JOURNAL OF CATALYSIS 104, 339–346 (1987)

# Hydrogenation of Carbon Dioxide into Light Hydrocarbons at Atmospheric Pressure over $Rh/Nb_2O_5$ or $Cu/SiO_2$–$Rh/Nb_2O_5$ Catalyst

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Received May 28, 1986; revised December 2, 1986

$Rh/Nb_2O_5$ or $Cu/SiO_2$–$Rh/Nb_2O_5$ catalyst gives $C_{2+}$ hydrocarbons consisting mainly of $C_2H_6$ and $C_3H_8$ with 30–50% selectivity at temperatures ranging from 250 to 350°C even at atmospheric pressure. Both the activity and the selectivity of the $Cu/SiO_2$–$Rh/Nb_2O_5$ catalyst, in which $Cu/SiO_2$ and $Rh/Nb_2O_5$, having different selectivities, are piled up in two layers, are significantly greater than those of $Rh/Nb_2O_5$ alone. In the $Cu/SiO_2$–$Rh/Nb_2O_5$ double-layer catalyst, $Cu/SiO_2$ is placed at the inlet of catalyst bed and is responsible for the conversion of $CO_2$ into CO at a significant magnitude. Some characteristic data of supported Rh catalysts relating to chemisorption of $CO_2$, CO, and $H_2$ were obtained by pulse-flow adsorption measurements. In order to speculate the reaction scheme, a relationship between the catalytic activity and the chemisorption data is discussed.

## INTRODUCTION

A large number of investigations have been made on the hydrogenation of CO into $C_{2+}$ hydrocarbons (hereafter referred to as $C_{2+}$-HC) or alcohols and thus many interesting informations are now available (*1*).

In contrast the hydrogenation of $CO_2$ into $C_{2+}$-HC or alcohols has been less studied than that of CO. However, it has been recently reported that, in the studies on the interaction between $CO_2$ and $H_2$ or $CO_2$ and $H_2O$, hydrogenation using metal catalyst (*2–5*), metal oxide catalyst (*6–9*), or metal complex catalyst (*10–12*), photoassisted reduction (*13*) and electrolytic reduction (*11, 14*) are able to form $C_{2+}$-HC or alcohols, although their rates of formation and selectivities are not always high.

On the other hand, the hydrogenation of $CO_2$ or CO into $CH_4$ has been widely investigated over various metal catalysts and is well known to occur readily in the $CO_2$–$H_2$ reaction rather than in the CO–$H_2$ reaction (*15–19*). Influences of supporting materials upon Rh catalysts in the $CO_2$–$H_2$ reaction have been also reported by several workers (*16–18*).

In general it is not easy to form $C_{2+}$-HC in the $CO_2$–$H_2$ reaction at atmospheric pressure. In preliminary experiments, however, we have observed that $Rh/Nb_2O_5$ catalyst give significant amounts of $C_{2+}$-HC even at atmospheric pressure. In this paper, details of the experimental results are reported together with a discussion of the relationship between catalyst activity data and chemisorption data.

## EXPERIMENTAL

*Catalyst preparation.* Most of the catalysts used in this study was prepared by the usual impregnation method. Commercially available $SiO_2$, $Al_2O_3$, and $TiO_2$ pellets (DIA Catalysts & Chemicals Ltd., 1–2 mm diameter × 2–3 mm long) were used as a supporting material of the catalysts without further pretreatment. $Nb_2O_5 \cdot nH_2O$ powder (Companhia Brasileira de Metalurgia e Meneracao Ltd.) was also used as a supporting material after washing with distillated water and drying at 150°C. These supporting materials were calcined at 400°C for 2 h in a stream of air. The BET surface areas were as follows: $SiO_2$: 380; $Al_2O_3$: 210; $TiO_2$: 35; and $Nb_2O_5$: 47 $m^2/g$. $ZrO_2$ support was prepared by the hydrolysis of an aqueous $ZrOCl_2$ solution with $NH_4OH$.

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Amorphous $Zr(HPO_4)_2$ support was prepared from $ZrOCl_2$ and $H_3PO_4$ according to the method of Clearfield and Stynes (*20*). The BET surface areas of $ZrO_2$ and $Zr(HPO_4)_2$ were 67 and 79 $m^2/g$, respectively.

