JOURNAL OF CATALYSIS **68**, 371–382 (1981)

Methanation of CO_2 on Supported Rhodium Catalyst

F. SOLYMOSI, A. ERDÖHELYI, AND T. BÁNSÁGI

Reaction Kinetics Research Group, The University, 6701 Szeged, P.O. Box 105, Hungary

Received July 8, 1980; revised October 31, 1980

The synthesis of methane from CO_2 and H_2 was investigated on supported Rh catalysts. The adsorbed species present on the catalysts were characterized by infrared spectroscopy. The hydrogenation of CO_2 on Rh/Al_2O_3 occurred at a measurable rate above 443 K, yielding exclusively methane. The rate of methane formation on Rh/Al_2O_3 is described by the expression $N_{CH_4} = 2.69 \times 10^6 \exp(-16.200/RT) P_{H_2}^{0.61} \cdot P_{CO_2}^{0.26}$. From a comparison of the specific activities of Rh/Al_2O_3 in the $H_2 + CO_2$ and $H_2 + CO$ reactions it appears that the hydrogenation of CO_2 occurs much faster than that of CO. The support exerted a marked influence on the specific activity of Rh. The most effective support was TiO_2 and the least effective one SiO_2. Infrared spectroscopic measurements revealed that linearly bonded CO (perturbed by hydrogen adsorbed on the same Rh atom) and adsorbed formate species were present on the catalyst surface during the reaction. Evidence is presented to show that the surface formate is located not on the Rh, but rather on the support. The formation of surface C was also detected. Its amount slightly increased during the conditioning period and also with temperature elevation. It is proposed that the important steps in CH_4 formation are the dissociation of CO_2 promoted by adsorbed hydrogen, the subsequent dissociation of CO into reactive surface carbon, and hydrogenation of the latter. The possible reasons for the different methanation rates of CO_2 and CO are discussed.

INTRODUCTION

The current energy problem has initiated great interest in the study of the catalytic hydrogenation of CO to methane and other hydrocarbons, and also in the search for new carbon sources which can be converted into hydrocarbon fuels. The results and the proposed mechanisms of hydrogenation of CO have been described extensively in different reviews (*1–4*). Relatively little attention has been paid so far to the catalytic transformation of CO_2, although the hydrogenation of CO_2 is less exothermic than that of CO (which is not a negligible point in the designing of a reactor), and it yields methane almost exclusively (*5, 6*).

In a short note we recently reported that, from among the noble metals, alumina-supported Ru and Rh exhibited very high activities and selectivities in the hydrogenation of CO_2 (*7*). In another paper we examined in detail the low-temperature interaction between H_2 and CO_2 on supported Rh by adsorption and infrared spectroscopic measurements (*8*).

In the present report we give a detailed account of the catalytic behavior of Rh. The primary concern of this work is to evaluate the mechanism of the methanation of CO_2. Special attention is focused on the surface processes, on the identification of surface species during this reaction, and on the effects of various supports. It is hoped that such an evaluation of the main features of the hydrogenation of CO_2 may contribute to a better understanding of the hydrogenation of CO as well.

A long-term aim of our research program is to develop efficient catalytic processes whereby CO_2 can be transformed into more valuable carbon-containing compounds.

EXPERIMENTAL

Materials

The catalysts were prepared by impregnating the supports with solutions of

0021-9517/81/040371-12$02.00/0

$RhCl_3 \cdot 3H_2O$ to yield a nominal 1 and 5 wt% metal. The impregnated powders were dried at 373 K. Before any measurements, small fragments of pellets made from the catalyst were oxidized for 30 min and reduced for 60 min at 673 K *in situ*. After oxidation and reduction the sample was cooled to the reaction temperature in flowing H_2. For infrared studies, transparent thin wafers (30 × 10 mm) were prepared at high pressure (1600 atm).

The following powder supports were used: Al_2O_3 (Degussa Pl10 Cl), SiO_2 (Aerosil 200), MgO (DAB 6), and TiO_2 (Degussa P25). The characteristic data for the supports and supported Rh are shown in Table 1.

The gases used were of commercial purity. They were carefully purified by fractional distillation (CO_2) or by adsorbing the impurities with a molecular sieve at the temperature of liquid air.

Methods

Catalytic investigations were carried out in a flow microreactor made from an 8-mm-i.d. Pyrex glass tube. Its length was 100 mm. The dead volume was filled with glass beads. The reactor was heated by an external oven. A small glass tube containing an Fe–Ko thermocouple was placed in the middle of the catalyst bed. No increase in the catalyst temperature was observed during the reaction. The amount of catalysts used was 0.3–0.6 g. The ratio of H_2/CO_2 in the reacting gas mixture was in general 4/1. Helium was used whenever a diluent was needed. Analyses of the exit gases were performed with a Hewlett–Packard 5750 gas chromatograph equipped with a 3370 electronic digital integrator. An effluent splitter in the gas chromatograph permitted simultaneous detection by thermal conductivity and flame ionization detectors. A 2-m-long 0.25-in.-diameter column packed with Porapak QS allowed complete separation and determination of reactants and products.

