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Hydrogenation of CO on Supported Rh Catalysts[1]

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The hydrogenation of CO on supported Rh was investigated in a flow technique. Special attention was focused on the identification of surface species formed during the reaction. The reaction occurred at measurable rate above 473 K. The product distribution sensitively depended on the support; while on Rh/SiO_2 mainly CH_4 was formed, on Rh/TiO_2 a number of C_2–C_5 compounds were also produced. *In situ* infrared spectroscopic measurements showed that only the linearly bonded CO exists with a detectable concentration on the surface during the reaction. It appeared, however, at lower frequencies than that corresponding to the Rh–CO species. In addition, the absorption bands characteristic for the formate ion and CH_x compounds were also identified. The formation of surface C was also detected. Its amount increased during the conditioning period and also with temperature elevation. The specific rate of CH_4 formation on Rh/TiO_2 was more than one order of magnitude higher than that of the less effective Rh/MgO and Rh/SiO_2 catalysts. From the behaviors of surface formate under different conditions it was inferred that it does not play an important role in hydrocarbon synthesis on Rh catalysts. It is proposed that the important steps in CH_4 formation are the dissociation of CO promoted by adsorbed hydrogen and the subsequent hydrogenation of surface carbon. As regards the high activity of Rh/TiO_2 it is assumed that an electronic interaction operates between the TiO_2 and Rh influencing the bonding and reactivity of chemisorbed species.

1. INTRODUCTION

In an investigation of the methanation of CO_2 on an alumina-supported noble metal catalyst we found that Rh exhibits outstanding catalytic performance in this reaction (*1*, *2*). Its specific activity was influenced dramatically by the support (*2*). As the methanation of CO_2 very probably occurs through the transient formation and subsequent dissociation of CO, it seemed important to examine the hydrogenation of CO on such catalysts more thoroughly, with special emphasis on the surface processes, the formation and reactivity of surface carbon, and the effects of the supports on these reactions.

Kinetic data relating to the hydrogenation of CO and the product distribution on Rh samples have been determined previously (*3*). No attention was paid, however, to the identification of the surface species formed during the reaction. Sexton and Somorjai (*4*) investigated the reaction on Rh foil. Auger analysis revealed that carbon was deposited on the surface during the reaction. The specific rate and the activation energy of the methanation agreed very well in the two cases. Fujimoto *et al.* (*5*) recently studied the hydrogenation of chemisorbed CO on alumina and silica-supported Rh by a temperature-programmed desorption method. They concluded that the "bridge" CO was hydrogenated at a lower temperature than the linear CO.

2. EXPERIMENTAL

2.1. Materials. The same catalyst samples were used as in the case of the hydrogenation of CO_2 (*2*). Their characteristic data are shown in Table 1. They were prepared by impregnation of the supports with solutions of $RhCl_3 \cdot 3H_2O$. For adsorption and catalytic studies, fragments of slightly compressed pellets were used; for ir spectroscopic measurements, the samples were compressed at high pressure (~1600) atm into transparent thin wafers. The sample

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TABLE 1

Kinetic Data for the Hydrogenation of CO on Supported Rh Catalysts

	Area of the supports (m^2/g)	The amount of chemisorbed H_2 (μmol H_2/g catalyst)	Rh dispersion[a] (%)	N_{CH_4}[b]	N_{i,CH_4}[c]	E (kcal/mol)	A (s^{-1} atm^{-x-y})	X[d]	Y[d]
				$\times 10^3$, at 548 K					
TiO_2 (Degussa, 200)	150	10.83	22.3	61.6	321	18.3 ± 2.3	4.76×10^5	0.75 ± 0.09	−0.88 ± 0.04
Al_2O_3 (Degussa P110 C 1)	100	14.67	30.2	11.3	39	24.0 ± 2.6	3.3×10^7	0.9 ± 0.06	−0.42 ± 0.09
MgO (DAB 6)	170	7.58	15.6	3.36	4.5 (82)[e]	23.7 ± 1.9	6.47×10^6	0.8 ± 0.07	−0.50 ± 0.13
SiO_2 (Aerosil 200)	240	16.13	33.2	4.14	5.64 (51)[e]	22.6 ± 1.1	4.10×10^6	0.57 ± 0.15	−0.20 ± 0.06

[a] Rh dispersion = percentage exposed of Rh. The amount of Rh was 1 wt%.

[b] N_{CH_4} = turnover number (molecules formed /metal site × sec) at the steady state.

[c] N_{i,CH_4} = initial turnover number extrapolated to zero time.

[d] The partial pressure of H_2 (X) and CO (Y) were varied between 0.09–0.9 atm for H_2 and 0.08–0.42 atm for CO.

[e] At 613 K.

thickness was in the range 15–20 mg/cm^2.

Before any measurements, the catalyst was oxidized with 100 Torr O_2 for 30 min and reduced with 100 Torr H_2 for 30 min at 673 K *in situ*. After oxidation and reduction, the sample was evacuated prior to adsorption and infrared spectroscopic measurements for 30 min up to 10^{-5} Torr vacuum. The gases used were carefully purified by adsorbing the impurities with a molecular sieve at the temperature of liquid air. Their purities were checked by mass spectrometry.

2.2 Methods. Adsorption measurements were carried out in a Sartorius microbalance. The dispersity of the supported Rh was determined by H_2 chemisorption at 298 K. Infrared spectra were recorded with a Specord 75 IR double-beam spectrometer (Carl Zeiss, Jena). For room-temperature measurements, a Kiselev ir cell was used with NaCl windows; a detailed description of the cell has been given elsewhere (*6*). For spectroscopic measurements during the catalytic reaction, a high-temperature ir cell was used (*7*).

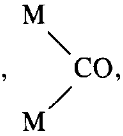
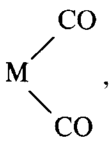
The hydrogenation of CO was investigated in a flow microreactor at atmospheric pressure. The space velocities were 3000–6000 hr^{-1}. In the kinetic measurements the conversion of CO was kept less than 10–15%. The absence of diffusional limitation was confirmed by the method suggested by Körös and Nowak (*8*). Analyses of the gases were performed with a Hewlett–Packard and with a Chrom-4 gas chromatograph. A 2-m-long 0.25-in.-diameter column packed with Poropak QS allowed complete separation and determination of reactants and products.

Pulse experiments were carried out in a microcatalytic pulse system. The microreactor was incorporated between the sample inlet and the analytical column of the gas chromatograph. The reactor was made from 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 catalyst used was 0.3–0.6 g. The ratio of H_2/CO in the reacting gas mixture was in general 3 : 1. Helium was used whenever a diluent was needed.

