JOURNAL OF CATALYSIS 95, 41–48 (1985)

Effect of Potassium and Phosphorus on the Hydrogenation of CO over Alumina-Supported Ruthenium Catalyst

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Received September 17, 1984; revised March 15, 1985

The effects of additives such as K, B, and P to Ru/Al_2O_3 catalysts were investigated with regard to the adsortion and the catalytic hydrogenation of CO. Thermal desorption of CO and infrared bands of CO adsorbed indicated that the addition of K increased the strength of CO adsorption, by enhancing the back-donation from Ru to CO. As for the catalytic hydrogenation of CO, the addition of K significantly increased the olefin/paraffin ratios in product hydrocarbons and suppressed the methane formation, while the catalytic activity decreased by the addition. On the other hand, the addition of P or B brought about opposite changes in both CO adsorption and CO hydrogenation. The relationships between the electronic state of Ru and the activity and selectivity for this reaction have been interpreted on the basis of the inhibiting effect of strongly adsorbed CO for the hydrogenation.

INTRODUCTION

Chemical modification of catalysts by additives often brings about significant increases in the catalytic activity and selectivity, e.g., for the synthesis of methanol (*1*) or ethanol (*2–4*) from CO and H_2. In Fischer–Tropsch synthesis, alkali metals are effective additives for the formation of olefinic hydrocarbons over Fe (*5, 6*), Ni (*7*), and Ru (*8, 9*) catalysts. Recent studies showed that the deposition of alkali metals to single crystals of metals such as Ni and Fe resulted in (i) increase in the strength of adsorption of CO and (ii) increase in the rate of its dissociation (*7, 10*). Oxygen, carbon, sulfur, and phosphorus also affected the CO adsorption, where the effects of these materials were opposite to alkali metals (*11–14*). However, as for supported metal catalysts, there are very few instances in which these effects were studied concurrently.

In the present work, we studied the effects of the addition of K, B, and P to Ru supported on Al_2O_3 on both the adsorption and the hydrogenation of CO. Since an intimate contact between additives and metals is likely important to enhance their effects (*6, 8*), highly dispersed Ru catalysts prepared from $Ru_3(CO)_{12}$ were used to obtain better contact.

EXPERIMENTAL

Catalyst. γ-Al_2O_3 (Reference Catalyst of Catalysis Society of Japan, ALO-4, 170 $m^2\ g^{-1}$) was used as a support. Al_2O_3 was pretreated with K, P, or B as follows. An appropriate amount of K_2CO_3, P_2O_5, or H_3BO_3 was dissolved in water to wet completely Al_2O_3. After impregnation with the solution at room temperature, they were dried at 100°C and calcined in air at 500°C for 10 h. Two series of Ru catalysts were prepared. The first series was prepared by adsorption of $Ru_3(CO)_{12}$ as described previously (*15*). These catalysts contained, in addition to 2.5% Ru, 1 or 3% K, 0.9% P, or 0.8% B by weight. These are denoted as $Ru/Al_2O_3(A)$ or Ru/1% K-$Al_2O_3(A)$, etc. The second series was prepared by impregnating an aqueous solution of $RuCl_3 \cdot 3H_2O$ (Koso Chemicals) onto Al_2O_3 or Al_2O_3 pre-

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0021-9517/85 $3.00

treated with K. These catalysts are denoted as Ru/Al_2O_3(B) and Ru/1% K-Al_2O_3(B).

Procedure. The hydrogenation of CO was carried out in a continuous flow reactor (glass tubular reactor, 12 mm diam.). The catalyst of 0.2–1.0 g was reduced at 450°C for at least 2 h in flowing H_2 (1 atm). After the sample was cooled to 260°C in H_2, a 1 : 2 mixture of CO and H_2 which was purified by passing through a molecular sieve 5A column, was fed over the catalysts under 1 atm pressure. Gas chromatographic measurement of CH_4 and CO using a molecular sieve 5A column was made at 15-min intervals. At the initial stage of the reaction, the rate of methane formation decreased with time. A nearly steady rate (about $\frac{2}{3}$ that of the initial value) was obtained after about 1 h. The analysis of the entire product hydrocarbons was carried out after 2 h by using an FID gas chromatograph (Yanagimoto GC-2800). C_1–C_4 hydrocarbons were analyzed by a VZ-10 column, of which the temperature was raised from 40 to 80°C at 2°C/min. For the analysis of C_5–C_{12} hydrocarbons, a silicon SE-30 column (Gasukuro Kogyo, Inc.) was used, and the column temperature was increased from 30 to 150°C at 5°C/min. CO_2 was analyzed by using a Porapak Q column.