The supported catalysts were prepared by impregnating $SiO_2$, $Al_2O_3$, $TiO_2$, $Nb_2O_5$, $ZrO_2$, or $Zr(HPO_4)_2$ with the prescribed amounts of an aqueous solution of $Rh(NO_3)_3$ or $Cu(NO_3)_2$ *etc.*, and then calcined at 500°C for 2 h in a stream of air. Several kinds of commercial catalysts were also used after calcining at 500°C.

*Catalytic activity test.* The hydrogenation reaction of $CO_2$ (or CO) was carried out in a conventional flow apparatus operating at atmospheric pressure. The reactor consisted of a 18-mm-diameter glass tube, and it contained a packed bed consisting of 1.0 g of the catalyst and small glass beads in the ratio of 1 : 10 by volume, thereby improving the isothermal conditions during the course of reaction. Before the start of the hydrogenation reaction, the catalyst was reduced with a stream of $H_2$ at 400°C for 2 h, and then cooled to the reaction temperature in a stream of $H_2$. A mixture of $CO_2$ (or CO) and $H_2$ was admitted into the reactor at a constant flow rate. After we had ascertained that the flow system had attained a stationary state, we began to analyze the product stream. The reaction products and the reactor feed were introduced at regular time intervals into two sets of gas chromatographic units: one was used for the quantitative analysis of produced hydrocarbons and it consisted of a 3-m column of Porapak R operating at 120°C, and the other was used for the analysis of $C_1$ compounds ($CO_2$, CO, and $CH_4$) and it was consisted of a 4-m column of Porapak R operating at room temperature.

The selectivity was defined as the fraction of $CO_2$ (or CO) converted to the respective product (the basis of carbon atoms of $CO_2$ or CO fed).

*Adsorption measurement by pulse method.* The chemisorption behaviors of $CO_2$, CO, and $H_2$ onto the supported Rh catalysts were investigated by pulse-flow method. The $CO_2$ or CO adsorption measurements were conducted by the use of He as the carrier gas, whereas $N_2$ carrier was used in the $H_2$ adsorption measurements.

The samples of catalysts or supporting materials were crushed and sieved to obtain the 10–20 mesh fraction and then were weighed and packed into a 4mm-i.d.-diameter, 40-cm-long glass tube column. Prior to adsorption measurement, all samples were reduced at 400°C for 2 h in a stream of $H_2$. After the catalyst sample had been allowed to stand for 1 h in a stream of He or $N_2$ carrier gas in order to eliminate the hydrogen chemisorbed on the sample, it was cooled to the prescribed temperature in a stream of carrier gas. The pulse of $CO_2$ CO, or $H_2$, the volume of which was 0.56 ml (NTP) per pulse, was repeatedly injected into the sample column at regular time intervals by the use of doser consisting of a six-way valve system.

The elution curves of the repeated pulse injections were recorded as a function of pulse numbers by using a unit equipped with a thermal conductivity detector connecting directly with the exit of sample column.

## RESULTS AND DISCUSSION

### *Activities and Selectivities of Various Catalysts in the Hydrogenation of $CO_2$*

The results of catalytic tests for seven kinds of $Al_2O_3$-supported catalysts are shown in Table 1. The changes in activities and selectivities with process time were usually slight. Table 1 indicates that hydrogenation activity per unit weight of the catalysts decreases in this order: Ni > Rh ≅ Ru > Cu > Pt > Pd > Re. The activity sequence should be defined by turnover frequencies; however, we leave unsolved the subject in this reaction. The selectivity differs from one another in such a way that it can be roughly classified into four groups: the catalyst giving $CH_4$ only (Ni, Rh, Ru, Pt), the catalyst giving CO only (Cu), the