3. RESULTS

3.1. Low-Temperature Interaction

In the study of the adsorption of CO_2 on Rh/Al_2O_3 we observed that the presence of H_2 *greatly* enhanced the uptake of CO_2 (*9*). Infrared spectroscopic studies revealed that CO and formate ion are formed in the surface interaction of $H_2 + CO_2$. A similar conclusion was reached for the Rh/MgO and Rh/TiO_2 (*10*). On Rh/SiO_2, only very slight enhanced adsorption was experienced (*10*).

In the case of the adsorption of CO at 298–373 K, however, the presence of H_2 exerted no or only a slight influence on the adsorption of CO (Fig. 1). The adsorption of CO on reduced Rh/Al_2O_3 at 298 K produced four bands in the range of CO stretching; these correspond to the formation of linearly bonded CO, M–CO, absorbing at 2060–2070 cm^{-1}, bridged CO,  , absorbing at 1850–1910 cm^{-1}, and twin CO,  , absorbing at 2101 and 2030 cm^{-1} (Fig. 2). Only very slight change in the spectrum was experienced when the adsorption temperature was raised to 373 K, and the spectrum was taken at this temperature in the presence of gaseous CO or after its pumping off at 298 K.

The presence of H_2 had only a small influence on the infrared spectra at 298 K (Fig. 2). At 373 K, however, in accordance

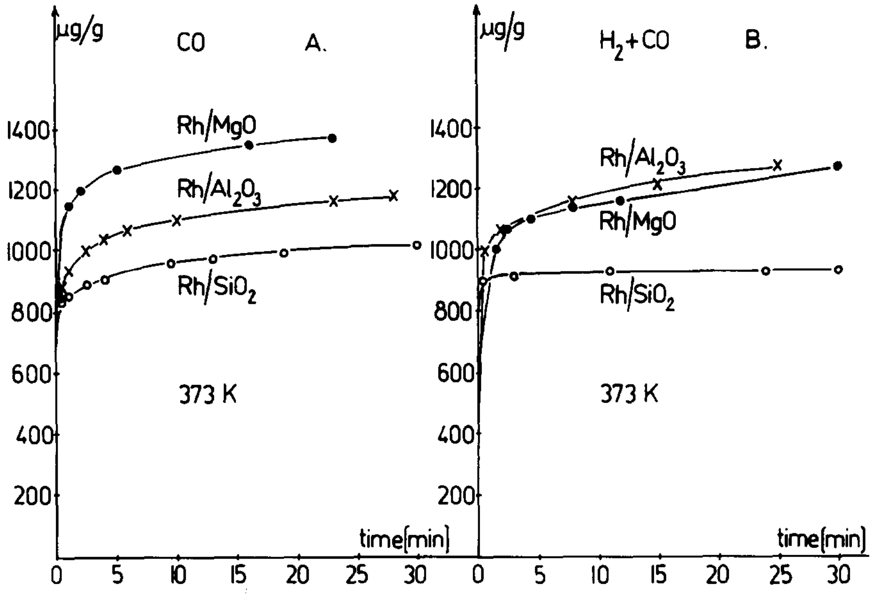


FIG. 1. Adsorption of 20 Torr CO (A) and 40 Torr H_2 + CO (1 : 1) (B) on reduced Rh samples at 373 K. In the latter case the ordinate refers to total gas (H_2 + CO) uptake. The amount of samples was 200 mg.

with the results of Yang and Garland (*11*), the intensity of the twin band was greatly decreased, and the band due to linearly bonded CO was shifted to slightly lower frequency (Fig. 2). At 298–373 K there was no indication of the presence of any new band in either the low (1200–1700 cm^{-1}) or high-frequency (2500–3000 cm^{-1}) range. Similar phenomena were observed for Rh supported by other oxides.

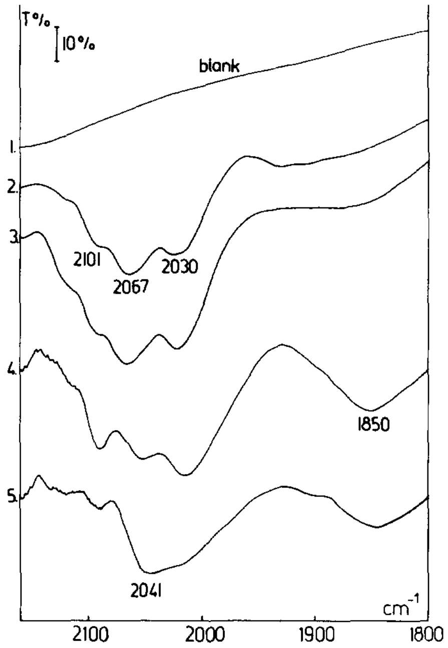


FIG. 2. Infrared spectra of Rh/Al_2O_3 in the presence of CO at 298 K (2); and in the flow of reacting gas mixture (H_2 : CO : N_2) at 298 K for 10 min (3); at 298 K for 30 min (4); at 373 K for 15 min (5). The flow rate was 32 ml/min. The mole ratio of reacting gas mixture was 3 : 1 : 20.

3.2. Kinetic Measurements

The temperature range of measurable rates of CH_4 formation depended on the support. On all the catalyst samples, considerable decreases in the conversion and CH_4 formation occurred as time passed. This is in contrast with the hydrogenation of CO_2, where practically no deactivation of the supported Rh catalysts was experienced. Before kinetic measurements the catalyst was treated with the reacting gas mixture at the highest reaction temperature used (ca. 10–15% conversion) until a steady-state activity (constant activity) was obtained. This required in general 30–120 min.

The selectivity for CH_4 formation depended on the support. In the steady state it was 92–94% on Rh/SiO_2, 82–86% on Rh/Al_2O_3, 71–75% on Rh/TiO_2, and 60–65% on Rh/MgO. With the exception of Rh/SiO_2, it showed only little variation during the decrease of the activity. In the case of Rh/SiO_2 a well-reproducible increase was observed, from an initial value of 83% (5 min) to 94%. In the temperature range to achieve 1–12% conversion, the selectivity for CH_4 formation was practically constant, with the exception of Rh/MgO, where it increased with the rise of the reaction temperature from 548 to 623 K. It is likely that the selectivity change for Rh/MgO is due to the higher conversion.

