JOURNAL OF CATALYSIS **84**, 446–460 (1983)

Effects of the Support on the Adsorption and Dissociation of CO and on the Reactivity of Surface Carbon on Rh Catalysts

A. ERDÖHELYI AND F. SOLYMOSI

Reaction Kinetics Research Group, University of Szeged, P.O. Box 105, H-6701 Szeged, Hungary

Received May 9, 1983; revised July 4, 1983

The adsorption, desorption, and dissociation of CO on supported Rh have been investigated by means of infrared spectroscopy, pulse technique, thermal desorption, and temperature-programmed reaction spectroscopy. The reactivity of surface carbon produced by the disproportionation of CO has been also examined. Special attention has been paid to the effect of supports (TiO_2, Al_2O_3, SiO_2, MgO) on these processes. Adsorption of CO on differently supported Rh samples at 300 K produced almost identical infrared spectra; the dominant feature was the appearance of the twin CO band. The desorption temperature of CO, T_{max} = 463–473 K, was practically the same for all samples. The efficiency of the supports in promoting the dissociation of CO over Rh decreased in the order $TiO_2 > Al_2O_3 > SiO_2 > MgO$. Temperature-programmed reaction spectroscopy revealed that different kinds of surface carbon are produced by CO dissociation. The ratios of these forms depends on the temperature of their production, as well as on their thermal treatments. The surface carbon reacted with H_2 at a lower temperature on Rh/TiO_2, but the aging of carbon was also fastest on this sample. The activation energy of the hydrogenation of the reactive surface carbon increased in the order $Rh/TiO_2 < Rh/Al_2O_3 < Rh/SiO_2$.

INTRODUCTION

Recently we investigated the hydrogenation of CO_2 and CO on rhodium, with particular emphasis on the effect of the support (*1–4*). An exceptionally high activity was exhibited by Rh/TiO_2. This catalyst displayed an outstanding catalytic performance in the NO + CO reaction (*5–8*), indicating that TiO_2 not only provides a high surface area for the metal but that, through metal–support interaction, it strongly influences the catalytic behavior of the metal.

A strong electronic interaction between a metal and TiO_2 support was first proposed more than 2 decades ago by Szabó and Solymosi (*9*) following a study of formic acid decomposition on Ni/TiO_2. It was shown that changing the electron concentration in the *n*-type TiO_2, by doping it with altervalent cations, influences the value of the activation energy of the catalytic reaction on Ni. It was concluded that *an electronic interaction occurs between Ni and TiO_2, electrons being transferred from the TiO_2 support to the Ni* (*9*). It was also pointed out that complete reduction of the NiO in the preparation of Ni/support samples is very important from the aspect of the evaluation of the effect of the support, as a similar electronic interaction operates between Ni and unreduced NiO (*9–12*). Due to the high electron hole concentration, NiO exerted a dramatic influence on the catalytic properties of Ni (*10, 11*). The high efficiency of Ni/Al_2O_3 + 5% NiO observed by Schwab *et al.* (*13*) compared to Ni/Al_2O_3 was attributed in that case to the formation of an effective Ni/NiO contact, i.e., not to an electronic interaction between Ni and doped Al_2O_3 (*9–12*). Results showing the importance of electronic interaction between metals and supports have been summarized in two reviews (*9, 14*).

The fact that TiO_2 is an especially effective support and the proposed explanation (*9*) for the interaction between Ni and TiO_2 were almost completely neglected. The support effect of TiO_2 was rediscovered only recently.

0021-9517/83 $3.00

The electronic interaction between Ni and TiO_2 has been *confirmed* by Kao *et al.* (*15*, *16*) by using the combined methods of UPS/XPS and Auger electron spectroscopy. They showed that electrons are transferred from TiO_2 to Ni. The amount of charge transfer is ~0.1 electron per nickel atom when the nickel "coverage" (*16*) is 1.0 Å. They also assumed that this charge transfer may be the cause for the increase in the CO hydrogenation activity on Ni/TiO_2 (*16*).

