over the whole catalysts, ethylene formation was not observed and only ethane formed as a C_2 product, but propylene and butene formation along with propane and butane was observed in some cases as C_3 and C_4 products. The products higher than C_5 and oxygenated compounds were negligible over the whole catalysts. The activation energies of both reactions are shown in Table 2. The activation energies of the $CO_2 + H_2$ reaction were always less than those of the $CO + H_2$ reaction over the whole catalysts. The oxidized $Rh\text{-}ZrO_2$ and $Rh\text{-}Al_2O_3$ catalysts showed considerably higher catalytic activity and higher selectivity toward higher hydrocarbons in the $CO + H_2$ reaction than those over the original catalysts. The preoxidation of catalyst showed no effect for the reaction of $CO_2 + H_2$.

TABLE 3

H–D Isotope Effect

Catalyst	Reaction	
	$CO + H_2 (D_2)$	$CO_2 + H_2 (D_2)$
$Rh\text{-}ZrO_2$	$(k_H/k_D) = 0.67$	$0.72 \sim 0.83$
$Rh\text{-}Al_2O_3$	$(k_H/k_D) = 0.82$	1

TABLE 4

Dispersion of Rh Metal

Catalyst	H/Rh	CO/Rh
$Rh\text{-}ZrO_2$	0.51	0.74
$Rh\text{-}Al_2O_3$	0.60	0.56
$Rh\text{-}SiO_2$	0.27	0.26
$Rh\text{-}MgO$	0.27	0.21

The complete conversion of CO was attained over $Rh\text{-}ZrO_2$ but was not in the case of CO_2 over the same catalyst. Over the oxidized $Rh\text{-}ZrO_2$, the selectivity for higher hydrocarbons was very low in the complete conversion condition.

The H–D isotope effect was studied in the recirculation reactor over $Rh\text{-}ZrO_2$ and $Rh\text{-}Al_2O_3$. The result is summarized in Table 3. The inverse kinetic isotope effect was observed in the reactions of $CO + H_2$ and $CO_2 + H_2$ over $Rh\text{-}ZrO_2$, and in the reaction of $CO + H_2$ over $Rh\text{-}Al_2O_3$, but the effect was not observed in the reaction of $CO_2 + H_2$ over $Rh\text{-}Al_2O_3$.

The partial pressure dependencies of reaction rate with respect to CO and CO_2 were almost O order and 0.4 order, respectively, over $Rh\text{-}ZrO_2$.

The dispersion of Rh metal was estimated by the adsorption of H_2 and CO on each catalyst. The results are shown in Table 4. On $Rh\text{-}Al_2O_3$ catalyst, the adsorbed amount of H_2 was high compared to the other catalysts. However, the adsorbed amount of CO on $Rh\text{-}ZrO_2$ was larger than that of $Rh\text{-}Al_2O_3$. The dispersion of Rh metal on MgO and SiO_2 was low compared to $Rh\text{-}ZrO_2$ and $Rh\text{-}Al_2O_3$.

DISCUSSION

As a support of methanation catalyst, Al_2O_3 and SiO_2 are widely used. However, in this work, ZrO_2 was found to be superior to those oxides as the support of rhodium catalyst for the hydrogenation of CO and CO_2. Not only the activity but also the selectivity was different on Rh–ZrO_2 in the reaction of CO and H_2. Ichikawa (*7*) has published results indicating that Rh–ZrO_2 is a selective catalyst for the synthesis of ethyl alcohol from CO and H_2. Thus it would be interesting to study the surface character of Rh–ZrO_2 in relation to the reaction mechanism of CO and CO_2 hydrogenation.