Amounts of H_2 and CO chemisorption were measured with a conventional high vacuum system at room temperature as described previously (*15*).

Infrared measurements. Forty milligrams of catalyst which was pressed into a 2-cm-diameter wafer was used for the infrared measurement. Apparatus and procedure were the same as described previously (*15*). In thermal desorption of CO adsorbed, the catalyst was exposed to CO (20 Torr; 1 Torr = 133.3 Pa) at room temperature for 30 min, and then the temperature was raised stepwise, holding at each temperature for 1 h. The amount of CO adsorbed was estimated from the integrated IR bands. The amounts of carbon deposited on the surface during thermal desorption were measured in separated runs as follows. The catalyst (0.5 g) was exposed to CO (20 Torr) for 30 min, and was evacuated at room temperature. Then the temperature was raised to 200°C under vacuum. After that, the surface CO and C were oxidized (80 Torr O_2) to CO_2 at 400°C and determined volumetrically. CO, which remained undissociated, was estimated from the infrared band. Then, the amounts of carbon formed by dissociation of CO were estimated by the difference of these two values. In the case of infrared measurement in the presence of reactant gas, a mixture of CO (60 Torr) and H_2 (200 Torr) was introduced to the sample heated at 250°C. The spectral changes were followed for 2 h. Then the sample was cooled to desired temperatures. After it was allowed to stand for 1 h at each temperature, the spectra were recorded. Relative absorption coefficient at each temperature was estimated as follows: Ru/Al_2O_3(A) reduced at 400°C was exposed to CO at 25°C, and was evacuated at 250°C for 2 h. After the spectra of CO adsorbed were recorded at 250°C, the sample was cooled to each temperature under vacuum. By assuming that the absolute amount of CO adsorbed was constant during this procedure, the relative absorption coefficient at each temperature can be estimated by integrating the absorbance of the band of CO. The relative absorption coefficient was changed from 1.00 to 0.76 in the range of 25 to 250°C.

RESULTS

Adsorption of H_2 and CO. Uptakes of H_2 or CO on fresh catalysts (prereduced at 450°C) are summarized in Table 1, together with their surface areas. The amounts of chemisorption are expressed by H/Ru or CO/Ru which is "the number of hydrogen atoms or CO molecules chemisorbed divided by the number of Ru atom loaded." Addition of 1% K and 0.9% P, where K or P-to-Ru ratio was 1 in atomic ratio decreased H/Ru to some extent, and the addition of 3% K or 0.8% B decreased the ratio

TABLE 1

Chemisorption of H_2 and CO on Fresh Ru Catalysts

Catalyst	Additives	H/Ru	CO/Ru	d (Å)	SA^a (m^2 g^{-1})
$Ru/Al_2O_3(A)^b$	None	0.80	1.00	10	170
	K (1 wt%)	0.69	0.83	12	150
	K (3 wt%)	0.47	0.18	18	180
	P (0.9 wt%)	0.61	1.07	14	134
	B (0.8 wt%)	0.37	0.18	22	166
$Ru/Al_2O_3(B)^c$	None	0.21	0.32	40	170
	K (1 wt%)	0.21	0.30	40	150

[a] Surface area of catalyst measured by BET method using N_2.

[b] Prepared from $Ru_3(CO)_{12}$.

[c] Prepared from $RuCl_3$.

considerably. By assuming that a hydrogen atom is adsorbed on an Ru atom at 1 : 1 stoichiometry, the average particle sizes of Ru estimated from the uptakes of hydrogen were less than about 20 and 40 Å for a series of $Ru/Al_2O_3(A)$ and $Ru/Al_2O_3(B)$, respectively.