The system was operated at a total pressure of 1 atm. High space velocities of 3000–6000 hr^{-1} were used. The CO_2 conversion was in general less than 10–15%. The absence of diffusional limitation was confirmed (*9*).

Pulse experiments were conducted in a microcatalytic pulse system. The microreactor was incorporated between the sample inlet and the analytical column of the gas chromatograph. Details of the reactor have been described elsewhere (*10*).

The greaseless vacuum ir cell used was similar to that described by Amenomiya (*11*). Spectra were recorded with a double-beam ir spectrometer (*8*).

The dispersity of the supported metals was determined by H_2 chemisorption at 298 K by use of dynamic impulse methods (*8*).

RESULTS

1. Kinetic Measurements in a Flow System

The hydrogenation of CO_2 on alumina-supported Rh occurred at a measurable rate above 443 K. Before kinetic measurements the catalyst sample was treated with the reactant gas mixture at the highest reaction temperature (10–15% conversion) until steady-state activity was obtained. The conversion of CO_2 slightly increased during this conditioning period. The selectivity toward CH_4 formation approached 99–100%.

When the alumina was replaced by some other support, the temperature range of measurable activity changed considerably; this range was the lowest on Rh/TiO_2 and the highest on Rh/SiO_2. The high selectivity of the catalyst remained the same, and it was easy to reach the steady-state activity in 20–30 min. An exception was the Rh/MgO sample. In this case a marked decay in activity was observed at 563 K. The selectivity of CH_4 formation also decreased from 98% to 88% and CO was produced.

Variation of the H_2/CO_2 ratio exerted very little influence on the selectivities of

TABLE 1

Kinetic Data for the Hydrogenation of CO_2 on Supported Rh Catalysts

	Area of the supports (m^2/g)	Amount of Rh (wt%)	Rh dispersion (%)	$N_{CH_4} \times 10^3$ (sec^{-1})		E_{CH_4} (kcal/mol)	A (sec^{-1} atm^{-x-y})	x	y	Ref.
				at 473 K	at 548 K					
Al_2O_3 (Degussa P110 Cl)	100	5	30.2	20.4	230[a]	16.2 ± 0.4	2.69×10^6	0.61	0.26	Present work
SiO_2 (Aerosil 200)	240	5	22.8	4.4	53[a]	17.3 ± 0.6	1.3×10^6	0.64	0.27	Present work
TiO_2 (Degussa P25)	150	1	22.3	150	2400[a]	19.4 ± 1.0				Present work
				H_2 + CO reaction						
Al_2O_3 (Degussa P110 Cl)	100	5	30.2	0.45	13.5	23.7	2.2×10^7	0.95	0.40	(*10*)
η-Al_2O_3	200	1	51	0.38[a]	13	24.0 ± 0.4	5.2×10^7	1.04	−0.20	(*13*)

Note. 1 cal = 4.187 J.

[a] Extrapolated values.

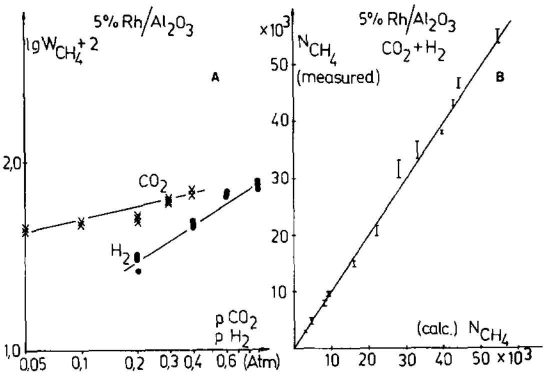


FIG. 1. (A) Dependence of rate of CH_4 formation on the partial pressure of CO_2 and H_2. (B) Comparison of experimental and calculated rates of methane synthesis. N_{CH_4} = turnover number of CH_4 formation (sec^{-1}).

the Rh catalysts. The conversion of CO_2 increased with the partial pressure of H_2 in all cases.

Sensitive gas-chromatographic analysis revealed that on Rh/Al_2O_3 and on Rh/TiO_2 small amounts of CO (less than 1% of the methane) were also formed. On Rh/TiO_2, traces of ethane were also detected.

The dependence of the rate of methanation on the partial pressures of CO_2 and H_2 was determined from the slope of log–log plots of the rate against the reactant partial pressure (Fig. 1). The rate of CH_4 formation on supported Rh catalysts can be described with the following empirical equation:

$$N_{CH_4} = A \cdot e^{-E/RT} P_{H_2}^{x} \cdot P_{CO_2}^{y},$$

where N_{CH_4} is the rate of CH_4 formation per surface Rh site, A is the preexponential factor, E is the apparent activation energy, and x and y are the exponents of the partial pressures of H_2 and CO_2, respectively. A comparison of the experimental and calculated rates of methane formation based on the kinetic data given in Table 1 is shown in Fig. 1.