A further advance in this field occurred when reliable methods were developed for the determination of metal surface areas. Tauster *et al.* (*17*, *18*) found that when titania-supported Ni (and other transition metals) were reduced at ca. 773 K, a complete suppression of hydrogen and carbon monoxide chemisorption occurred, which was interpreted by assumption of the occurrence of a "strong metal–support interaction."

The high efficiency of Ni/TiO_2 catalyst has been found in a number of cases (*19–24*). It is noteworthy that although some authors explicitly assume that an electronic interaction between Ni and TiO_2 also contributes to the high efficiency of Ni/TiO_2 catalyst, almost all these authors failed to make reference to the work (*9*) which first examined the interaction between Ni and TiO_2 and explained its catalytic behavior in terms of the strong electronic interaction.

In an attempt to establish the possible mechanisms of the hydrogenation of CO and CO_2 on Rh and to explain the exceptionally high efficiency of the TiO_2 support, the present study was undertaken to investigate the effect of the support on the dissociation of CO and on the reactivity of the surface carbon formed, these processes presumably playing important roles in the methanation reaction on supported Rh catalysts (*1–4*).

EXPERIMENTAL

Materials. The catalysts were prepared by impregnating the supports with a solution of $RhCl_3 \cdot 3H_2O$ to yield 0.3, 1, or 5 wt% metal. The impregnated powders were dried at 373 K. Before any measurements the catalysts were oxidized for 30 min at 673 K and reduced for 60 min at 473 or 673 K *in situ*. For infrared studies, transparent thin wafers, 30 × 10 mm, were prepared at high pressure.

The following powder supports were used: Al_2O_3 (Degussa P110 Cl), TiO_2 (Degussa P25), MgO (DAB 6), and SiO_2 (Aerosil 200).

The gases used were of commercial purity. The carrier gas He (99.99%) was purified with an Oxy-trap and by adsorbing the other impurities with a molecular sieve at the temperature of liquid air. The hydrogen was purified by passage at the temperature of liquid air through a trap filled with molecular sieve.

Methods. Infrared spectra were recorded with a Specord 75 IR double-beam spectrometer (Zeiss, Jena). Two different cells were used. In the high-temperature cell, the spectra were taken at the reaction temperature *in vacuo* or in the gas flow. In a Kiselev-type infrared cell all spectra were recorded at the temperature of the infrared beam, ~313 K.

The pulse reactor was incorporated between the sample inlet and the analytical column of the gas chromatograph (Hewlett–Packard 5750 equipped with a 3370 digital integrator).

Temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) experiments were carried out in a pulse reactor made from an 8-mm-i.d. quartz tube. The dead volume was filled with quartz beads. The amount of catalyst used was 0.2–0.3 g. The reactor was heated by an external oven. A small glass tube containing an Fe–constantan thermocouple was placed in the middle of the catalyst bed. A temperature programmer was used to control catalyst heating at a linear rate and most experiments reported in this paper involved heating rates of 40 K min^{-1} to a final temperature of 873 K. In these cases

TABLE 1

Characteristics of Supported Rh Catalysts Reduced at 673 K

	Area of the support (m^2/g)	0.3 wt% Rh	1 wt%/Rh	
		CO/Rh[a]	CO/Rh[a]	H/Rh
Al_2O_3 (Degussa P110 Cl)	100	1.64	0.35	0.33
TiO_2 (Degussa P25)	150	—	0.29	0.22
MgO (DAB 6)	170	0.64	0.18	0.15
SiO_2 (Aerosil 200)	240	0.53	0.39	0.33

[a] Extrapolated values at zero CO pressure. The values are corrected for the adsorption of CO on the supports.

the columns were removed from the gas chromatograph.

In the TPD experiments the carrier gas was He, and the desorbed gases were analyzed with a thermal conductivity detector. For TPR experiments, the He stream was replaced by H_2 before the catalyst was heated. In this case the products were analyzed with a flame ionization detector.