Hydrogenation of carbon monoxide. The dependence of the conversion on W/F was measured for these catalysts, where W is the catalyst weight and F is the flow rate of CO. When W/F was less than 60 g · h · (CO mol)$^{-1}$, the conversion based on CO increased almost linearly with W/F. So the activity of catalyst was compared in this range of W/F, where the conversion was less than 20%. Distribution of carbon number in the products was almost independent of W/F. The detailed product distributions at the conversion level of 8–13% are presented in Table 2, except for Ru/3% K-Al_2O_3(A) in which the conversion was 2.5%. In all cases, the fraction of CO_2 in the products was less than 3 mol% and the carbon balance between the inlet and outlet of reactor was usually more than 95% at the stationary state.

In the case of $Ru/Al_2O_3(A)$, the addition of 1 and 3% K decreased the rate to about $\frac{1}{3}$ and $\frac{1}{100}$, respectively. In contrast, the rate somewhat increased by the addition of P or B. As for the selectivity, it was found that the addition of K suppressed the formation of methane; the fraction of methane was 27%, or 15% over Ru/1% K-Al_2O_3(A) or Ru/3% K-Al_2O_3(A), while 45% methane was formed over $Ru/Al_2O_3(A)$. Furthermore, olefin/paraffin ratios in C_2, C_3, and C_4 hydrocarbons greatly increased upon the addition of K. A similar effect of K was observed for $Ru/Al_2O_3(B)$ catalyst, of which

TABLE 2

Activity and Selectivity in Hydrogenation of CO over Ru Catalysts[a]

Catalyst	W/F^b	Conv. (%)	$Rate^c$	Selectivity^d (wt%)										α^e
				C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	
$Ru/Al_2O_3(A)$	19.9	12.6	6.3	45.8	11.3 (0.2)	13.2 (1.7)	10.9 (3.6)	6.7	4.4	2.6	2.2	1.9	0.9	0.54
Ru/1% K-Al_2O_3(A)	54.2	13.6	2.5	26.9	8.7 (0.7)	20.4 (9.7)	16.6 (7.6)	10.3	7.1	5.0	3.8	2.3	1.0	0.65
Ru/3% K-Al_2O_3(A)	400	2.5	0.06	14.7	6.8 (10.2)	14.3 (17.7)	15.7 (17.0)	11.3	10.4	9.4	9.6	7.8	0	0.73
Ru/P-Al_2O_3(A)	10.8	7.7	7.1	47.3	12.7 (0.1)	15.5 (0.4)	10.2 (1.0)	6.1	3.5	2.4	1.4	1.0	0.1	0.48
Ru/B-Al_2O_3(A)	10.6	8.9	8.4	48.1	11.0 (0.1)	16.1 (1.4)	10.4 (2.6)	5.6	3.6	2.0	1.8	1.0	0.1	0.48
$Ru/Al_2O_3(B)$	24.0	9.7	8.0	46.8	11.2 (0.1)	15.5 (1.6)	11.5 (3.4)	6.3	3.7	2.2	1.3	0.6	0.1	0.53
Ru/1% K-Al_2O_3(B)	48.8	12.9	5.3	40.8	10.5 (0.2)	17.5 (4.6)	16.4 (4.9)	7.8	5.1	3.1	2.2	1.0	0.1	0.58

[a] Reaction conditions: 260°C, 1 atm, $H_2/CO = 2$.

[b] g-cat h (CO-mol)$^{-1}$.

[c] 10^{-3} mol (CO) g^{-1} h^{-1}.

[d] Figures in parentheses are olefin/paraffin ratio.

[e] Propagation probability.

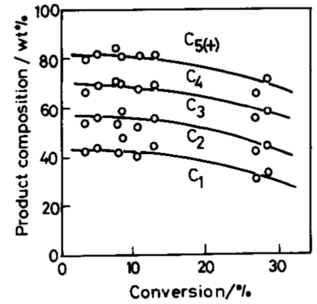

FIG. 1. Dependence of product distribution on the conversion in the CO hydrogenation over Ru/Al_2O_3(A) (T = 260°C, P = 1 atm, H_2/CO = 2).

the dispersion was lower, but the effects were less significant.