The activation energy of the reaction was determined from the temperature dependence of the rate at the steady state. The activation energy was almost the same (16–19 kcal/mol) for Rh/Al_2O_3, Rh/TiO_2, and Rh/SiO_2. Some Arrhenius diagrams are shown in Fig. 2. Due to a continuous decay in the activity of Rh/MgO, reliable kinetic data could not be determined in this case.

The specific activities of the catalysts (in terms of turnover numbers) were calculated by taking into account the dispersity of the Rh on the different samples. These values are also shown in Table 1. It appears that the most active catalyst is Rh/TiO_2 and the least effective one Rh/SiO_2.

As the methanation of CO_2 proceeds at a measurable rate at 443–473 K, where the methanation of CO is very slow, it was interesting to see how the presence of CO influenced the hydrogenation of CO_2 in this temperature range. The results obtained are shown in Fig. 3. It can be seen that a small

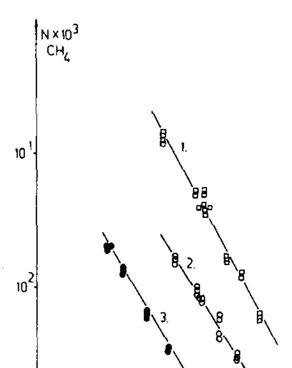


FIG. 2. Arrhenius plots for Rh/TiO_2 (1), Rh/Al_2O_3 (2), and Rh/SiO_2 (3).

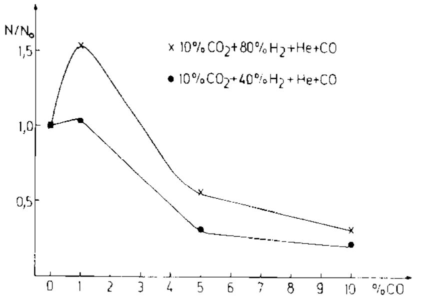


FIG. 3. The relative rate of CH_4 formation in the $H_2 + CO_2$ reaction on Rh/Al_2O_3 at 463 K as a function of added CO. N_0 = turnover number of CH_4 formation in the absence of added CO. N = turnover number of CH_4 formation in the presence of CO.

amount of CO slightly promotes the production of CH_4. With the increase of the partial pressure of CO, however, the hydrogenation of CO_2 is gradually decreased.

2. *Infrared Spectroscopic Measurements during the Catalytic Reaction*

In order to identify the surface species formed during the catalytic reaction, infrared spectroscopic measurements were performed at the temperatures of the reaction. The flow rate of the $H_2 + CO_2$ (4 : 1) mixture was the same as during the kinetic experiments. Some spectra taken at different intervals are given in Fig. 4.

Upon introduction of the $H_2 + CO_2$ reactant gas mixture at 523 K, absorption bands appeared at 1380, 1596, 1625, and 2020 cm^{-1}. Weak bands were also observed at 2914–2910 cm^{-1}. Their intensities remained at a low level during the reaction at different temperatures. These bands were also observed in the low-temperature interaction of $H_2 + CO_2$ (*8*). Taking into account the infrared spectra of adsorbed formic acid and CO on Rh/Al_2O_3 (*8*), the 1596- and 1380-cm^{-1} bands are assigned to the asymmetric and symmetric O–C–O stretching vibrations of adsorbed formate ion. The weak band at 2914–2921 cm^{-1} is attributed to the CH stretching vibration and the bands at 2020 cm^{-1} to CO adsorbed on Rh.

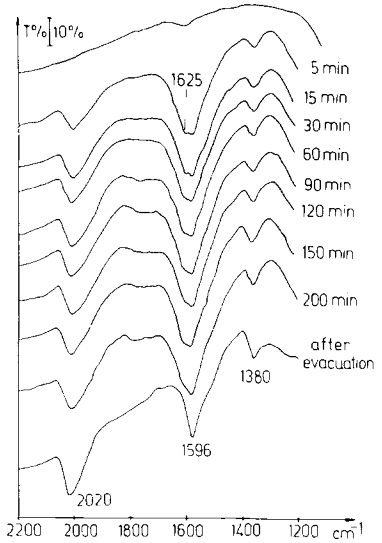


FIG. 4. Infrared spectra taken during the $H_2 + CO_2$ reaction on Rh/Al_2O_3 at 523 K. The flow rate of $H_2 + CO_2$ mixture (mole ratio 4 : 1) was 25 ml/min. The sample weight was 60 mg.

The 1625-cm^{-1} band is due to the carbonate species.