The product distributions on the different catalysts are shown in Fig. 3. The values refer to the steady state, when the conversion of CO was about 8–12%.

In addition to methane, a large number of hydrocarbons were formed on Rh/Al_2O_3 and Rh/TiO_2. Although both the methanation and the overall activities decayed with time, the relative yields of higher molecular weight products to methane, C_n/C_1, increased during the conditioning period. This is illustrated for Rh/TiO_2 in Fig. 4, which also shows the changes in the amounts of the products during the conditioning period. An increase in the absolute values during the conditioning period was observed only for propylene.

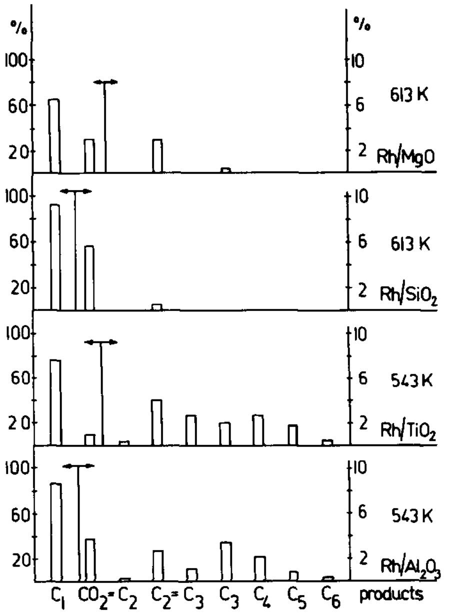


FIG. 3. Product distribution for the H_2 + CO reaction on different Rh samples at the steady state.

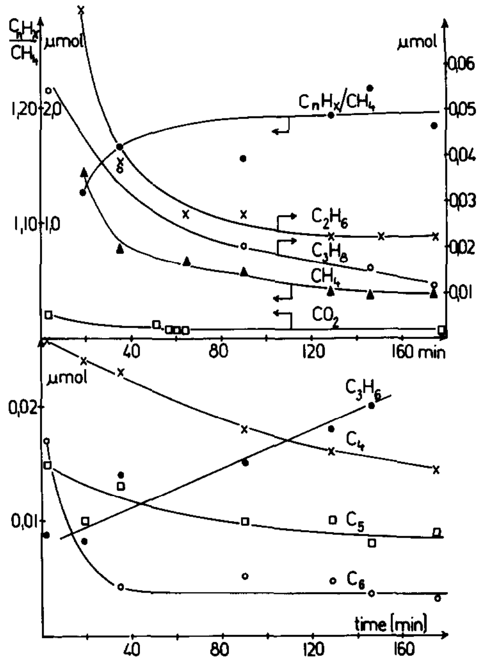


FIG. 4. Variations of the products of the H_2 + CO reaction over Rh/TiO_2 during the conditioning period at 543 K.

On Rh/SiO_2 and on Rh/MgO the extents of CO_2 formation were higher than on the other samples; in these cases only C_2 and C_3 (Rh/MgO) compounds were identified from among the higher molecular weight products. On Rh/TiO_2 and on Rh/MgO a small amount of methanol was also produced.

The variation of the rate of methane production with the partial pressures was determined from the slope of log–log plots of the rate against the reactant partial pressure (Fig. 5). The following empirical equation was used to describe the rate of CH_4 formation:

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

where N_{CH_4} is the rate of CH_4 formation per

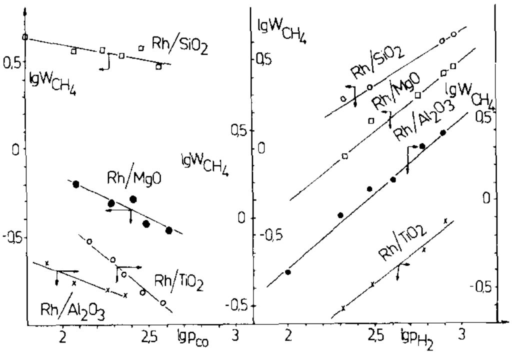


FIG. 5. Dependence of rate of CH_4 formation on the partial pressures of CO and H_2 at 3–5% conversion.

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, respectively. Arrhenius diagrams for the four samples are shown in Fig. 6. The rate parameters and kinetic data are listed in Table 1.

It appears that the most active catalyst is Rh/TiO_2, but its catalytic activity decays to the greatest extent.

3.3. *Examination of the Catalyst Surfaces during and after the Reaction*

In the subsequent experiments we examined what kinds of surface species are formed during the catalytic reaction on different Rh samples. First ir spectroscopic measurements were carried.

In situ ir spectroscopic measurements. The disk made from the catalyst powders underwent the same treatment as before the catalytic studies. The background spectra were taken in vacuum and in H_2, and no difference was observed. The flow of reacting gas mixture was 32 ml/min.

Figure 7 shows the spectra obtained for Rh/Al_2O_3 at 473–548 K. In the range of C–O stretching vibrations bands appeared at 1850 and 2040 cm^{-1}. The intensities of these bands hardly changed in time, and were almost the same at 473 and 548 K. Another spectral feature is the appearance of a strong band at 1595 cm^{-1}, a weaker one at 1380 cm^{-1}, and a shoulder at 1393 cm^{-1}. A very weak band at 2914 cm^{-1} was also identified. The intensities of these bands increased as the reaction time was lengthened at 473 K. When the temperature was raised to 523–573 K, they appeared at lower intensities. As these bands were also observed during the adsorption of formic acid on alumina (*12*) and on Rh/Al_2O_3 (*9, 10*), we feel justified in attributing them to *the adsorbed formate ion.* The 1595 cm^{-1} band is due to the asymmetric and the 1380 cm^{-1} band to the symmetric O–C–O stretching vibrations of formate ion. The very weak band at 2914 cm^{-1} is probably due to a CH stretching vibration, while the band at 1393 cm^{-1} relates to a C–H deformation mode. This assignment is confirmed by using D_2 instead of H_2.

Bands also developed at 1625, 1450 and

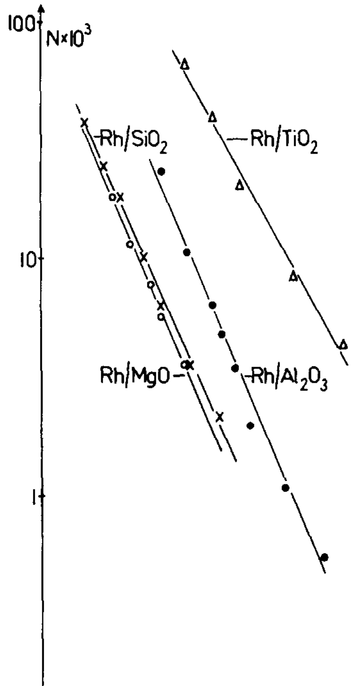


FIG. 6. Arrhenius plots for Rh samples. N_{CH_4} = turnover number, rate of CH_4 formation per surface Rh sites.