The molecular weight distribution of hydrocarbons followed Schultz–Flory distribution law (the propagation probability, α, calculated from the slopes and intercepts agreed essentially). As shown in Table 2, α increased from 0.54 to 0.65 by the addition of 1% K, but decreased to 0.48 by the additions of P and B to Ru/Al_2O_3(A).

The product distributions of carbon number are shown as a function of conversion in Figs. 1, 2, and 3 for Ru/Al_2O_3(A) and Ru/1% K-Al_2O_3(A) and Ru/P-Al_2O_3(A), respectively. In all cases, the distribution did not change much with conversion, where a slight shift toward higher hydrocarbons was observed at high conversions for the former and a small deviation at low conversions for the latter. In cases of Ru/Al_2O_3(B) and Ru/1% K-Al_2O_3(B), the change was also small.

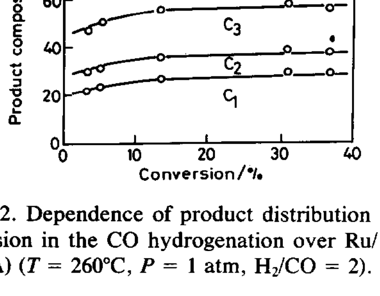

FIG. 2. Dependence of product distribution on the conversion in the CO hydrogenation over Ru/1% K-Al_2O_3(A) (T = 260°C, P = 1 atm, H_2/CO = 2).

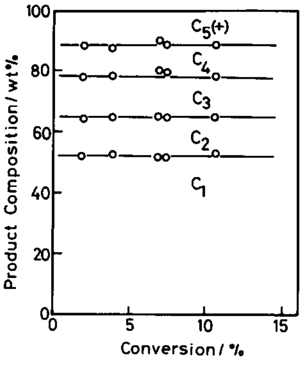

FIG. 3. Dependence of product distribution on the conversion in the CO hydrogenation over Ru/P-Al_2O_3(A) (T = 260°C, P = 1 atm, H_2/CO = 2).

In Fig. 4, turnover frequency (abbreviated as TOF) of CO hydrogenation and the olefin/paraffin ratios in C_2, C_3, and C_4 hydrocarbons are shown as a function of the K content in Ru/K-Al_2O_3(A), where the conversion level was 3–7%. The TOF significantly decreased as the K content increased, and the olefin/paraffin ratios increased markedly.

The effects of additives are compared in Fig. 5. In this figure the propene/propane ratios are plotted against conversion. In the case of Ru/Al_2O_3(A), as the conversion increased from 3 to 28%, the ratio lowered from 4 to 0.5 over Ru/Al_2O_3(A). When K

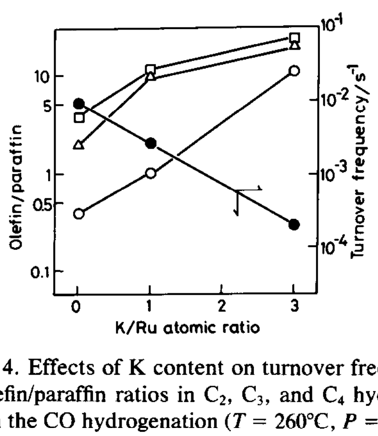

FIG. 4. Effects of K content on turnover frequency and olefin/paraffin ratios in C_2, C_3, and C_4 hydrocarbons in the CO hydrogenation (T = 260°C, P = 1 atm, H_2/CO = 2). Conversions are 3.5, 3.3, and 2.5% over the catalysts containing 0, 1, and 3% of K, respectively. (○) Ethylene/ethane, (△) propene/propane, (□) butene/butane.

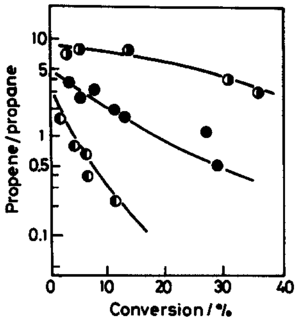

FIG. 5. Changes in propene/propane ratio as a function of the conversion over Ru catalysts (260°C, 1 atm, $H_2/CO = 2$). (○) Ru/Al$_2$O$_3$(A), ◐) Ru/P-Al$_2$O$_3$(A), (◑) Ru/1% K-Al$_2$O$_3$(A).

was added, the ratio retained rather a high value even at a high conversion. On the other hand, the addition of P caused a greater decrease in the ratio; the ratio was only 0.2 at 10% conversion.