TABLE 1

Conversions and Selectivities of Various $Al_2O_3$-Supported Catalysts at Atmospheric Pressure[a]

| Catalyst[b] | Reaction temperature (°C) | Conversion of $CO_2$ (%) | Selectivity to products (carbon basis, %) | | |
|---|---|---|---|---|---|
| | | | $CH_4$ | CO | $C_{2+}$-HC |
| Ni (0.5)[c] | 250 | 30 | 100 | — | — |
| | 300 | 78 | 100 | — | — |
| | 350 | 91 | 100 | — | — |
| Rh (0.5)[c] | 250 | 28 | 100 | — | — |
| | 300 | 67 | 100 | — | — |
| | 350 | 93 | 100 | — | — |
| Ru (0.5)[d] | 250 | 22 | 100 | — | — |
| | 300 | 70 | 100 | — | — |
| | 350 | 87 | 100 | — | — |
| Cu (12)[c] | 250 | 10 | — | 100 | — |
| | 300 | 17 | — | 100 | — |
| | 350 | 28 | — | 100 | — |
| Pt (0.5)[d] | 250 | 8 | 100 | — | — |
| | 300 | 17 | 100 | — | — |
| | 350 | 23 | 100 | — | — |
| Pd (0.5)[d] | 250 | 5 | 60 | 40 | — |
| | 300 | 14 | 79 | 21 | |
| | 350 | 24 | 84 | 16 | — |
| Re (5.0)[c] | 250 | 3 | 50 | 48 | 2 |
| | 300 | 9 | 53 | 47 | (trace) |
| | 350 | 19 | 61 | 39 | — |

[a] Reaction conditions: catalyst weight: 1.0 g; total feed rate of reactant mixture ($CO_2 + H_2$): 100 ml/min; feed mole ratio of $CO_2/H_2$: $\frac{1}{4}$.

[b] Number in parentheses denotes wt% in the catalyst composition.

[c] Laboratory-made catalyst prepared by the usual impregnation method.

[d] Commercial catalyst supplied from Nippon Engelhard Co.

catalyst giving both $CH_4$ and CO (Pd), and the catalyst simultaneously giving small amounts of $C_{2+}$-HC with a large quantity of $CH_4$ and CO (Re).

All the $Al_2O_3$-supported metal catalysts, except for $Re/Al_2O_3$, showed no detectable formation of $C_{2+}$-HC and alcohols in the $CO_2$–$H_2$ reaction at atmospheric pressure, similar to the results in the published papers (*2, 21, 22*). $Fe_2O_3$ (10 wt%)/$Al_2O_3$ catalysts was also tested under the same reaction conditions as for Table 1; however, it was found to be inferior to $Re/Al_2O_3$ in both activity and selectivity to $C_{2+}$-HC.

Recently, in the CO–$H_2$ reaction at atmospheric pressure Phadke and Ko (*23*) reported that $Fe/SiO_2$ or $Fe/Nb_2O_5$ yielded $C_1$–$C_5$ hydrocarbons at a CO conversion level of about 1.5%. However, the $CO_2$–$H_2$ reaction was not given in their report.

It is already known that, in the hydrogenation of CO, Rh catalyst results in a high selectivity to $C_{2+}$-HC when $ZrO_2$ or $Nb_2O_5$ is chosen as the supporting material (*24*). In the hydrogenation of $CO_2$, therefore, we have attempted to investigate influences of supporting materials upon the activity of the supported Rh catalysts. The results are shown in Table 2. It has become apparent from Table 2 that the catalyst selectivity is significantly affected by the selection of supporting material. When Rh is supported on $TiO_2$, the catalyst gives $CH_4$ only and has no selectivity to form $C_{2+}$-HC. In contrast, when Rh is supported on $Nb_2O_5$, $ZrO_2$, or $Zr(HPO_4)_2$, the supported catalyst develops an activity to form $C_{2+}$-HC and CO together with the formation of $CH_4$, although the conversion of $CO_2$ is relatively low compared to those of $Rh/Al_2O_3$ or $Rh/TiO_2$ catalyst. In particular, it is worth noting in Table 2 that the selectivity to $C_{2+}$-HC in the $Rh/Nb_2O_5$ catalyst is as high as 30–40%. Since every supporting material itself did not promote any catalytic reaction, it was considered that the selectivity to form $C_{2+}$-HC was attributed to some effects of the interaction between Rh and supporting material. This characteristic effect probably arises from the so-called strong metal–support interactions (SMSI).