As for the difference of catalytic activity, the dispersion of Rh metal would be important. The dispersion on the supports of SiO_2 and MgO is not high compared to other supports. However, it is impossible to explain the activity difference among those catalysts in terms of dispersion of Rh on the surface, because the turnover frequency of the CO hydrogenation reaction on the basis of H_2 adsorption over Rh–ZrO_2 is almost 10^3 times higher than that over Rh–MgO. The turnover frequency over Rh–Al_2O_3 is almost comparable to that over Rh–SiO_2 in both reactions of CO + H_2 and CO_2 + H_2. The adsorbed amount of CO on Rh–ZrO_2 considerably exceeds that of H_2 at room temperature in contrast with the other catalysts. On the infrared spectroscopic experiment (*8*), the formation of adsorbed CO_2 species on the Rh–ZrO_2 surface was observed when CO adsorbed on the reduced catalyst at room temperature but not on the surface of Rh–Al_2O_3, Rh–SiO_2, and Rh–MgO. This indicates that CO can easily dissociate on the surface of Rh–ZrO_2 even at room temperature but not on the other catalysts. Recently, experimental evidence supporting the idea that dissociation of CO to form carbon is an essential initial step in the synthesis of hydrocarbon has been presented (*9*). From these facts, it will be suggested that the dissociation of CO is a key to obtain a high catalytic activity of the hydrogenation of carbon oxides.

Upon the adsorption of CO_2 over Rh–Al_2O_3, the formation of linear CO species was observed in ir study (*10*) and the intensity of the CO band was enhanced strongly by the presence of hydrogen. This fact suggests that CO_2 hydrogenation proceeds via the dissociation of CO_2 to CO and O atom and then CO dissociates to carbon on the surface. However, CO did not form in the gas phase noticeably under the reaction condition. In this case, the hydrogenation of intermediate to hydrocarbon would be favorable compared to that in the presence of gas phase CO. This is one reason why CO_2 hydrogenation proceeds more easily than that of CO. We will discuss this point later.

As for the isotope effect in the hydrogenation of CO, several attempts have been made, but the results available thus far have been contradictory. In early studies by Jungers *et al.* (*11*) the hydrogenation of CO to CH_4 over Ni was observed to proceed more rapidly with D_2 than H_2. Recently Mori *et al.* (*12*) also observed the fact that methanation over Ni is 1.4 time faster with D_2 than with H_2. They proposed that the rate-limiting step of this reaction was the step of C–O bond cleavage of the hydrogenated species. Sakharov and Dokukina (*13*) also observed an inverse isotope effect for a Co/ThO_2/Kieselguhr catalyst. In contrast to these results, Dalla Betta and Shelef (*14*) reported that no isotope effect could be discerned for either CH_4 or total hydrocarbon formation over Ni/ZrO_2, Ru/Al_2O_3, or Pt/Al_2O_3. Based on this evidence it was suggested that CO dissociation is likely to be the rate-determining step in CO hydrogenation. More recently, Tamaru *et al.* (*15*) reported the existence of the inverse isotope effect over Ru/SiO_2 not only in the hydrogenation of CO but also in the hydrogenation of dissociated carbon, and they concluded that the rate-determining step was the hydrogenation of carbon formed by dissociative adsorption of CO. Kellner and Bell (*16*) also reported the inverse isotope effect over Ru catalyst. In this work, the inverse effect was observed over Rh–ZrO_2 in both reactions of CO + $H_2(D_2)$ and CO_2 + $H_2(D_2)$, but the effect was small in the case of CO_2 hydrogenation compared to the CO reaction. This fact would correlate with a lower energy barrier of intermediate hydrogenation in the CO_2 reaction compared with that in CO hydrogenation. Moreover, the isotope effect was nothing in the case of CO_2 hydrogenation over Rh–Al_2O_3. However, in the reaction of CO + H_2, the effect was still inverse but smaller than that on Rh–ZrO_2. From these facts, the inverse isotope effect seems to become larger when CO can dissociate easily on the surface. The inverse isotope effect can be interpreted by the stability difference between CD_x and CH_x species on the surface because of the thermodynamic stability of CD_x (*17*). If the rate-determining step involves hydrogenation of partially hydrogenated $CH_x(CD_x)$ species as reported by Happel *et al.* (*18*), the CD_x species must be abundant compared to the CH_x species and this increases the rate for the formation of deuterated products. From this point of view, the dissociation step to carbon is expected to become slower over Rh–Al_2O_3 compared to Rh–ZrO_2. This corresponds to the fact that the dissociation of CO is easier on Rh–ZrO_2 as observed by ir experiments (*8*). In particular, the dissociation step to carbon on Rh–Al_2O_3 in CO_2 hydrogenation would become an important step, because the isotope effect was not observed in this case in contrast with the reactions of CO and CO_2 over Rh–ZrO_2 and CO over Rh–Al_2O_3.