Figure 6 shows the effect of addition of ethylene to the feed gas for Ru/Al$_2$O$_3$(A) and Ru/1% K-Al$_2$O$_3$(A). The experiments were carried out according to a method similar to that described by Dwyer *et al.* (*16*). In these experiments, after the measurement of product distribution at a stationary state, the feed gas was changed from CO + H_2 (1 : 2 in molar ratio) to CO + H_2 + C_2H_4 (1 : 2 : 0.1). Then after a nearly stationary state was reached after 2 h, the product distribution was measured again. A considerable part of ethylene added was hydrogenated to ethane over both catalysts; ethylene/ethane ratios were 0.67 and 0.51 for Ru/Al$_2$O$_3$(A) and Ru/K-Al$_2$O$_3$(A), respectively. As for the products other than C_2, as the results in Fig. 6 show, the addition of ethylene in the gas phase suppressed methane formation and increased the rate of formation of C_3–C_5 hydrocarbons by a factor of about 2 in the case of Ru/Al$_2$O$_3$(A). In contrast, the effect was small for Ru/1% K-Al$_2$O$_3$(A). When the feed gas was changed to CO + H_2 again, the products after 1 h became quite similar to those before the ethylene addition.

Infrared studies of CO adsorbed. Figure 7 shows the thermal desorption of CO. The amounts of remaining CO relative to the amount just after the evacuation at 25°C are shown in this figure. It is noted that CO adsorbed on Ru/P-Al$_2$O$_3$(A) was more readily desorbed than CO on Ru/Al$_2$O$_3$(A), but it was more strongly bonded on Ru/1% K-Al$_2$O$_3$(A). For example, after the evacuation at 300°C, the relative amounts of CO held were 20, 8, and 0% for Ru/1% K-Al$_2$O$_3$(A), Ru/Al$_2$O$_3$(A), and Ru/P-Al$_2$O$_3$(A), respectively. Table 3 shows the amount of

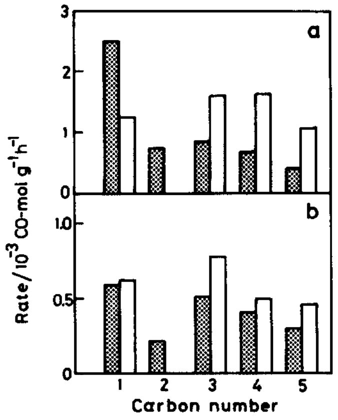

FIG. 6. Effect of the addition of ethylene in gas phase upon the rate of the hydrogenation of CO over (a) Ru/Al$_2$O$_3$(A) and (b) Ru/1% K-Al$_2$O$_3$(A) at 260°C. (▨) CO + H_2 (1 : 2 mole ratio; no ethylene addition), (□) CO + H_2 + C_2H_4 (1 : 2 : 0.1).

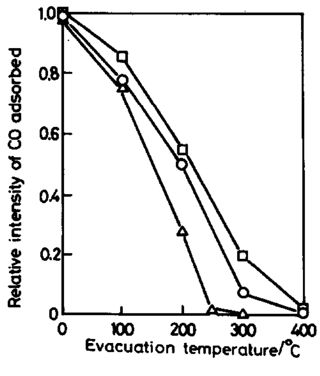

FIG. 7. Relative amount of CO held during stepwise thermal desorption over Ru catalysts. The ordinates are the integrated intensities of CO after evacuation at various temperatures divided by the integrated intensity after 25°C evacuation. (○) Ru/Al$_2$O$_3$(A), (△) Ru/P-Al$_2$O$_3$(A), (□) Ru/1% K-Al$_2$O$_3$(A).