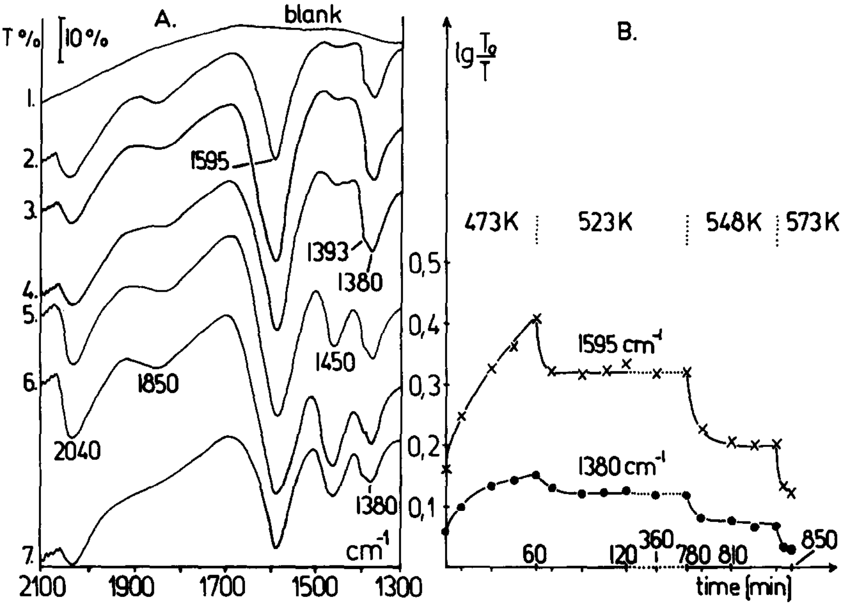


FIG. 7. (A) Infrared spectra taken during the H_2 + CO reaction on Rh/Al_2O_3. The flow rate of H_2 : CO : N_2 mixture (mole ratio 3 : 1 : 20) was 32 ml/min. (1) Blank; (2) 473 K for 10 min; (3) 473 for 60 min; (4) 523 K for 10 min; (5) 523 K for 360 min; (6) 523 K for 780 min; (7) 548 K for 60 min. (B) Changes in the intensities of formate bands at ~1595 and 1380 cm^{-1}.

1210 cm^{-1}, which can be attributed to the formation of surface carbonate and adsorbed water (1625 cm^{-1}).

When H_2 and CO were eluted and the flow contained only N_2, the intensities of all bands gradually decreased. When only CO was eluted from the gas mixture, the elimination of formate bands occurred much faster.

Similar measurements were performed on Rh/MgO and Rh/SiO_2.

Absorption bands due to adsorbed CO on Rh/MgO appeared at the beginning of the catalytic reaction, at 2045 and 1910 cm^{-1}. With the progress of the reaction and particularly at higher temperature, that at 2045 cm^{-1} was shifted to lower frequencies (as far as 2030 cm^{-1}), without any change in its intensity. The location and the intensity of the band at 1910 cm^{-1} remained unchanged during the experiments. A strong formate band at 1600 cm^{-1} was also produced by the reaction. It behaved similarly as in the case of Rh/Al_2O_3. When formic acid was injected into the reacting gas mixture, the intensities of the formate bands temporarily increased, but soon decreased to the values observed before its introduction.

On Rh/SiO_2 there was no indication of the formation of the formate band, and the presence of adsorbed CO was indicated only by the appearance of the bands at 2050 and at 1884–1894 cm^{-1}. No shift of these bands was observed with the progress of the reaction or on increase of the temperature.

Attempts were made to perform similar measurements with Rh/TiO_2 catalyst. The marked decrease in the transmittance of the sample in the presence of H_2 + CO mixture, however, made this program impossible.

Isotopic substitution. In order to ascertain whether the formate ion formed during the methanation of CO participates in the reaction or is a totally inactive species, isotope substitution experiments were performed and the reactivity of the formate species toward H_2 was investigated. In order to save D_2, these experiments were carried out in a closed circulation system, in which a high-temperature ir cell served as reactor.

H_2 + CO was reacted over the catalyst at 473 K for 60 min, and then the gases were evacuated and D_2 + CO was introduced. The results obtained on Rh/Al_2O_3 are shown in Fig. 8.

It can be seen that significant changes occurred in the spectra even after 30 min. The 2915, 2850, and 1395 cm^{-1} bands decreased in intensity to very low values. The intensities of the 1595 and 1380 cm^{-1} bands remained the same, and they shifted only slightly, to 1588 and 1349 cm^{-1}. When the gaseous phase was removed from the cell, a new band became apparent at 2200 and a very weak one at 2098 cm^{-1}.

Similar spectral changes were observed when formic acid was adsorbed on Rh/Al_2O_3 and, after evacuation, D_2 + CO was reacted on this surface at 473 and 523 K.

No such phenomena were experienced on pure Al_2O_3, however; in this case the positions of the intense absorption bands observed at 1585, 1392, and 1370 cm^{-1} after adsorption of formic acid hardly changed in the presence of D_2 or D_2 + CO at 473 or 523 K.

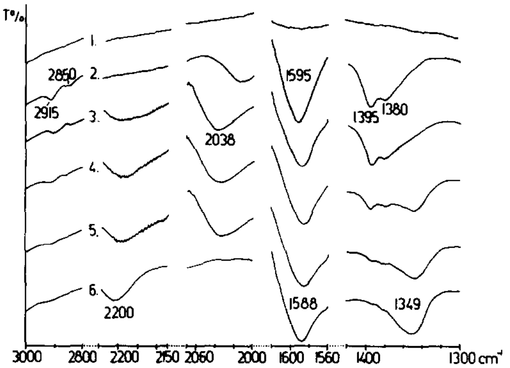


FIG. 8. Isotope substitution during the H_2 + CO reaction on Rh/Al_2O_3. (1) Blank, (2) spectra taken in vacuum after circulating 100 Torr H_2 + CO mixture over the catalyst disk at 473 K for 60 min. Spectra taken at 523 K after admission of 100 Torr D_2 + CO on the previous sample, reaction times: 5–25 min (3); 55–75 min (4); 80–100 min (5); and after evacuation at 473 K (6).