The activity difference between CO + H_2 and CO_2 + H_2 reactions has been noticed by several workers in relation to their reaction mechanism. Over Rh catalyst, it is known that the rate of CO_2 hydrogenation per unit surface area is considerably higher than that of hydrogenation of CO either on polycrystalline Rh (*2*) or on alumina-supported Rh (*3*) at around 170 ~ 250°C. This phenomenon was also observed over all catalysts in this work. Particularly over Rh–ZrO_2, CO_2 was hydrogenated to CH_4 even at 50°C, while CO reacted with H_2 at a temperatures higher than 130°C and the activation energy of the CO + H_2 reaction was almost a half of that of CO + H_2. When the catalysts of Rh–ZrO_2 and Rh–Al_2O_3 were oxidized, the rate of the CO + H_2 reaction increased remarkably. Sexton and Somorjai (*2*) reported the same phenomenon over Rh metal foil catalyst. On Rh–ZrO_2 or Rh–Al_2O_3, the amount of adsorbed CO which was observed in ir study (*8*) was reduced remarkably by the oxidation of catalysts. Thus, the increase of activity would be due to the decrease of CO coverage on the Rh surface. The reaction order with respect to CO was almost 0 order in this work and moreover the negative order was reported in some cases (*19*). This indicates that CO adsorbs very strongly on the Rh site and even acts as a poison for H_2 adsorption. However, the reaction order with respect to CO_2 was about 0.4 order. Thus, the adsorption of CO_2 on Rh is weaker than that of CO and will not act as a poison for H_2 adsorption; the hydrogenation step of intermediate will then be faster in the case of the CO_2 reaction than that in CO. Very recently, Solymosi *et al.* (3b) published a paper about the hydrogenation of CO_2 over Rh metal supported on TiO_2, Al_2O_3, or SiO_2. In the sense mentioned above, we generally agreed with their conclusion that the greater activity observed for CO_2 + H_2 as compared with CO + H_2 was ascribed to the lower concentration of adsorbed CO in the former case. However, we have a different opinion about the adsorption model of CO formed from CO_2 on the Rh surface which has been proposed by Solymosi *et al.* (*3b*). They assumed that the CO is bonded to Rh which is also linked to one or two H atoms to explain the shift of CO formed from CO_2 to lower frequency compared to that of pure CO. They stated that the dissociation of CO in these forms occurred more easily, as the electron transfer from H atom increased the Rh–C bond strength, and at the same time weakened the C–O bond. In our case, the difference in CO frequency was not discernible in both cases of CO_2 in the presence or absence of H_2 (*10*). Thus, we concluded the shift of CO frequency was only due to a weak coverage of CO on the surface.

Solymosi *et al.* also assumed that the carbon formed in the $CO_2 + H_2$ reaction was less likely to accumulate and age, which would lead to less reactive forms of carbon. As mentioned above, CO hydrogenation showed a larger inverse isotope effect in both cases of Rh–ZrO_2 and Rh–Al_2O_3 than in the CO_2 reaction. This would be due to the increase of the energy barrier in the hydrogenation step of intermediates in the CO reaction compared to that in CO_2 as assumed by Solymosi *et al.* (*3b*), because CD_x species should be accumulated in the prestep of the rate-limiting barrier step.