TABLE 3

Amounts of CO and Carbon on the Surface

Catalyst	After evacuation at			
	25°C	200°C		
	CO/Ru[a]	CO/Ru[b]	(CO + C)/Ru[c]	C/Ru
$Ru/Al_2O_3(A)$	1.00	0.50	0.57	0.07
$Ru/1\%\ K\text{-}Al_2O_3(A)$	0.83	0.46	0.56	0.10
$Ru/P\text{-}Al_2O_3(A)$	1.07	0.32	0.47	0.14

[a] Measured by adsorption.
[b] Determined by infrared measurement.
[c] Measured by oxidation at 400°C.

carbon formed by the dissociation of CO during the thermal desorption up to 200°C. Less than 14% of CO present at 25°C dissociated during the thermal desorption up to 200°C. Therefore, the main species present on the surface was molecular CO and desorbed as molecular CO during the thermal desorption.

Infrared spectra taken at several temperatures in the presence of a mixture of CO and H_2 are shown in Fig. 8. The intensity of adsorbed CO decreased with time at 250°C. However, the decrease was less than about 10% at the initial 1 h, and after 1 h the decrease was very small. The change was much less at lower temperatures. Data in Fig. 8 were taken after 1 h. As can be seen in Fig. 8, the position of the band shifted to a lower frequency by about 8 cm^{-1} as the temperature increased. The band of CO appeared around 2024 cm^{-1} over $Ru/Al_2O_3(A)$, and the addition of K shifted the band by about 40 cm^{-1} to a lower frequency. In contrast, the band shifted to a higher frequency by 16 cm^{-1} upon the addition of P.

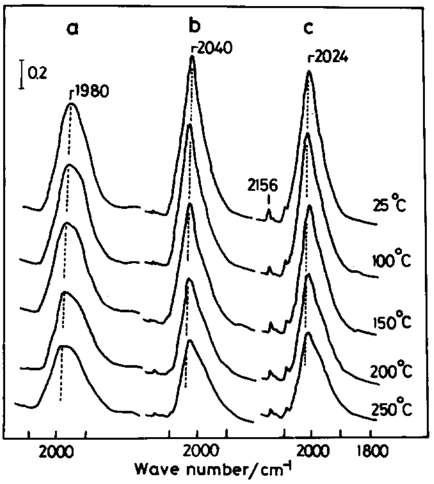

FIG. 8. Infrared spectra of CO adsorbed taken at various temperatures in the presence of CO (60 Torr) and H_2 (200 Torr). (a) $Ru/1\%\ K\text{-}Al_2O_3(A)$, (b) $Ru/P\text{-}Al_2O_3(A)$, (c) $Ru/Al_2O_3(A)$.

The changes in the surface coverage of adsorbed CO in the presence of a reactant gas mixture (CO + H_2) are shown in Fig. 9. Since the coverage of CO at 25°C can be assumed to be 1, the coverage was expressed by the ratio of the integrated intensities of CO adsorbed at given temperatures to those at 25°C. The addition of K increased the surface coverage of CO at each temperature, while the coverage decreased by the addition of P.

DISCUSSION

Effects of additives on CO adsorption. The data of thermal desorption shown in Fig. 7 clearly show that the addition of K and P changed the strength of CO adsorption in an opposite manner. The addition of K enhanced the strength of CO adsorption, and P reduced it. The shifts in the infrared band of CO by the addition of K and P (Fig. 8) indicate that these additives varied the electronic state of Ru. K donates electrons

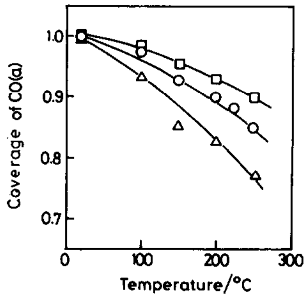

FIG. 9. Surface coverage of CO in the presence of CO (60 Torr) and H_2 (200 Torr) as a function of temperature. The ordinates are the integrated intensities of CO adsorbed at various temperatures divided by the integrated intensity at 25°C. (○) $Ru/Al_2O_3(A)$, (△) $Ru/P\text{-}Al_2O_3(A)$, (□) $Ru/1\%\ K\text{-}Al_2O_3(A)$.

to Ru, and by this, CO adsorption becomes stronger through the increase of back-donation in the metal–carbon bond. The effect of P can be explained by the opposite effect. This observation for K and P addition agrees in trend with that reported for Fe, Ni, and Pt (*10, 14, 17, 18*).