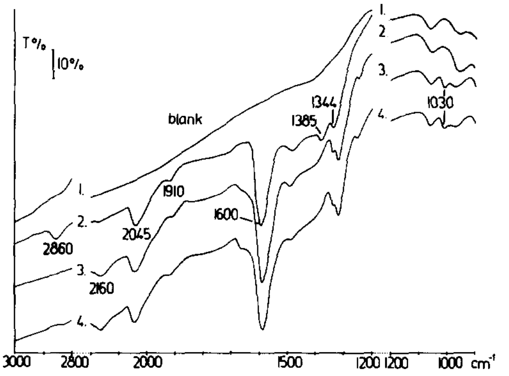


FIG. 9. Isotope substitution during the H_2 + CO reaction on Rh/MgO. (1) Blank, (2) spectra taken in vacuum after circulating 100 Torr H_2 + CO mixture over the catalyst disk at 473 K after 60 min. Spectra taken at 523 K after admission of 100 Torr D_2 + CO on the previous sample, reaction time: 15–30 min (3); 45–65 min (4).

When the surface formate was produced on Rh/Al_2O_3 by the reaction of D_2 + CO, absorption bands appeared at 2200, 2098, 1583, and 1347 cm^{-1} due to $DCOO^-$ (see Discussion), and at 2030 cm^{-1} due to adsorbed CO. After switching to a reaction mixture of H_2 + CO, the spectral changes were the opposite of those observed before. After 60 min at 473 K the same bands appeared as were obtained when H_2 + CO reacting gas mixture was admitted onto the clean reduced sample.

The same experiments were performed on Rh/MgO. The results are shown in Fig. 9. On replacing the H_2 + CO reacting gas mixture with D_2 + CO, we observed similar shifts in the ir spectra as for Rh/Al_2O_3. In addition, however, in the presence of D_2 a new band at 1030 cm^{-1} could also be well resolved.

It should be mentioned that no, or only very slight, changes occurred in the ir spectra of either Rh/Al_2O_3 or Rh/MgO below 473 K when the H_2 + CO mixture was switched to D_2 + CO, or when D_2 + CO was admitted onto the surface predosed with HCOOH.

Reaction of adsorbed formate with H_2. We recently observed that the stability of formate on Rh/Al_2O_3 (as indicated by its ir bands) is greatly decreased in the presence of H_2 at 425 K, with simultaneous formation of CH_4 (*13*). Under favorable conditions, one formate ion reacted with H_2 on Rh/Al_2O_3 was converted to approximately one CH_4 molecule. This occurred at 425 K, far below the methanation temperatures of CO and CO_2, when the decomposition of adsorbed formate was very slow. A similar phenomenon was experienced on Rh/MgO, but the conversion of formate into CH_4 in this case was much less.

In subsequent measurements we investigated the behavior of adsorbed formate ion on Rh/Al_2O_3 in the presence of H_2 at the reaction temperature of methanation of CO. Adsorbed formate ion was produced by the adsorption of formic acid at 298 K and by subsequent evacuation at 373 K. The changes in intensity of the formate bands were followed and the reaction product was analyzed. For comparison, we determined the stability of formate in a He flow at these temperatures (Fig. 10).

In this temperature range the stability of surface formate in a He flow was considerably less than that at 425 K, and the presence of H_2 exerted a smaller effect. Although methane formation was detected in this case too, it was found that even in pure H_2 only about 1–5% of the surface formate was converted into CH_4. The surface concentration of formate ion was calculated on the basis of the correlation between the absorbance of the formate band at 1595 cm^{-1} and the amount of formate ion present on alumina (*12*) or magnesia (*10*).

Formation of surface carbon during the H_2 + CO reaction. Although ir spectroscopic measurements revealed what kinds of adsorbed species exist on the catalyst surfaces during the reaction, they provided no information on the possible formation of surface carbon in the catalytic reaction.

In order to determine and follow the formation of surface carbon or carbonaceous species, designated here as "SC," the flow of reacting gas mixture (H_2 + CO + He) was stopped at certain times, and the reactor was flushed with a He stream for 10 min at 548 K; according to ir spectroscopic measurements, this is sufficient to remove all the chemisorbed species at this temperature. Afterward H_2 was passed through the

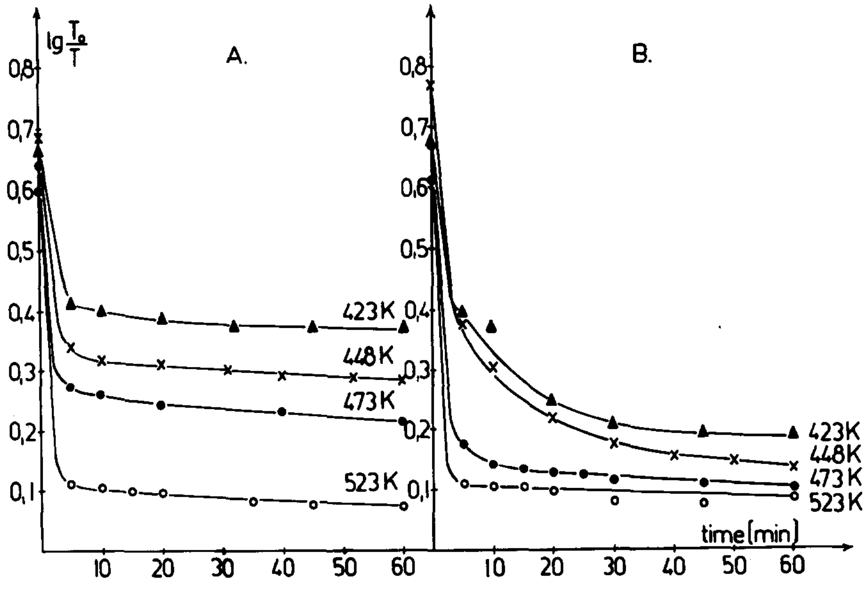


FIG. 10. Changes in the intensity of formate band at 1595 cm^{-1} at different temperatures. (A) In a He flow; (B) in a H_2 flow.

reactor and the hydrocarbons formed were determined by gas chromatography. In order to obtain a reliable value for the amount of "SC" and to establish the initial rate of its hydrogenation, the hydrocarbons formed in the first 3 min were trapped in a vessel cooled to 77 K. The results obtained for Rh/Al_2O_3 are shown in Fig. 11, while the data for other Rh samples are listed in Table 2.