### *Influences of Rh Content and Reduction Temperature of $Rh/Nb_2O_5$ Catalyst upon the $CO_2$–$H_2$ Reaction*

Table 2 shows that, in the case of $Rh/Nb_2O_5$ catalyst, both the conversion and the selectivity to $C_{2+}$-HC increase with increasing reaction temperature. However, when it is raised to temperatures near to 400°C, the hydrogenation into $CH_4$ proceeds drastically and thus the selectivity to $C_{2+}$-HC is exceedingly lowered.

The influence of $CO_2/H_2$ molar feed ratio upon the reaction is illustrated in Fig. 1. The conversion of $CO_2$ decreases with an increase in the $CO_2/H_2$ feed ratio, contrary to that the selectivity to $C_{2+}$-HC increases. This trend suggests that the concentration

TABLE 2

Conversions and Selectivities of Rh Catalysts Supported on Various Supports at Atmospheric Pressure[a]

| Catalyst[b] | Reaction temperature (°C) | Conversion of $CO_2$ (%) | Selectivity to products (carbon basis %) | | | $C_2H_6/C_3H_8$ (carbon basis) |
|---|---|---|---|---|---|---|
| | | | $CH_4$ | CO | $C_{2+}$-HC[c] | |
| $Rh/TiO_2$ | 250 | 29 | 100 | — | — | — |
| | 300 | 37 | 100 | — | — | — |
| | 350 | 47 | 100 | — | — | — |
| $Rh/Nb_2O_5$ | 250 | 4 | 70 | 5 | 25 | 1.2 |
| | 300 | 8 | 59 | 7 | 34 | 1.3 |
| | 350 | 11 | 58 | 5 | 37 | 1.7 |
| $Rh/ZrO_2$ | 250 | 8 | 88 | — | 12 | 5.0 |
| | 300 | 19 | 96 | — | 4 | — |
| | 350 | 30 | 100 | — | — | — |
| $Rh/Zr(HPO_4)_2$ | 250 | 2 | 60 | 10 | 30 | 9.0 |
| | 300 | 5 | 79 | 3 | 18 | 3.5 |
| | 350 | 8 | 86 | 4 | 10 | 0.9 |

[a] Reaction conditions are the same as those described in Table 1.

[b] All of these preparations were made to contain 0.5 wt% Rh in the final catalyst.

[c] $C_{2+}$-HC consisted mainly of $C_2H_6$ and $C_3H_8$. The amounts of olefins and $C_{4+}$-HC were negligibly small.

of hydrogen adsorbed dissociatively on the catalyst surface is enhanced with an increase in the partial pressure of $H_2$. Thus, it seems to vary in such a way that the formation of $CH_4$ is further enhanced and the formation of $C_{2+}$-HC is oppositely depressed.

The yields of $C_{2+}$-HC and CO (defined as the product of total $CO_2$ conversion and the selectivity to $C_{2+}$-HC or CO) have varied with W/F, as is shown in Fig. 2. The yield of $C_{2+}$-HC increases monotonically with an increase in W/F; whereas the yield of CO increases with W/F, passes through a maximum, and then decreases. These facts suggest that the hydrogenation of $CO_2$ into $C_{2+}$-HC proceeds consecutively, passing through CO as a gas-phase intermediate.

The influence of Rh content upon the reaction is shown in Fig. 3. The conversion of $CO_2$ increases with an increase in Rh content and appears to gradually level off, while the selectivity to $C_{2+}$-HC remains almost unchanged in the range of Rh content up to 2 wt%.

Influences of the reduction temperature in the catalyst preparation upon the activity and selectivity were investigated. When $Rh/Nb_2O_5$ catalyst was reduced with $H_2$ at

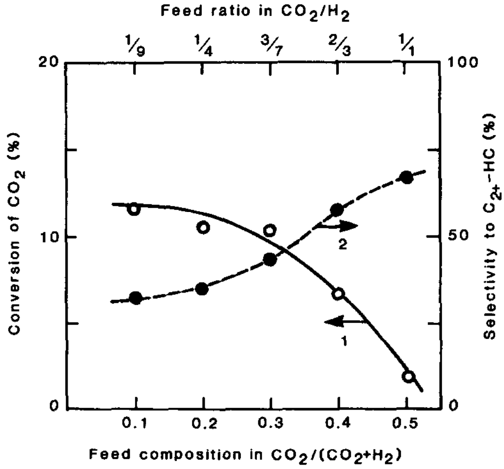


FIG. 1. Influence of feed composition upon $CO_2$ hydrogenation at atmospheric pressure over a Rh(0.5 wt%)/$Nb_2O_5$ catalyst. Reaction temperature: 300°C, catalyst weight: 1.0 g, total feed rate of reactant mixture ($CO_2$ + $H_2$): 100 ml/min. Curve 1: conversion of $CO_2$, 2: selectivity to $C_{2+}$-HC.