The intensities of the bands in the range 1370–2100 cm^{-1} varied only a little with the reaction time; their position was remarkably constant during the reaction (Fig. 4). The intensities and locations of these bands changed a little when the reactant gas mixture was replaced with pure N_2 at 523 K. In a pure H_2 flow, however, the band at 2020 cm^{-1} soon disappeared. The intensities of the bands at 1596 and 1380 cm^{-1} also decreased slowly.

Qualitatively similar results were obtained on Rh/MgO. The positions of the bands were somewhat different, and they were produced with higher intensities than on Rh/Al_2O_3 in the same reaction time (Fig. 5). The CO band appeared at 2035, the formate band at 1600 cm^{-1}. In the case of Rh/SiO_2, only a band at 2031 cm^{-1} was detected during the reaction (Fig. 6). Its intensity was lower than in the previous cases. There was no indication of the formation of formate ion or any other surface complexes. The low transmittance of the Rh/TiO_2 sample in the presence of H_2/CO_2

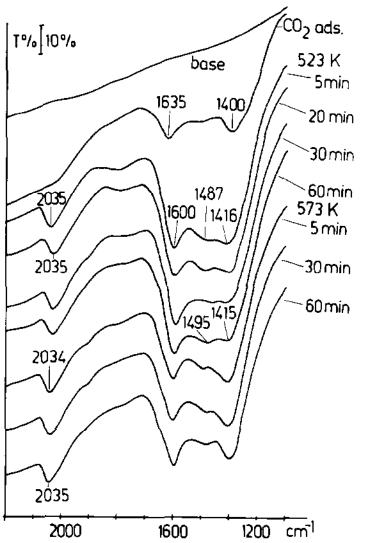


FIG. 5. Infrared spectra taken during the $H_2 + CO_2$ reaction on 1% Rh/MgO. The flow rate of $H_2 + CO_2$ mixture (mole ratio 4 : 1) was 25 ml/min. The sample weight was 60 mg.

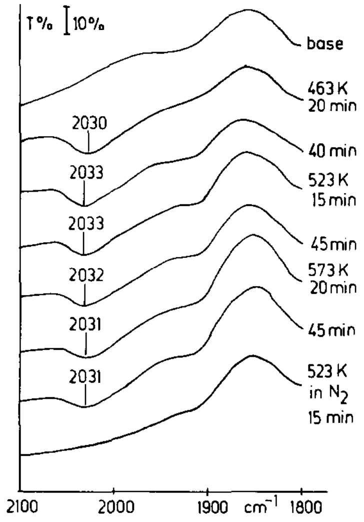


FIG. 6. Infrared spectra taken during the $H_2 + CO_2$ reaction on Rh/SiO_2. The flow rate of $H_2 + CO_2$ mixture (mole ratio 4 : 1) was 25 ml/min. The sample weight was 60 mg.

gas mixture prevented the performance of infrared spectroscopic measurements during the catalytic reaction.

3. *Formation and Reactivity of Surface Carbon*

After the catalytic run had been completed the surface of the catalysts was examined. When the $H_2 + CO_2 + He$ flow was replaced with He and then with a H_2 + He stream, the formation of CH_4 was observed for the next 10–20 min, but no other hydrocarbon was detected. The initial rate of methane formation on Rh/Al_2O_3 was practically the same as that observed at the steady state, but it fell quickly. Similar results were obtained on other Rh samples. It was revealed by ir spectroscopic measurements that in the case of the Rh/SiO_2 sample all the adsorbed CO was removed in 2–3 min in He at 573 K, and hence it may justifiably be assumed that the observed CH_4 evolution, at least in that case, is exclusively due to the hydrogenation of surface carbon formed in the $H_2 + CO_2$ reaction.

In order to establish the effects of the reaction time and the temperature on the carbon deposit, the Rh samples were treated with the reactant gas mixture under the same conditions, and the surface was then reacted with H_2 pulses (1 ml) in a He flow until CH_4 formation ceased. Some results for Rh/SiO_2 are shown in Fig. 7. The amount of carbon deposited increased initially but soon reached a steady value. Its limiting ratio to the number of surface Rh atoms, C/Rh_S, was 0.31. It varied only slightly with the reaction temperature.

Similar phenomena were observed on other Rh samples. In these cases, however, the study of carbon formation was somewhat more difficult, as formate and carbonate species were also present on the surface; their complete elimination required treatment above 573 K, where aging of surface C may be occurred to some extent. Nevertheless, the amount of surface carbon formed in the catalytic reaction on different Rh samples showed no significant variation with the supports. It should be mentioned here, that with a stoichiometric mixture of $H_2 + CO$ (3 : 1), the amount of the carbon

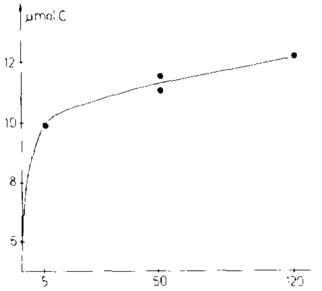


FIG. 7. The amount of surface carbon formed in the H_2 + CO_2 reaction at 573 K on Rh/SiO_2 at different reaction times. The amount of carbon was determined in the form of CH_4 by treating the surface with H_2. The sample was flushed with He before H_2 introduction. The amount of catalyst was 0.32 g.

deposit on Rh samples at 473–573 K was about 3–5 times higher than in this case. The hydrogenation of the surface carbon produced not only CH_4, but 1–3% ethane too. Interestingly, the initial rate of CH_4 production in this case was about 20 times higher than that measured at the steady state, indicating that the chemisorbed CO inhibits the reaction (*10*).