The dispersion of the rhodium was determined via H_2 adsorption at 298 K with the use of a dynamic impulse method (*2, 4*). Characteristic data for the supported Rh samples are shown in Table 1.

RESULTS

Infrared Spectroscopic Studies

Figure 1 shows the ir spectra of adsorbed CO on Rh samples reduced at 473 K. The samples contained 0.3 wt% Rh. Rh/Al_2O_3 and Rh/TiO_2 behaved similarly; adsorption of CO on both samples produced intense absorption bands at 2096 and 2029 cm^{-1}, which belong to the asymmetric and symmetric stretches of dicarbonyl species. There was no indication of the presence of linearly and bridge-bonded CO at any pressures at 300 K. On Rh/TiO_2 a shoulder also appeared at 2000 cm^{-1}, which can be attributed to CO bonded to the TiO_2 support. On Rh/SiO_2 the twin CO bands appeared at the same frequencies as on previous samples, but at much lower intensities. At higher CO exposure a weak band at 2065 cm^{-1} indicative of the terminal CO was also seen; it disappeared, however, on evacuation. On Rh/MgO only extremely weak twin CO bands were detected at this Rh content.

When the temperature of reduction was raised to 673 K the ir spectra of CO on Rh/Al_2O_3 remained the same (Fig. 1). The higher reduction temperature caused a loss in the transparency of Rh/TiO_2 and decreased the intensities of the twin CO band. At the same time, a weak band at 2060 cm^{-1} appeared on the spectra. On Rh/SiO_2 only a decrease of the intensities of CO bands was experienced.

When the Rh content was increased to 1 wt% and the samples were reduced at 473 K, the dominant absorption bands were again those due to dicarbonyl species. The linearly bonded CO at 2065–2068 cm^{-1} became apparent only at higher CO exposures, particularly on Rh/SiO_2. After reduction at 673 K this band became more pronounced. On Rh/MgO and on Rh/SiO_2 low exposures of Co produced one band at 2066 cm^{-1}.

Temperature-Programmed Desorption of CO

The adsorption of CO was performed on reduced samples by exposure to pure CO for 60 min at 373 K. Afterward the reactor