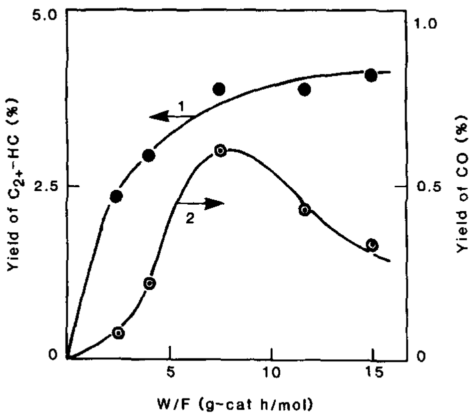


FIG. 2. Influence of W/F upon yields of $C_{2+}$-HC and CO. Catalyst: Rh(0.5 wt%)/$Nb_2O_5$, reaction temperature: 300°C, feed ratio of $CO_2/H_2$: $\frac{1}{4}$. Curve 1: $C_{2+}$-HC yield, 2: CO yield.

temperatures ranging from 300 to 450°C, subsequent $CO_2$–$H_2$ reaction was almost unaffected by the reduction temperature of catalyst. However, raising the reduction temperature up to 600°C drastically decreases the catalyst activity, although the selectivity to $C_{2+}$-HC is almost unaffected. Possibly this is due to a lowering of the surface area of both Rh and $Nb_2O_5$. Iizuka *et al.* (*25*) described that sintering of $Nb_2O_5$ became appreciable at a temperature as high as 600°C.

### *Adsorption Behavior of $CO_2$, CO, or $H_2$ onto the Catalysts*

When a $CO_2$ pulse was injected into sample column, the elution curve depicted the different shapes depending upon the samples, suggesting characteristic differences in the adsorption behavior.

In the case of $Nb_2O_5$, the injected pulse of $CO_2$ passes through sample column without any detectable change in both the pulse shape and the pulse volume. Thus it can be said that $Nb_2O_5$ behaves like an inert substance, in analogy with the case when $Al_2O_3$ was tested as the sample. In contrast, Rh/$Nb_2O_5$ catalyst strongly adsorbs a part of the injected $CO_2$ pulse and the resulting elution curve shows the complicated shape consisting of the one sharp peak and the other rounded hump. The former sharp peak with a short retention time corresponds to $CO_2$ which passes through the sample column without being adsorbed. The other broad signal with a long retention time consists mainly of CO which is formed by the following reaction: $CO_2(g) \rightarrow CO(g) + O_{ads}$, where $O_{ads}$ denotes the oxygen atoms chemisorbed irreversibly on the catalyst surface. In the case of Rh/$Al_2O_3$ catalyst, the elution curve indicates that only a part of the pulse-injected $CO_2$ flows out from the sample column and a large portion of $CO_2$ is irreversibly chemisorbed on the catalyst surface. The irreversible chemisorption of $CO_2$ is presumed to be produced by the following reaction: $CO_2(g) \rightarrow C_{ads} + 2O_{ads}$ or $\rightarrow CO_{ads} + O_{ads}$, where the subscript ads represents the dissociatively chemisorbed species which remains on the catalyst surface without desorption.

Adsorption measurements of CO and $H_2$ by the pulse-flow method have offered some characteristic data shown in Table 3. Table 3 indicates that both the CO and $H_2$ uptake in the Rh/$Al_2O_3$ catalyst are much larger than in the Rh/$Nb_2O_5$ catalyst. This is believed to be due to the fact that, in the