The activity of oxidized catalyst was enhanced remarkably in the CO reaction and gradually decreased due to the reduction of catalyst in a flow of CO and H_2 mixture and reached a steady state within 40 ~ 60 min, but was still higher than that on the reduced surface. In this case, we can deny the possibility that CO first converts to CO_2 over the surface and then CO_2 reacts with H_2 to form methane, because the increment of formed methane and CO_2 far exceeds the amount of oxygen on the surface, and the selectivity toward the higher hydrocarbons ($C_2 \sim C_4$) increased compared to that on the prereduced surface. This is in clear contrast with the fact that only CH_4 formed in the case of the $CO_2 + H_2$ reaction. However, on the complete conversion of CO over oxidized Rh–ZrO_2, only a few percent C_2 hydrocarbon formed with a large amount of CH_4. When the conversion decreased slightly, but still exceeded 99% conversion, the higher hydrocarbon ($C_2 \sim C_4$) appeared in the products. When the flow of CO was stopped in this stage, the products of $C_2 \sim C_4$ hydrocarbons disappeared instantly but CH_4 still formed even 30 min after stopping of the CO flow. However, on the surface which had been prereduced, $C_2 \sim C_4$ hydrocarbons formed even under the condition of complete conversion of CO. These facts would indicate that the propagation mechanism of hydrocarbon was different on the oxidized surface from that on the prereduced surface. Three types of propagation mechanisms have been proposed (*20*): (i) polymerization of CH_x units or hydrogenation of polymerized carbon atom chains, (ii) dehydrocondensation of alcohol-like units, and (iii) repeated CO insertion to M–CH_x species. Ekerdt and Bell (*21*) reported that ethane and propane along with CH_4 formed even in the absence of chemisorbed CO, and concluded that propagation proceeds by polymerization of methylene groups to form alkylidenes which in turn undergo rearrangement to form olefins or hydrogenation to form alkanes. In our work, over a prereduced surface, mechanism (i) can explain the experimental results, but the CO insertion mechanism will be likely over oxidized catalyst, because the propagation did not proceed under the condition of complete hydrogenation of adsorbed CO, but the products of $C_3 \sim C_4$ suddenly appeared along with the appearance of a small amount of CO in the gas phase. Probably, the nondissociated CO weakly adsorbed on Rh is important for the propagation of a chain on the oxidized surface.

REFERENCES

1. Vlasenco, V. M., and Yuzefovich, G. E., *Russ. Chem. Rev.* **38,** 728 (1969).

2. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46,** 167 (1977).

3. (a) Solymosi, F., and Erdöhelyi, A., *J. Mol. Catal.* **8,** 471 (1980); (b) Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981).

4. Sinfelt, J. H., *Catal. Rev.* **3,** 175 (1969).

5. Slinkin, A. A., and Fedorovskaya, E. A., *Russ. Chem. Rev.* **40,** 860 (1971).

6. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).

7. Ichikawa, M., *J. C. S. Chem. Commun.* 566 (1978).

8. Iizuka, T., Tanaka, Y., and Tanabe, K., *J.C.S. Farad. Trans.* **1,** in press.

9. Araki, M., and Ponec, V., *J. Catal.* **44,** 439 (1976).

10. Iizuka, T., and Tanaka, Y., *J. Catal.* **70,** 449 (1981).

11. Luytens, L., and Jungers, J. C., *Bull. Soc. Chim. Berg.* **54,** 303 (1945).

12. Mori, T., Masuda, H., Imai, H., Miyamoto, A., and Murakami, Y., *Shokubai* **22,** 7 (1980).

13. Sakharov, M. M., and Dokukina, E. S., *Kinet. Katal.* **2,** 710 (1961).

14. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **49,** 383 (1977).

15. Kobori, Y., Naito, S., Onishi, T., and Tamaru, K., *J. C. S. Chem. Commun.* 92 (1981).

16. Kellner, C. S., and Bell, A. T., *J. Catal.* **67,** 175 (1981).

17. Ozaki, A., "Isotopic Studies of Heterogeneous Catalysis. p. 170. Kodansha Academic Press, Tokyo, 1977.

18. Happel, J., Fthenakis, V., Suzuki, I., and Ozawa, S., Proc. 7th Int. Congr. Catal. A-37 (1980).

19. Vannice, M. A., *J. Catal.* **37,** 462 (1975).

20. Ponec, V., *Catal. Rev.* **18,** 151 (1978).

21. Ekerdt, J. G., and Bell, A. T., *J. Catal.* **58,** 170 (1979).