Several conclusions can be drawn from these experiments.

(i) The rate of CH_4 formation for 3 min is greater by a factor of 20 than the steady-state rate.

(ii) The hydrogenation of "SC" produces methane and ethane. The ratios of these products are very nearly the same as those observed during the reaction.

(iii) The formation of "SC" continues even after the stage when the catalyst reaches a constant activity.

(iv) Some of the "SC" can be hydrogenated at room temperature or 373 K, where the hydrogenation of CO does not occur to a measurable extent.

(v) The formation of "SC" and its reactivity depend sensitively on the support (Table 2).

4. DISCUSSION

The catalytic activity of alumina-supported Rh in the methanation of CO is about 1.5 orders of magnitude less than that of Ru, which is the most effective noble metal for this reaction (*3*). The activation energy of the reaction, however, is practically the same on these two catalysts.

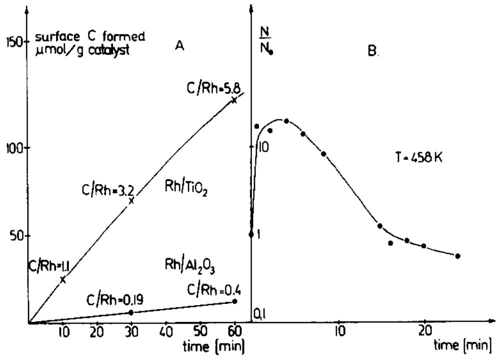


FIG. 11. (A) The amount of surface carbon formed in the H_2 + CO reaction at 548 K on Rh/Al_2O_3 and Rh/TiO_2 at different reaction times. (B) The relative rate of CH_4 formation on Rh/Al_2O_3. N_0 = turnover number of CH_4 formation at the steady state of the H_2 + CO reaction. N = turnover number of CH_4 formation following steady-state reaction in the absence of CO.

An interesting feature of the catalytic behavior of supported Rh is that, in contrast to other noble metals, its specific activity is markedly different in the methanations of CO and CO_2. In the hydrogenation of CO_2 its specific activity is more than one order of magnitude higher than in the case of the hydrogenation of CO, and exceeds that of Ru (*1*, *2*).

TABLE 2

The Amount of Carbonaceous Species Transformed into CH_4 (in μmol/g Catalyst) in the Reaction with H_2 at Different Temperature[a]

Catalyst	The conversion of CO[b] (%)	298 K	373 K	623 K	673 K	Total amount
Rh/TiO_2	40–10	0.14	2.4	70.8	53	126.34
Rh/Al_2O_3	22–9	0.3	1.38	9.3	0.5	11.48
Rh/MgO	~1.9–0.4	0.05	0.16	0.05	0.11	0.37
Rh/SiO_2	~2.2–1.0	0.12	0.22	1.86	1.17	3.37

[a] Surface carbon was produced by the H_2 + CO reaction on reduced Rh samples at 548 K for 60 min, then the reactor was flushed with a He stream for 10 min to remove all the chemisorbed species. Afterward the sample was cooled down in He to room temperature and exposed to H_2 pulses. After cessation of CH_4 formation, the reaction temperature was increased.

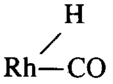
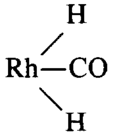
[b] The values show changes in the conversion of CO during the reaction.

Under the experimental conditions applied, the hydrogenation of CO on Rh samples depended on the support and occurred at a measurable rate in the temperature range 473–620 K. In contrast to the hydrogenation of CO_2, a significant decrease in activity was observed with time. The selectivity of Rh and the product distribution varied only slightly with the experimental conditions. Whereas the hydrogenation of CO_2 on these catalysts yielded practically only methane, in the present case, and particularly on Rh/TiO_2 and Rh/Al_2O_3, a number of C_2–C_5 compounds were also formed.

In order to propose a mechanism for the hydrogenation of CO on Rh, it is instructive to examine the nature and the reactivity of the surface species formed in the low-temperature interaction and in the high-temperature reaction of H_2 + CO on supported Rh.

4.1. *Low-Temperature Interaction*

In contrast to the adsorption of $H_2 + CO_2$ on supported Rh samples (*9, 10*), neither the adsorption nor the ir spectroscopy disclosed any detectable surface interaction leading to the formation of a surface complex at 298–373 K.

It was noticed, however, that the twin CO disappeared at lower temperatures than in the absence of H_2, and the band due to linearly bonded CO was shifted to slightly lower frequencies. A similar observation was made by Yang and Garland (*11*). This shift is probably due to the formation of  and/or  species, and to the increased π-donation from the Rh into the antibonding π-orbital of the CO (*9, 10, 14*).

4.2. *High-Temperature Reaction*

At higher temperature, when the hydrogenation of CO is appreciable or occurs rapidly, in addition to the linearly and bridged bonded CO, formate ion and surface carbon were detected.

Let us investigate more closely the behavior and possible roles of these surface species in the hydrogenation of CO.

Formate ion. Bands characteristic of the formate ion appeared in the ir spectra at 423–573 K. Their intensities were fairly constant at 523 K, but decreased somewhat when the temperature was raised from 523 to 573 K. Before going further into the discussion we should mention that formate ion was identified in the low-temperature interaction of $H_2 + CO_2$ at 298–423 K (*9, 10*) and in the methanation of CO_2 at 450–523 K on Rh/Al_2O_3 and Rh/MgO catalysts (*2*). Taking into account the constancy of the formate bands, the concentration of formate groups (which greatly exceeded that of surface metal atoms), and the fact that on Rh/SiO_2 neither the coadsorption of $H_2 + CO_2$ nor the adsorption of formic acid produced bands due to formate ion above 300 K, we came to the conclusion that the formate ion is located not on the Rh, but on the supports (*9, 10*). Although the formate ion was produced at a higher temperature and in a lower concentration in the present case, there is no reason to assume that the site of the formate ion would be different.

Besides the location of the formate ion, the Rh plays an important role in its formation, as the adsorption of H_2 + CO mixture on the supports alone produced no or much less formate species at 423–473 K. *We propose that the hydrogen activated on the Rh migrates onto the support, where it reacts with CO producing formate ion*

$$OH^- + CO \rightleftharpoons HCOO^-$$

In spite of the location of the formate group, however, it cannot be considered a *totally inactive* surface species. As no significant accumulation of formate group occurred on Rh/Al_2O_3 (the surface concentration of formate group remained the same even after 5 or 13 hr of reaction), it seems very likely that this surface concentration represents a steady-state value. This is supported by the observation that after the concentration of surface formate groups had been temporarily increased by HCOOH introduction into the reacting gas mixture (He + H_2 + CO), the concentration of surface formate decreased in some minutes to the previous value.