These changes in the electronic state of Ru reflected in the surface coverage of CO adsorbed in the presence of CO and H_2, as shown in Fig. 9. The coverage of CO increased by the addition of K, and decreased by the addition of P. These changes are closely related to the activity and selectivity of the hydrogenation of CO as will be described below.

Changes in catalytic activity by additives. We reported previously (*15*) that 4% Ru/Al_2O_3(A) was much more active than 5% Ru/Al_2O_3(B), and 2.5% Ru/Al_2O_3(A) was slightly more active than 2.5% Ru/Al_2O_3(B), when the reaction was carried out at 200°C and 0.7 atm in a closed circulation system. Under the present reaction conditions, 4% Ru/Al_2O_3(A) was also more active than 5% Ru/Al_2O_3(B), but 2.5% Ru/Al_2O_3(A) was less active than 2.5% Ru/Al_2O_3(B) (Table 2). However, the difference between 2.5% Ru/Al_2O_3(A) and 2.5% Ru/Al_2O_3(B) was small in both cases. Dependence on reaction conditions may be slightly different between the two catalysts.

The reaction rate dropped upon the addition of K and increased by the additions of P and B. The same effect of K has been reported for Fe, Ni, and Ru catalysts (*6–9*). Campbell and Goodman (*7*) found that the addition of K to Ni (100) enhanced CO dissociation, but the reaction rate was lowered by the addition of K. Therefore, they concluded that the rate-limiting step of this reaction was not CO dissociation, but probably the hydrogenation or hydrogen adsorption step. Several investigators (*19, 20*) also have inferred that the hydrogenation is the rate-limiting step.

If the dissociation of hydrogen is an important factor, the surface CO may influence the overall rate by inhibiting the dissociative adsorption of hydrogen. Since the addition of K increased the surface coverage of CO, the decrease in the rate is reasonably understood. It was reported that adsorbed CO which was inactive against hydrogenation was present on Ru/Al_2O_3 (*21, 22*), and the amount of the inactive CO increased by the addition of K (*22*). This latter effect may be another reason for the decrease in the activity.

Primary and secondary products. As shown in Figs. 2, 3, and 4, the product distribution of carbon number depended only moderately on the conversion, showing that hydrogenolysis of higher hydrocarbons to methane was not significant. Therefore, most of methane was the primary product. On the other hand, higher paraffins were mostly the secondary products. As shown in Fig. 5, the propene/propane ratio was considerably high at a low conversion level, and decreased with the conversion, indicating that propene was the primary product and that most of propane was formed by the subsequent hydrogenation of propene.

Besides hydrogenation, the incorporation of olefins to propagation step was reported in this reaction system (*16, 19, 23*). As shown in Fig. 6, ethylene added was converted to C_3–C_5 hydrocarbons over Ru/Al_2O_3(A). However, the effect of this reaction was probably small when ethylene was not intentionally added, since ethylene present during the ordinary reactions (for example, at 10% conversion) was less than $\frac{1}{50}$ that added in the experiments shown in Fig. 6. Therefore, it is most probable that olefins take a small part in the propagation step and are mostly hydrogenated to corresponding paraffins.

Selectivity changes by additives. The contrasting change in the selectivity between K and P or B (Table 2) can be explained as follows based on the changes in the strength of CO adsorption. For example, as described above, when the surface coverage of CO increased by the addition of K, the ability of catalyst for hydrogenation (dissociative adsorption of H_2) decreased, and the readsorption of olefins became difficult to occur. If so, it is reasonable that the formation of methane by the hydrogenation of methyl group on surface is suppressed, and the olefin/paraffin ratio in the primary products increases, and at the same time the hydrogenation of olefins once formed is depressed. The latter may be the reason why the high olefin/paraffin ratio was retained by the addition of K even at high conversions (Fig. 5). The effect of P and B can be explained by the opposite effect. These results obtained here indicate that changes in the electronic state of Ru caused by these additives are reflected directly to the catalytic activity and selectivity of Ru catalysts for CO hydrogenation.

ACKNOWLEDGMENTS

We gratefully acknowledge Mr. T. Enomoto and Mr. S. Lin for experimental assistance in part of this work. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 58045027 from the Ministry of Education, Science and Culture.

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