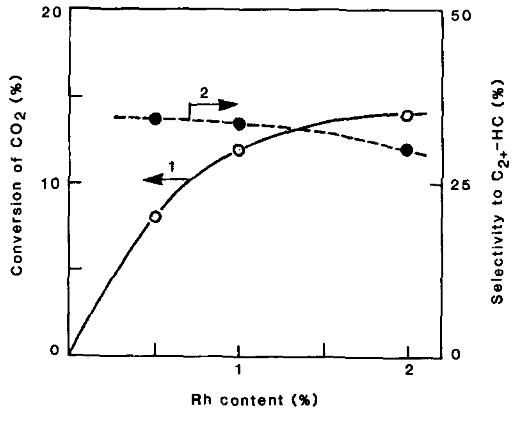


FIG. 3. Influence of Rh content in Rh/$Nb_2O_5$ catalyst upon the $CO_2$ hydrogenation at atmospheric pressure. Reaction temperature: 300°C, the other reaction conditions are the same as for Table 1. Curve 1: conversion of $CO_2$, 2: selectivity to $C_{2+}$-HC.

TABLE 3

Some Characteristics Data of Supported Rh Catalysts Relating to Chemisorption

| Catalyst | Surface area of the support ($m^2/g$) | Uptake (ml/g) | | $(2H/CO)_{ads}$ | CO/Rh | 2H/Rh |
|---|---|---|---|---|---|---|
| | | CO | $H_2$ | | | |
| Rh(0.5 wt%)/$Nb_2O_5$ | 47 | 0.5 | 0.07 | 0.28 | 0.21 | 0.06 |
| Rh(0.5 wt%)/$Al_2O_3$ | 210 | 2.2 | 1.0 | 0.91 | 0.93 | 0.85 |

case of Rh/$Nb_2O_5$ catalyst, surface area of $Nb_2O_5$ support is relatively smaller than that of the $Al_2O_3$ support and hence Rh dispersion is inferior to the case of Rh/$Al_2O_3$ catalyst. It is further noteworthy in Table 3 that $(2H/CO)_{ads}$ ratio of Rh/$Nb_2O_5$ is significantly smaller than that of Rh/$Al_2O_3$. This fact suggests that Rh/$Nb_2O_5$ catalyst is encountered with a remarkable depression of hydrogen chemisorption, *viz.*, SMSI effect.

### *A Comparison of $CO_2$–$H_2$ Reaction with CO-$H_2$ Reaction and Plausible Reaction Paths of the Hydrogenation of $CO_2$ into $C_{2+}$-HC*

In order to compare the hydrogenation of $CO_2$ with that of CO, the hydrogenation of CO was carried out over the same catalysts as used in the hydrogenation of $CO_2$. The results are shown in Figs. 4 and 5.

By comparison of the data of Rh/$Al_2O_3$ catalyst in Table 1 and Fig. 4, the conversions of $CO_2$ are found to be significantly higher than those of CO at the same temperature. That is, the hydrogenation rates of $CO_2$ into $CH_4$ are larger than those of CO. This fact agreed with the conclusions described in other published papers (*15–19*).

The other difference between $CO_2$–$H_2$ reaction and CO–$H_2$ reaction is noted in the selectivity. In the $CO_2$–$H_2$ reaction, Rh/$Al_2O_3$ gives $CH_4$ only; in contrast in the CO–$H_2$ reaction, Rh/$Al_2O_3$ is able to give significant amounts of $C_{2+}$-HC at temperatures below 350°C. In other words, suitable catalysts for $C_{2+}$-HC formation in the $CO_2$–

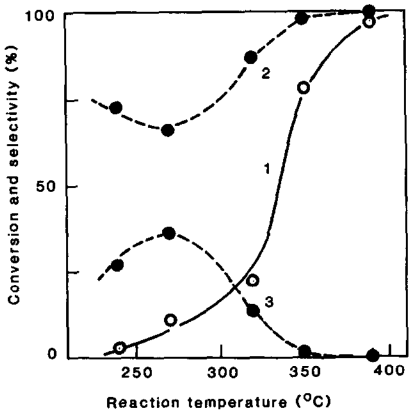


FIG. 4. CO hydrogenation at atmospheric pressure over Rh(0.5 wt%)/$Al_2O_3$ catalyst. Total feed rate of reactant mixture (CO + $H_2$): 100 ml/min, feed ratio of CO/$H_2$: $\frac{1}{2}$, catalyst weight: 1.0 g. Curve 1: conversion of CO, 2: selectivity to $CH_4$, 3: selectivity to $C_{2+}$-HC.