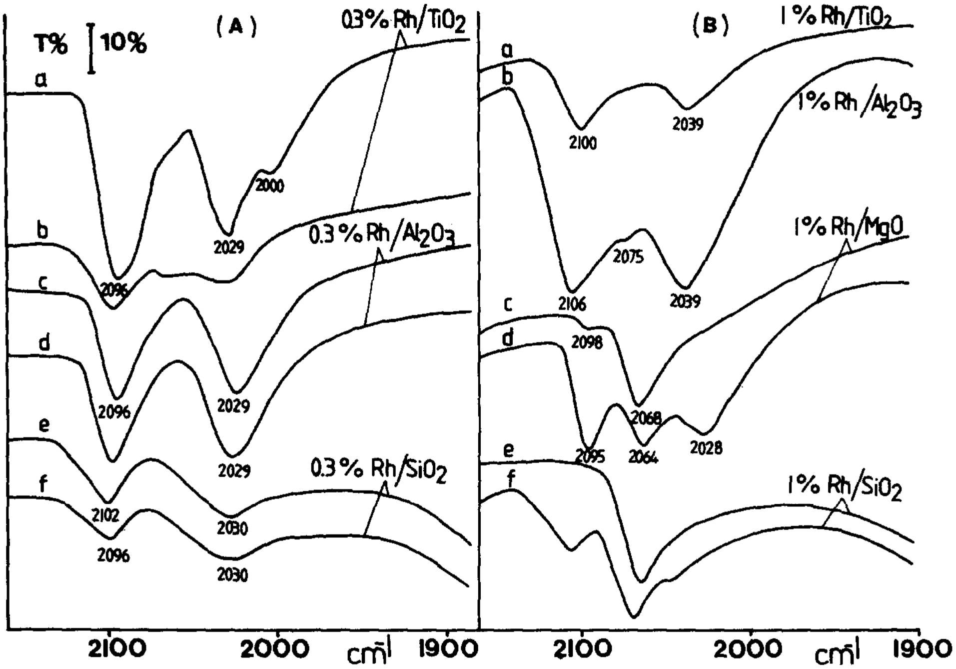

FIG. 1. Infrared spectra of adsorbed CO on supported Rh samples at 300 K. The spectra shown were obtained at saturation with CO and after short evacuation of the ir cell. (A) Reduction temperature: 473 K (a, c, e), 673 K (b, d, f). (B) Reduction temperature: 673 K. For (c) and (e) the CO pressure was only 5×10^{-2} Torr.

was flushed with He for 10 min and the sample was heated at a rate of 40 K min^{-1}. In the first experiment the total amount of gases was analyzed, while in the second experiment the CO_2 formed during the desorption was frozen in a trap cooled with liquid air. The TPD spectra are shown in Fig. 2.

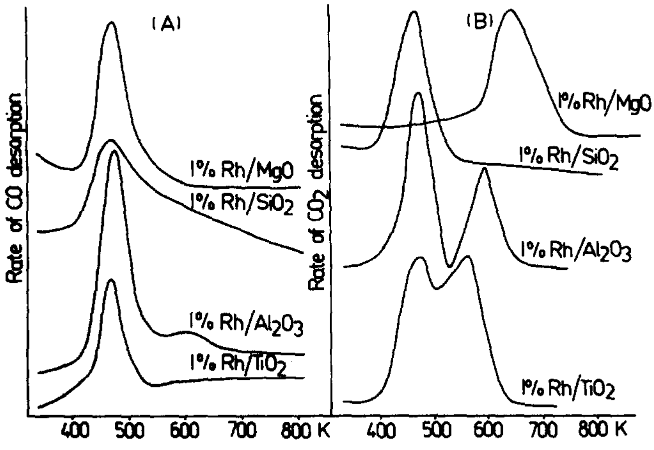

FIG. 2. TPD spectra from Rh samples reduced at 673 K after adsorption of CO for 60 min at 373 K. The flow rate of He was 40 ml/min. In order to avoid the effect of adsorbed H_2O and CO_2 the catalyst samples have been heated to 873 K in He flow after their reduction at 673 K. (A) CO desorption. (B) CO_2 desorption.

TABLE 2

Characteristics of Temperature-Programmed Desorption after Adsorption of CO at 373 K on Supported Rh Catalysts

	Desorption of CO		Desorption of CO_2			
	T_M (°K)	Amount of desorbed gas (μmol/g)	T_{M_1} (°K)	Amount of desorbed gas (μmol/g)	T_{M_2} (°K)	Amount of desorbed gas (μmol/g)
1% Rh/Al_2O_3	473	13.5	473	13.2	588	3.99
1% Rh/TiO_2	463	7.3	473	11.6	543	12.0
1% Rh/SiO_2	463	8.3	473	9.9	—	—
1% Rh/MgO	463	9.4	—	—	653	12.2

Note. T_M is the temperature where the rate of CO or CO_2 desorption is maximum.

It appears that the desorption temperature of CO, $T_{max} = 463–473$ K, is practically the same for all samples. Simultaneously with the desorption of CO, however, CO_2 was also desorbed. An exception was Rh/MgO.

A high-temperature stage of CO_2 desorption was also observed on Rh/Al_2O_3, Rh/TiO_2, and Rh/MgO. The peak temperature was 543 K on Rh/TiO_2, 588 K on Rh/Al_2O_3, and 653 K on Rh/MgO. This stage was not detectable on Rh/SiO_2. The characteristic data relating to the TPD measurements are collected in Table 2.