The reactivity of the surface carbon was investigated in greater detail by means of a more sensitive pulse technique. The following procedure was applied: after oxidation and reduction of the catalyst sample at 673 K, it was degassed in a He flow for 30 min at 673 K, and cooled down in He to the reaction temperature.

Upon admission of a H_2 + CO_2 pulse (molar ratio 4 : 1) onto the reduced Rh/SiO_2 at 523 K, 2% of the CO_2 was tranformed into CH_4. After He purging (at this temperature 15 min was required for elimination of the adsorbed gases) the sample was cooled down in He to different temperatures and exposed to several pulses of H_2. A small amount of surface carbon was hydrogenated to methane even at low temperature; at 300 K 0.17% and at 373 K 1.6% of the surface carbon reacted with H_2. At higher temperatures, methane formation was more considerable. At 523 K, 22% of the surface carbon reacted with the first two H_2 pulses, yielding methane, and an additional 18 H_2 pulses converted 65% of the remainder (Fig. 8). The rate of CH_4 production above 500 K depended on how rapidly the catalyst sample was brought into reaction with the H_2. When 30 min had passed between the injection of the H_2 + CO_2 and the H_2 pulses, much less CH_4 was produced in the first ten pulses.

The high reactivity of the surface carbon toward H_2 at low temperatures was also observed by Rabó *et al.* (*12*) in the case of Ni, Co, and Ru catalysts.

DISCUSSION

Supported Rh proved to be a very effective catalyst for the hydrogenation of CO_2. Kinetic data are listed in Table 1. For comparison, the data obtained for the H_2 + CO reaction on Rh/Al_2O_3 (*10*, *13*) are also shown. The reaction yields methane almost exclusively and on Rh/Al_2O_3 it occurs much faster than the hydrogenation of CO. The value of the activation energy, 16.2 kcal/mol, is also less.

The present data fit in quite well with the recent investigations of Sexton and Somorjai (*14*) over Rh foil; they also obtained 16 kcal/mol for the activation energy, and found a higher reaction rate than in the case of the hydrogenation of CO.

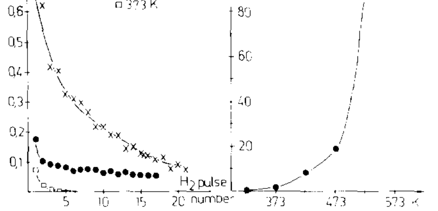


FIG. 8. (A) The formation of CH_4 in the reaction of surface carbon with H_2 pulses on Rh/SiO_2 at different temperatures. The carbon was produced by injecting one pulse (1 ml) of H_2 + CO_2 mixture (mole ratio 4 : 1) onto the sample at 523 K. The sample was flushed with He before H_2 introduction. One H_2 pulse contained 41.6 μmole H_2. (B) The maximum amount of surface carbon transformed into CH_4 in the reaction with H_2 at different temperatures.

This study, however, further demostrated that variation of the support drastically changes the specific activity of Rh. The most effective support was found to be TiO_2. The hydrogenation of CO_2 on Rh/TiO_2 occurred even at 403 K. Its specific activity was one order of magnitude higher, while that of Rh/SiO_2 was a factor of 4 lower than that of Rh/Al_2O_3.

As concerns the mechanism of the methanation of CO_2, two main routes can be considered:

(1) The reaction occurs through the formation of a surface complex.

(2) CO_2 first dissociates, and the further reactions are the same as in the case of the hydrogenation of CO.

Let us investigate these possibilities in more detail.

1. The Role of the Surface Formate Complex

In a study of the adsorption of H_2 and CO_2 on Rh/Al_2O_3 at low temperatures (298–373 K), we observed that the presence of H_2 resulted in a dramatic increase in the gas uptake (*8*). Infrared spectroscopic measurements showed that this was mainly due to formation of the formate group. The dominant role of the rhodium in the formation of the formate ion was clearly indicated by the following observations:

(i) no absorption bands due to formate were detected by ir spectroscopic measurements in the absence of Rh at such low temperatures;

(ii) the activation energy for the formation of the formate ion, 4.2 kcal/mol (*8*), was markedly less than that determined on pure alumina in a higher temperature range (*15*).

However, there was no indication of the presence of formate ions on Rh. Therefore, backed up by various control measurements, it was concluded that the formate ion is located not on the Rh, but rather on the support.