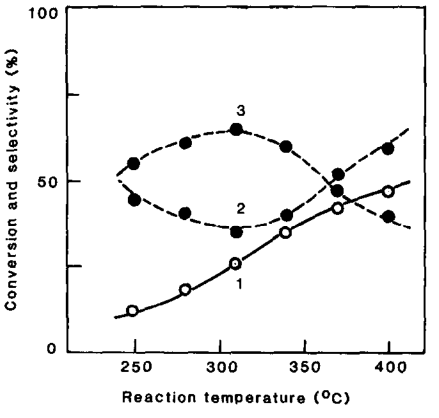
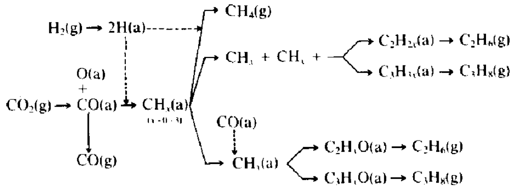


FIG. 5. CO hydrogenation at atmospheric pressure over Rh(0.5 wt%)/$Nb_2O_5$ catalyst. Reaction conditions and symbols in figure are the same as for Fig. 4.

$H_2$ reaction are not identical to those in the CO–$H_2$ reaction.

The adsorption mechanism of $CO_2$ or CO over the Rh catalysts has been described by many workers (*16–18*). In the methanation of $CO_2$, carbonyl hydride species (*18*) or reactive surface carbon (*16*) is found to be the key surface intermediate. In our present study, the detailed reaction scheme is still not understood because of the lack of IR measurements and surface residues during the course of $CO_2$–$H_2$ reaction. However, we would like to tentatively speculate the reaction pathways over $Rh/Nb_2O_5$ catalyst as follows:



(a) denotes the adsorbed state, and $CH_x$, $C_2H_{2x}$, etc., represent the intermediate hydrogenated state.

Considering the results of adsorption measurements, the surface concentration of H(a) in the $Rh/Nb_2O_5$ catalyst is presumed to be relatively low. In addition, $Rh/Nb_2O_5$ catalyst simultaneously forms CO as a gas-phase intermediate during the course of reaction. Thus, the condensation reaction of $CH_x(a)$ or the insertion reaction of CO onto $CH_x(a)$ leading to $C_2H_6$ or $C_3H_8$ is liable to be encountered on the surface of $Rh/Nb_2O_5$ catalyst. The $Rh/Al_2O_3$ catalyst, on the contrary, possesses a high concentration of H(a) and does not form CO. Consequently, in the hydrogenation of $CO_2$, $Rh/Al_2O_3$ catalyst results in a preferential formation of $CH_4$ without leading to $C_{2+}$-HC.

### *The Hydrogenation of $CO_2$ over $Cu/SiO_2$–$Rh/Nb_2O_5$ Catalyst*

The results obtained in the activity tests of the $Cu/SiO_2$–$Rh/Nb_2O_5$ catalyst, in which $Cu/SiO_2$ and $Rh/Nb_2O_5$, which have different selectivities are piled up in two layers, are shown in Fig. 6. In this $Cu/SiO_2$–$Rh/Nb_2O_5$ double-layer catalyst, $Cu/SiO_2$ was placed at the inlet of catalyst bed. By comparison of Fig. 6 and Table 2, it can be seen that both the conversion of $CO_2$ and the selectivity to $C_{2+}$-HC are significantly improved by application of a $Cu/SiO_2$–$Rh/Nb_2O_5$ double-layer catalyst, compared with those of $Rh/Nb_2O_5$ alone. This result suggests that the hydrogenation of $CO_2$ to $C_{2+}$-HC proceeds via the consecutive steps of $CO_2 \rightarrow CO \rightarrow C_{2+}$-HC and the combined action of $Cu/SiO_2$ (which is mainly responsible for the conversion of $CO_2$ into CO) with $Rh/Nb_2O_5$ (which plays a role in the transformation of CO into $C_{2+}$-HC with a high efficiency) has led to an excellent catalytic activity superior to the one-stage process by $Rh/Nb_2O_5$ alone.