Dissociation and Disproportionation of Adsorbed CO

The dissociation of CO was investigated first with the pulse technique. The extent of CO disproportionation was calculated by determination of the CO_2 evolved. It soon appeared, however, that calculation of the extent of disproportionation or dissociation of CO on this basis may easily lead to false results, as traces of H_2O present can convert CO to CO_2 at higher temperature. Therefore, great care was devoted to working under dry conditions and to eliminating traces of water. Exploratory measurements were made with 5% Rh/Al_2O_3. One CO pulse contained 125 μmol CO, which was about 2.6 times larger than the molar quantity of surface Rh atoms on Al_2O_3. A considerable amount of CO was adsorbed at 298 K on a reduced Rh/Al_2O_3 surface, but only a very small amount of CO_2 (<1% of the CO pulse) was found in the effluent at 373 K. Subsequent CO pulses did not produce CO_2, indicating that neither disproportionation nor dissociation of CO occurred at this temperature.

The disproportionation of CO took place at higher temperatures, however. At 473 K, about 16% of the CO pulse underwent disproportionation, the corresponding value at 573 K being about 20% (Fig. 3).

More detailed measurements, which included a study of the effect of the support, were performed at 548 K. In order to increase the dispersion of the Rh, samples containing 1% Rh were used. In this experimental series we also determined the amount of carbon deposited on the surface as a result of disproportionation of CO. This was calculated from the amount of CH_4 formed in the reaction of surface carbon with H_2, the reaction being followed until methane formation ceased. Adsorbed CO was eliminated from the surface by He flushing at 548 K before hydrogenation. The results are summarized in Table 3. In this case one CO pulse contained 41.6 μmol CO.

With the exception of Rh/TiO_2, the amount of carbon formed increased only slightly with increase of the number of CO

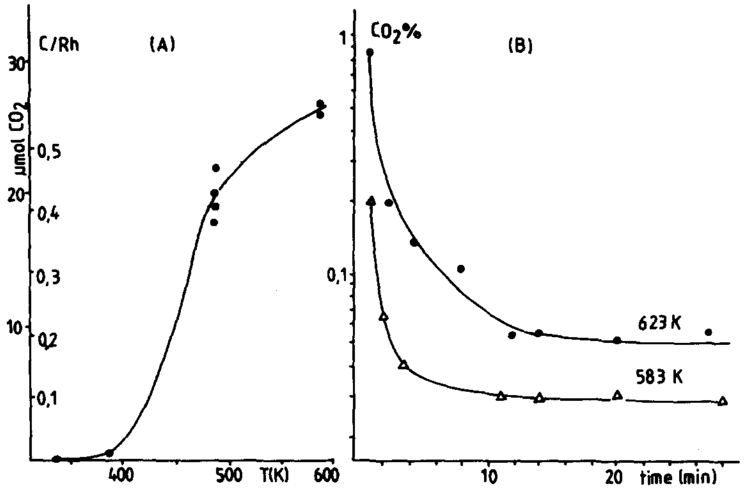

FIG. 3. The disproportionation of CO on Rh/Al_2O_3 catalysts. (A) The amount of CO_2 formed by injecting one CO pulse (125 μmol) on 5% Rh/Al_2O_3 at different temperatures. (B) The formation of CO_2 in a stream of He + CO (10%) gas mixture on 1% Rh/Al_2O_3 at different temperatures. The amount of Rh/Al_2O_3 was 0.33 g.

pulses. There was no significant difference in the final values. If we relate the amount of surface carbon to the number of Rh atoms, it appears that at 548 K the disproportionation of CO occurs to the greatest extent on Rh/TiO_2; this is followed by Rh/Al_2O_3, then by Rh/SiO_2, and finally by Rh/MgO. In this experiment the C/Rh ratios varied between 0.6 and 1.3.

Attempts were made to determine the apparent activation energy of CO disproportionation on 1% Rh/Al_2O_3. This was done in a flow system at 513–623 K. CO (~10%) was added to a flowing stream of He, and CO_2 formation was followed as a function of time. Before these runs, the catalyst was oxidized and reduced at 673 K. The rate of CO_2 formation declined very quickly initially, but after 3–6 min achieved a nearly constant value (Fig. 3). The activation energy of the CO disproportionation was calculated from the initial rate and from the pseudo-steady-state rate, and an average value of 50 kJ/mol was obtained. Similar measurements were performed on a 5% Rh/Al_2O_3 sample. In this case the extent of CO disproportionation was larger, but the specific rate of disproportionation was practically the same as on 1% Rh/Al_2O_3. The values of the activation energy of the reaction, as calculated from the initial rate, were also the same for the two samples within the estimated error of ±3 kJ/mol.