Isotope substitution experiments confirm this view. As the results in Fig. 8 show, on switching from the H_2 + CO mixture to D_2 + CO at 473–523 K, the C–H bands at 2914 and 2850 cm^{-1} and the formate C–H deformation band at 1395 cm^{-1} decreased in intensity. In parallel, new bands appeared at 2200–2100 cm^{-1} (C–D stretching), indicating the occurrence of the decomposition of $HCOO^-$ and the formation of $DCOO^-$ species. The band due to the C–D deformation mode of surface formate (~1050 cm^{-1}) cannot be seen in the spectra; it is probably obscured by the steep background. Shifts in the opposite direction were observed when the D_2 + CO reaction mixture was replaced with H_2 + CO after a 1 hr reaction time.

Similar observations were made on Rh/MgO (Fig. 9). In this case a band at 1030 cm^{-1} due to the C–D deformation mode of adsorbed formate was identified too. We note that the positions of the C–D bands agreed very well with those observed during the adsorption of deuterated formic acid on Al_2O_3 and MgO (*15, 16*).

It appears to be important that these shifts occurred only at the temperatures where the hydrogenation of CO proceeded; below these temperatures the shifts occurred very slowly, if at all.

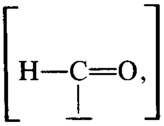
These observations are in contrast with those of Dalla Betta and Shelef (*17*) on Ru/Al_2O_3. In this case the infrared bands due to formate ion were formed slowly and continued to grow in intensity even after the reaction had reached a steady state. In addition, no isotope substitution was observed during the reaction.

Another important observation was that in the presence of H_2 the stability of the formate decreased appreciably, and simultaneously CH_4 was formed. This was clearly manifested at 425 K, when the decomposition of surface formate is slow and the methanation of CO is negligible; hydrogen activated by Rh, however, can react with formate adsorbed on the support to yield methane (*13*). In the temperature range of methanation of CO on Rh/Al_2O_3 and Rh/MgO, however, the stability of formate ion is considerably less, and only a small fraction of it reacts with activated hydrogen (Fig. 10).

In this case the effect of hydrogen can be attributed mainly to the occurrence of the reaction:

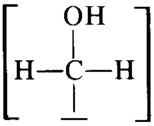
$$H_{(a)} + HCOO_{(a)} \rightleftharpoons HCOOH_{(a)}$$

The adsorbed formic acid may migrate to the Rh particles and decompose to CO_2(CO) and H_2(H_2O), or desorb as such. As the decomposition of adsorbed formate yields CO and CO_2 in this temperature range, it cannot be established with certainty whether the slight CH_4 formation is a result of hydrogenation of adsorbed formate through a different surface complex,



$$\left[\begin{array}{c}\mathrm{H{-}\underset{|}{C}{=}O,}\end{array}\right]$$

and



$$\left[\begin{array}{c}\mathrm{H{-}\overset{\overset{OH}{|}}{\underset{|}{C}}{-}H}\end{array}\right]$$

as was proposed for the low-temperature reaction (*13*), or whether it is a product of hydrogenation of CO or CO_2 formed in the decomposition of adsorbed formate.

Taking into account all these observations and results, we may conclude that the surface formate is a by-product of the H_2 + CO reaction; its surface concentration is controlled by the temperature and pressures of the reacting gases. It seems very likely that the production of CH_4 and other hydrocarbons in the hydrogenation of CO on supported Rh occurs only to a negligible extent through the formation and reactions of surface formate. This view is further supported by the observation that the formation of the formate ion was not detected on Rh/SiO_2 at either temperature, although the hydrogenation of CO proceeded rapidly on this sample above 573 K.

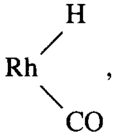
Surface carbon; the dissociation of CO on Rh. There is a certain controversy in the literature concerning the dissociation of CO on Rh surfaces. Measurements carried out so far refer to the adsorption of CO on Rh foil and single-crystal surfaces at low pressures. Whereas Somorjai *et al.* (*18–20*) stated that at elevated temperatures CO dissociates on Rh surfaces with irregularities (steps, kinks, and defects), Yates *et al.* (*21, 22*) concluded that the probability of dissociation of CO on Rh is negligible at 300–870 K.

As the occurrence of the dissociation of CO is of great relevance to the mechanism of the hydrogenation of CO, in a separate work we investigated the adsorption of CO and its dissociation on supported Rh at high pressures (*23*). In harmony with theoretical considerations (*24, 25*), CO undergoes far less dissociation on supported Rh than on Ni, Ru, etc. (*26–29*), but *dissociation does occur* to a small extent above 473 K. The dissociation is influenced by the support; it was the largest on Rh/TiO_2, followed by Rh/Al_2O_3, Rh/SiO_2, and Rh/MgO.

At the temperature of dissociation of CO (473–574) only the linearly bonded and bridged CO was present on the surface; the twin CO desorbed before this temperature, in agreement with the recent study of Fujimoto *et al.* (*5*). Taking into account the stability of these surface species, it was proposed that dissociation of CO mainly occurs in the bridged form.

In the study of the reactivity of surface carbon it was found that some of the surface carbon is hydrogenated to CH_4 even at 300–373 K (*23*), i.e., at a temperature where no hydrogenation of adsorbed CO in either form was detected.

On examination of the catalysts at different stages of the H_2 + CO reaction, we found a considerable amount of carbonaceous deposit on the surface: the quantity was larger than that formed in the dissociation of CO under similar conditions, but in the absence of H_2 (Table 2).

These results clearly demonstrated that the dissociation of CO is promoted by H_2, which may be envisaged as occurring through the formation of the Rh–carbonyl–hydride,  $\mathrm{Rh}{<}^{\mathrm{H}}_{\mathrm{CO}}$, species. The electron transfer from the H to the CO through Rh (described previously) increases the Rh–C bond strength, and at the same time weakens the C–O bond on the surface.