In the ir spectra taken under the reaction conditions, the absorption bands characteristic of the formate ion (1596 and 1380 cm^{-1}) also appeared (Fig. 4). Their intensities were somewhat less than for the low-temperature adsorptions, and they reached the highest values at the beginning of the reaction, indicating that the main route of the $H_2 + CO_2$ reaction now is the production of CH_4. Taking into account the correlation between the absorbance of the formate band at 1596 cm^{-1} and the amount of the formate ion (*11*), the surface concentration of the formate ion on Rh/Al_2O_3 at 523 K was calculated to be 193 μmol/g catalyst. This value is almost 1.3 times higher than the number of surface Rh atoms.

This behavior makes it unlikely that the formate ion is a real surface intermediate in the hydrogenation of CO_2. This conclusion is supported by the observation that the formation of the formate ion was not observed on Rh/SiO_2 at either temperature, although the hydrogenation of CO_2 occurred rapidly above 473 K (Fig. 6). The formate group was detected on Ru/Al_2O_3 in the H_2 + CO (*16*) and $H_2 + CO_2$ (*17*) reactions, when its role in the methanation was also discounted.

2. The Role of the Dissociation of CO_2

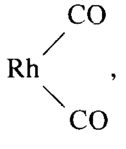
Let us deal now with the possibility of dissociation of CO_2. There is considerable uncertainty in the literature concerning the adsorption and dissociation of CO_2 on Rh. In the early studies on polycrystalline Rh (*18*), on Rh films (*19*), and on supported Rh (*20*) the adsorption of CO_2 was found to be very weak and nondissociative. Recently Somorjai *et al.* (*21–23*) showed that the dissociation of CO_2 does occur on several single-crystal and polycrystalline samples, CO and CO_2 gave an identical series of LEED patterns on both (111) and (100) Rh surfaces. Electron energy loss spectra of chemisorbed CO and CO_2 on Rh(111) were also identical, but CO_2 required a fivefold higher exposure to achieve the same surface structure.

On supported Rh, different observations have been made. Using ir spectroscopic measurements, Yang and Garland (*20*) found no evidence for the dissociation of CO_2 on Rh/Al_2O_3 at 300 K. No band due to adsorbed CO was identified on Rh/zeolite (*24*), but a CO band was detected on Rh/Al_2O_3 (*8*, *24*).

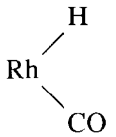
As the dissociation of CO_2 is very probably affected by the adsorbed gases (adsorbed hydrogen may promote dissociation, while adsorbed oxygen exerts an opposite effect), great care should be exercised to eliminate these gases from the surface. In addition the dispersity of the Rh may also be important factor.

Infrared, TPD, and pulse experiments unambiguously show that CO is formed on the surface both in the low-temperature interaction of $H_2 + CO_2$ (*8*) and at methanation temperatures. Its formation is assisted by the presence of H_2, as on this relatively poorly dispersed Rh in the absence of H_2 CO was not formed, or in only extremely small concentration. The surface concentration of adsorbed CO remained at a very low level during the catalytic reaction, and it disappeared when CO_2 was removed from the gas phase; it might thus be considered as one of the surface intermediates of the $H_2 + CO_2$ reaction (intermediate I). Taking into account the observation that the adsorption of formic acid on supported Rh produced adsorbed CO species even at low temperatures (*8*), we cannot exclude the possibility that the formation of CO in the $H_2 + CO_2$ reaction occurs through the formation and decomposition of formate ion.

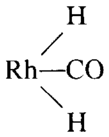
The structure and the reactivity of this adsorbed CO, however, differ markedly from those resulting from the adsorption of CO (*24–29*). The CO formed in the $H_2 + CO_2$ reaction is very probably bonded only in the linear form. The twin CO structure,



absorbing at 2104 and 2035 cm^{-1}, was completely missing, and the bridged, CO gave only a very weak band at 1850 cm^{-1}. In addition, the bands due to the CO formed in the $H_2 + CO_2$ reaction appeared at lower frequencies (2030 and 2020 cm^{-1}) than those corresponding to the Rh–CO species (~2060 cm^{-1}). This could be due to the weak CO coverage (*23*, *24*). On the basis of the effect of hydrogen on the ir spectra of chemisorbed CO (*8*, *20*, *27*, *29*), however, we may assume that the CO is bonded to Rh which is also lined to one or two H atoms; thus