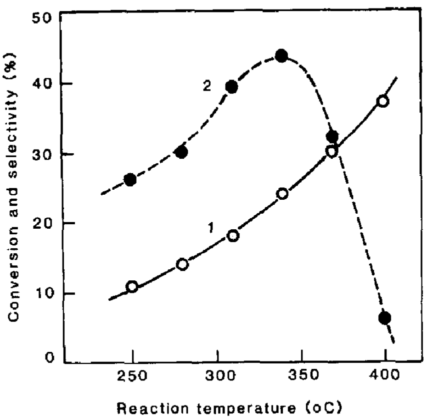


FIG. 6. $CO_2$ hydrogenation at atmospheric pressure over Cu(12 wt%)/$SiO_2$–Rh(0.5 wt%)/$Nb_2O_5$ catalyst being piled up in two layers. Weight of catalyst used: $Cu/SiO_2$ 3.0 g and $Rh/Nb_2O_5$ 1.0 g; the other reaction conditions are the same as those described in Table 1. Curve 1: conversion of $CO_2$, 2: selectivity to $C_{2+}$-HC.

## REFERENCES

1. For example, Sheldon, R. A., *in* "Chemicals from Synthesis Gas, Catalytic Reaction of CO and $H_2$." Reidel, Dordrecht, 1983.
2. Solymosi, F., and Erdöhelyi, A., *J. Mol. Catal.* **8**, 471 (1980).
3. Ramaroson, E., Kieffer, R., and Kiennemann, A., *J. Chem. Soc. Chem. Commun.*, p. 645 (1982).

*4.* Iizuka, T., Kojima, M., and Tanabe, K., *J. Chem. Soc. Chem. Commun.*, p. 638 (1983).

*5.* Weatherbee, G. D., and Bartholomew, C. H., *J. Catal.* **87,** 352 (1984).

*6.* Kiennemann, A., Kieffer, R., and Chornet, E., *React. Kinet. Catal. Lett.* **16,** 371 (1981).

*7.* Barrault, J., Forguy, C., Menzo, J. C., and Maurel, R., *React. Kinet. Catal. Lett.* **17,** 373 (1981).

*8.* Tatsumi, T., Muramatsu, A., and Tominaga, H., *Chem. Lett.* p. 593 (1985).

*9.* Baussart, H., Delobel, R., Bras, M., Maguer, D., and Leroy, J., *Appl. Catal.* **14,** 381 (1985).

*10.* Naito, S., Ogawa, O., Ichikawa, M., and Tamaru, K., *J. Chem. Soc. Chem. Commun.*, p. 1266 (1972).

*11.* Denise, B., and Snneden, R. P. A., *CHEMTECH*, February, p. 108 (1982).

*12.* Behr, A., *in* "Catalysis in $C_1$-Chemistry" (W. Keim, Ed.), p. 169. Reidel, Dordrecht, 1983.

*13.* Vjayakumar, K. M., and Lichtin, N. N., *J. Catal.* **90,** 173 (1984).

*14.* *Chem. Eng. News*, July 8, p. 29 (1985).

*15.* Inui, T., and Funabiki, M., *Chem. Lett.*, p. 251 (1978).

*16.* Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981).

*17.* Iizuka, T., Tanaka, Y., and Tanabe, K., *J. Catal.* **76,** 1(1982).

*18.* Henderson, M. A., and Whorley, S. D., *J. Phys. Chem.* **89,** 1417 (1985).

*19.* Solymosi, F., Tombácz, I., and Koszta, J., *J. Catal.* **95,** 578 (1985).

*20.* Clearfield, A., and Stynes, J. A., *J. Inorg. Nucl. Chem.* **26,** 117 (1964).

*21.* Maatman, R., and Hiemstra, S., *J. Catal.* **62,** 349 (1980).

*22.* Ferkul, H. E., Stanton, D. J., McCowan, J. D., and Baird, M. C., *J. Chem. Soc., Chem. Commun.*, p. 955 (1982).

*23.* Phadke, M. D., and Ko, E. I., *J. Catal.* **100,** 503 (1986).

*24.* Iizuka, T., Tanaka, Y., and Tanabe, K., *J. Mol. Catal.* **17,** 381 (1982).

*25.* Iizuka, T., Ogasawara, K., and Tanabe, K., *Bull. Chem. Soc. Japan* **56,** 2927 (1983).