After removal of CO from the reacting gas mixture, and the adsorbed species from the surface, the rate of methane formation in the hydrogenation of surface carbon was

TABLE 3

Effect of Ethylene and Propylene on the Product Distribution of the Hydrogenation of CO on Rh/Al_2O_3 at 548 K and Atmospheric Pressure[a]

Products (mole %)	Feed I $CO/H_2/N_2$	Feed II $CO/H_2/C_2H_4/N_2$	Feed III $C_2H_4/H_2/N_2$	Feed IV $CO/H_2/C_3H_6/N_2$	Feed V $C_3H_6/H_2/N_2$
CH_4	6.45	2.26	4.74	5.98	6.99
C_2H_4	0.030	6.62	0.82	0.08	0
C_2H_6	0.148	4.91	5.57	0.50	2.25
C_3H_6	0.12	0.49	0	3.55	2.06
C_3H_8	0.198	0.20	0.07	3.48	4.06
C_4H_8	0.018	0.048	0	0.15	0.04
C_4H_{10}	0.033	0.077	0	0.25	0

[a] The amount of C_2H_4 and C_3H_6 added was ~6 vol%. In the cases of Feed I, III, and V, the catalyst was cleaned (oxidized and reduced) before the experiments.

higher than the steady-state rate measured in the reacting gas mixture (Fig. 11).

In spite of the high reactivity of surface carbon, however, a substantial amount of it accumulated on the catalyst (particularly on Rh/TiO_2 and Rh/Al_2O_3) during the reaction. A possible reason for the carbon accumulation is that CO blocked some of the active Rh sites, which, by decreasing the extent of activation of the H_2, led to a reduced rate of hydrogenation of the carbon. As a result, not all the surface carbon can be hydrogenated in the first instant, and there will be sufficient time for a proportion of the carbon to be transformed to less reactive forms. Aging of surface carbon was observed in other cases, too; this can very probably be attributed to the transformation of carbidic carbon into the less reactive form (*27*).

4.3. A Possible Mode of Hydrogenation of CO

On the basis of the above considerations, we propose that the hydrogenation of CO on supported Rh proceeds through the following steps:

$$\begin{array}{lll}
CO & \rightleftharpoons & CO_{(a)} \\
CO_{(a)} & \rightleftharpoons & C_{(carbidic)} + O_{(a)} \\
H_2 & \rightleftharpoons & 2\,H_{(a)} \\
C + 4\,H_{(a)} & \rightleftharpoons & CH_4 \\
O_{(a)} + CO & \rightleftharpoons & CO_2 \\
O_{(a)} + H_2 & \rightleftharpoons & H_2O \\
C_{(carbidic)} & \rightarrow & C_{(amorphous)}
\end{array}$$

The hydrogenation of surface carbon possibly occurs in a stepwise manner, through CH_2 or CH_3 surface species (*29–33*). On the ir spectra taken during the catalytic reaction there were some indications of the presence of these surface species. We note here that in addition to formate species, ethylidene has been observed with tunneling spectroscopy to form on Rh/Al_2O_3 in the reaction of adsorbed CO with H_2 at 420 K (*34*).

We attempted to prove the presence of the CH_x surface species by the addition of ethylene and propylene to the reacting gas mixture at the steady state, in the same way as done by Eckerdt and Bell (*33*). In the presence of ethylene, the amounts of propylene increased considerably (Table 3). The addition of propylene to the feed during synthesis enhanced the formation of butene and butane. When the admission of olefins was stopped, the original product distribution was reached in some minutes. When the concentration of olefins was raised, the amounts of the above products further increased. It is to be mentioned that the highest values were obtained immediately after the introduction of the olefins, their production afterward decreasing. All these results provide evidence for the presence of methylene groups on the catalyst surface.

4.4. The Effects of the Supports

The catalytic performance of Rh was influenced drastically by the support. On the basis of the specific activity (N_{CH_4}, the rate of CH_4 formation per surface Rh sites), the most effective support was TiO_2. The specific activities of Rh/MgO and Rh/SiO_2 were lower by more than an order of magnitude. On the basis of initial activities, N_{i,CH_4}, the high efficiency of Rh/TiO_2 catalyst was more pronounced (Table 1). A similar activity sequence was established in the methanation of CO_2 on Rh (*2*) and on Ru (*35*).

The behavior of TiO_2 as a support was investigated first more than two decades ago (*36, 37*). As a change in the Fermi level of the electrons in TiO_2 affected the catalytic performance of the metal, it was inferred that an electronic interaction occurred between TiO_2 and the metal (*36, 37*). The importance of electronic interactions in the carrier effect, first proposed by Schwab *et al.* (*38*) and Szabó and Solymosi (*39*), has been observed in many cases (*37, 40*), and confirmed recently by modern surface techniques (*41–44*).

We believe that this type of interaction between the support and Rh operates in this case, too, influencing the bonding and reactivity of the chemisorbed species.

The high efficiency of the *n*-type TiO_2 support can be attributed to an enhanced partial electron transfer from TiO_2 to Rh, which increases the electron donation from Rh into an antibonding π-orbital of the CO, thereby strengthening the Rh–C bond and weakening the C–O bond. This proposal seems to be backed by the study of the effects of the supports on the dissociation of CO over Rh, where efficiency of the supports decreased in the order

$$TiO_2 > Al_2O_3 > SiO_2 > MgO.$$

The fact that the product distribution in the hydrogenation of CO depended on the support (on Rh/Al_2O_3, and particularly on Rh/TiO_2, a large number of hydrocarbons were produced) is probably due to the surface concentration of carbon being greater on these contacts. As a consequence, the lifetime and the surface population of the CH_x species (which now seems responsible for the formation of higher molecular weight hydrocarbons (*29–33*)) will also be considerably larger on these catalysts.

The high activity of Rh/TiO_2 in the dissociation of CO, particularly in the presence of H_2, is demonstrated by the much larger accumulation of surface carbon on Rh/TiO_2 during the reaction (Table 2): its amount exceeds the number of surface Rh atoms by a factor of 5. Although a larger proportion of this surface carbon should reside on the TiO_2 (Rh cannot accommodate such an amount of carbon), the drastic decrease of the catalytic activity of Rh is probably due to the accumulation of surface carbon on the Rh or at the Rh/TiO_2 interface.

Another explanation for the high initial activity of Rh/TiO_2 is that during the high-temperature reduction of the catalyst a chemical reaction occurs between TiO_2 and Rh ("strong metal–support interaction" (*45–47*)), in which a new, more effective compound is formed. However, the fact that the temperature of reduction of Rh/TiO_2 exerted a very slight influence on its catalytic performance suggests that this explanation is not very likely in this case (*48*).

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