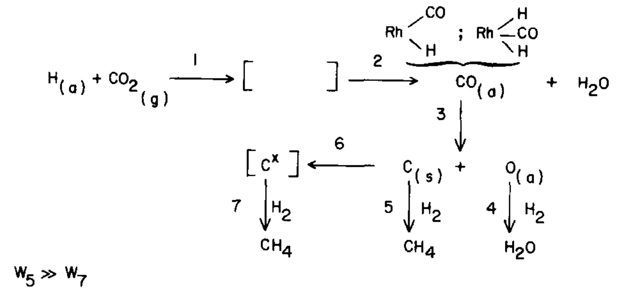
and



are formed. As the H bonded to a Rh atom of a carbonyl complex is electron donating, which increases the π-donation from the Rh into an antibonding π-orbital of the CO, resulting in a decrease of ν_{CO}, the shift to lower frequency is understandable. Calculation showed, however, that this shift cannot be greater than about 10 cm^{-1} for each hydrogen ligand added (*29*). As a CO band was observed at 2030–2020 cm^{-1}, it may be assumed that the surface carbon formed in the reaction also contributes to the shift to lower frequencies (*16*, *17*, *30*). The dissociation of CO in these forms occurs more easily, as the above-described electron transfer increases the Rh–C bond strength, and at the same time weakens the C–O bond. Experiments have confirmed that in the $H_2 + CO_2$ reaction surface C did form (we denote this as intermediate II), which can be readily hydrogenated to methane.

3. *A Possible Mode for the Methanation of* CO_2

Accordingly, we may propose the following reaction scheme for the hydrogenation of CO_2:



Although we could not identify partially hydrogenated carbon, CH_2 or CH_3, by ir spectroscopic measurements (probably due to the small amount of carbon formed), it seems plausible that the hydrogenation of carbon occurs in a stepwise manner.

As the rate of methanation of CO_2 is much higher than that of CO, the dissociation of CO_2 cannot be the rate-limiting step. This is supported by the observation that the dissociation of CO_2, i.e., the formation of adsorbed CO, was already observed in the low-temperature interaction of H_2 + CO_2, where there was no methane formation at all.

In this case the question arises as to why the formation of CH_4 is faster and occurs with lower activation energy than when we use the H_2 + CO mixture. In our opinion the surface concentrations of CO and C play the key roles. When we use CO_2, the concentration of adsorbed CO, and hence the concentration of surface carbon, is relatively low. The carbon formed can react quickly with the large excess of H_2, and there is less possibility for the accumulation and aging of surface C. In contrast, when a H_2 + CO gas mixture is used, the surface concentration of adsorbed CO is greatly increased and thus the formation of surface carbon in a given time will be much larger. As a consequence, not all the surface carbon can be hydrogenated in the first instant, and there will be time for part of the carbon to be transformed to less reactive forms [C^x] (intermediate III), the hydrogenation of which is slower and requires a higher activation energy.

The aging of carbon is well illustrated by the study of the reaction of surface carbon (formed in either the H_2 + CO_2 reaction or the H_2 + CO reaction (*10*)) with H_2 pulses. The first two H_2 pulses produced more CH_4 than the subsequent four H_2 pulses; at 523 K about 22% of the surface C reacted with the first two H_2 pulses. Similarly as observed by McCarty and Wise (*31*) on Ni/SiO_2, the reactivity of the surface carbon formed in the disproportionation of CO depended on the temperature of its formation and also on the time between its formation and its coming into contact with H_2 (*10*).

On the other hand, when we use a H_2 + CO mixture, CO adsorbed on Rh can function as a poison toward hydrogen chemisorption, and hence results in a decreased methanation rate. This is well illustrated in Fig. 3, where the rate of hydrogenation of CO_2 on Rh/Al_2O_3 is plotted against the percentage of CO added to the H_2 + CO_2 + He mixture. Whereas a small amount of added CO promoted methane formation, very probably due to the increased production of surface carbon, CO in higher concentration definitely inhibited the hydrogenation of CO_2, i.e., the formation of CH_4.

In our view the high methanation selectivity observed in the hydrogenation of CO_2 can also be attributed to the low surface concentration of carbon. As a consequence of this, the lifetime and the surface population of CH_x species [the polymerization of which now seems responsible for the formation of higher-molecular-weight hydrocarbons (*32–34*)] will be considerably less than in the case of the hydrogenation of CO.

4. *The Effects of the Supports*

Kinetic data showed that variation of the support greatly influenced the specific methanation activity of the Rh catalyst. An exceptionally high activity was exhibited by the Rh/TiO_2 sample (Table 1). Renewed interest has recently been shown in the TiO_2 support (*35–39*). Metals on titania exhibited an outstanding catalytic performance in the NO + CO reaction (using noble metal catalysts) (*35*) and in the H_2 + CO reaction (using nickel catalyst) (*36*).

In our opinion the effect of the support in the present case can be attributed to different extents of electronic interaction between the Rh and the support, influencing the bonding and the reactivity of the chemisorbed species (*40*). As TiO_2 is an n-type semiconductor, a much greater electronic interaction can be expected in this case than with alumina or silica. In harmony with this, changing the Fermi level of the electrons in TiO_2 affects the catalytic activity of the metal more sensitively (*40, 41*).

Another factor which should be taken into account is that a chemical reaction can occur between TiO_2 and the metal during the reduction of titania-supported metals ("strong metal–support interaction" (*37–39*)); this may also play a role in the catalytic efficiency of Rh/TiO_2.

In order to reach a final conclusion concerning this problem, it is necessary to investigate the effects of the support on the H_2 + CO reaction, on the dissociation of CO, and on the reactivity of surface carbon formed on a Rh catalyst. Studies are also required to establish to what extent an electronic interaction and the formation of new compounds are responsible for the high activity of the Rh/TiO_2 sample.

REFERENCES

1. Vlasenko, V. M., and Yuzefovich, G. E., *Russ. Chem. Rev.* **38**, 728 (1969).
2. Mills, G. A., and Steffgen, F. W., *Catal. Rev.* **8**, 159 (1975).
3. Vannice, M. A., *Catal. Rev. Sci. Eng.* **14**, 153 (1976).
4. Ponec, V., *Catal. Rev. Sci. Eng.* **18**, 151 (1978).
5. Lunde, P. J., and Kester, F. L., *J. Catal.* **30**, 423 (1973).
6. Phyng Quach, T. Q., and Rouleau, D., *J. Appl. Chem. Biotechnol.* **26**, 527 (1976).
7. Solymosi, F., and Erdöhelyi, A., *J. Mol. Catal.* **8**, 471 (1980).
8. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Catal.* **65**, 428 (1980).
9. Körös, R. M., and Nowak, E. J., *Chem. Eng. Sci.* **22**, 470 (1967).
10. Erdöhelyi, A., thesis, The University, Szeged, 1977; Solymosi, F., Tombácz, I., and Erdöhelyi, A., to be published.
11. Amenomiya, Y., *Appl. Spectrosc.* **32**, 484 (1978).
12. Rabó, J. A., Risch, A. P., and Poutsma, M. L., *J. Catal.* **53**, 295 (1978).
13. Vannice, M. A., *J. Catal.* **37**, 499 (1975).
14. Sexton, B. A., and Somorjai, G. A., *J. Catal.* **46**, 167 (1977).
15. Amenomiya, Y., *J. Catal.* **57**, 64 (1979).
16. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **48**, 111 (1977).
17. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Chem. Soc. Faraday Trans. I*, in press.
18. Campbell, C. T., and White, J. M., *J. Catal.* **54**, 289 (1978).
19. Collins, A. C., and Trapnell, B. M. W., *Trans. Faraday Soc.* **53**, 1436 (1957).
20. Yang, A. C., and Garland, C. W., *J. Phys. Chem.* **61**, 1504 (1957).
21. Castner, D. G., Sexton, B. A., and Somorjai, G. A., *Surface Sci.* **71**, 519 (1978).
22. Castner, D. G., and Somorjai, G. A., *Surface Sci.* **83**, 60 (1979).
23. Dubois, L. H., and Somorjai, G. A., *Surface Sci.* **91**, 514 (1980).
24. Primet, M., *J. Chem. Soc. Faraday Trans. I* **74**, 2570 (1978).
25. Arai, H., and Tominaga, H., *J. Catal.* **43**, 131 (1976).
26. Solymosi, F., and Sárkány, J., *Appl. Surface Sci.* **3**, 68 (1979).
27. Yates, J. T., Duncan, T. M., Worley, S. D., and Vaughan, R. W., *J. Chem. Phys.* **70**, 1219 (1979).
28. Yates, D. J. C., Murrell, L. L., and Prestridge, E. B., *J. Catal.* **57**, 41 (1979).
29. Yates, J. T., Worley, S. D., Duncan, T. M., and Vaughan, R. W., *J. Chem. Phys.* **70**, 1225 (1979).
30. Eckerdt, J. G., and Bell, A. T., *J. Catal.* **58**, 170 (1979).
31. McCarty, J. G., and Wise, H., *J. Catal.* **57**, 406 (1979).

32. Ponec, V., and van Barneveld, W. A., *Ind. Eng. Chem. Prod. Res. Develop.* **18,** 268 (1979).
33. Biloen, P., Helle, J. N., and Sachtler, W. M. H., *J. Catal.* **58,** 95 (1979).
34. King, O. L., *J. Catal.* **61,** 77 (1980).
35. Solymosi, F., Völgyesi, L., and Sárkány, J., *J. Catal.* **54,** 336 (1978); Solymosi, F., Völgyesi, L., and Raskó, J., *Z. Phys. Chem. N.F.* **120,** 79 (1980).
36. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. soc.* **100,** 170 (1978).
37. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
38. Baker, R. T. K., Prestridge, E. B., and Garten, R. L., *J. Catal.* **59,** 293 (1979).
39. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).
40. Solymosi, F., *Catal. Rev.* **1,** 233 (1967).
41. Szabó, Z. G., and Solymosi, F., *in* "Proceedings 2nd International Congress on Catalysis," p. 1627. Editions Technip, Paris, 1961.