TABLE 3

The Effect of Supports on the Disproportionation of CO on Rh at 548 K

Samples[a]	Amount of carbon (μmol/g catalyst)[b]	C/surface Rh
1% Rh/Al_2O_3	32.6	1.01
1% Rh/TiO_2	26.4	1.21
1% Rh/SiO_2	20.5	0.63
1% Rh/MgO	9.1	0.6

[a] The catalysts were reduced at 673 K.

[b] These values approach the maximum amount of surface carbon which can be attained by CO disproportionation at 548 K.

Reactivity of Surface Carbon

In subsequent measurements we investigated the reactivity of surface carbon formed in the disproportionation of CO on supported Rh samples. Carbon was pro-

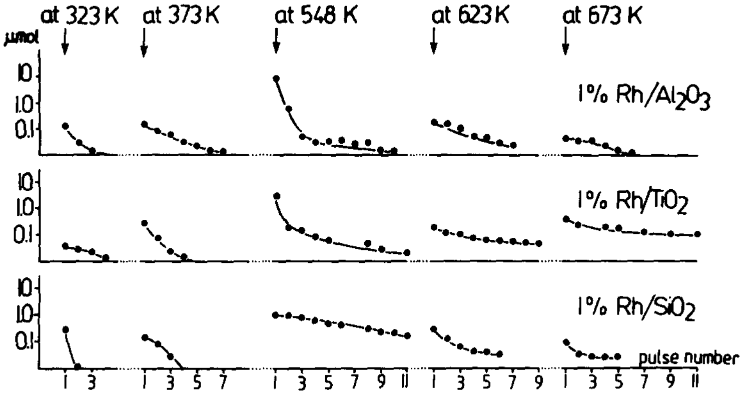

FIG. 4. The amount of CH_4 formed by treating the Rh samples containing surface carbon with H_2 pulses at different temperatures. Surface carbon was produced by adding CO pulses onto reduced surfaces at 548 K. The amount of Rh/Al_2O_3 was 0.33 g. The carbon content was about 20 μmol/g Rh samples. One H_2 pulse contained 41.6 μmol H_2.

duced by injection of 5–10 CO pulses in a He stream flowing over reduced Rh samples at 548 K. In order to have a reliable basis for comparison of the reactivity of carbon, care was taken to produce similar amounts of carbon on different samples by variation of the number of CO pulses. The amounts of CO_2 formed and of CO unreacted were determined. Afterward the reactor was flushed with He at 548 K for 10 min which, according to ir spectroscopic studies, is sufficient to remove adsorbed gases, and then cooled in a He flow to different temperatures.

The reactivity of surface carbon was investigated first with a *pulse technique* in a He flow until CH_4 formation ceased, or decreased to very small values. All experiments were carried out on freshly reduced samples. Results are shown in Fig. 4. It appears that a small proportion of the surface carbon (1–2%) can be hydrogenated to CH_4 on every sample even at room temperature. At 373 K the proportion of the total surface carbon hydrogenated on Rh/SiO_2 and Rh/TiO_2 amounts to 8.3%, on Rh/MgO to 2.7%, and on Rh/Al_2O_3 to 6.5%. It must be emphasized that the CO adsorbed on Rh samples does not react with H_2 under these conditions.

At higher temperatures the extent of methane formation was more considerable. At 548 K in the case of Rh/Al_2O_3 somewhat more than 80% of the surface carbon reacted *with the first H_2 pulse*. In the case of Rh/TiO_2 the corresponding value was fractionally smaller (45%), but it was much less (20 and 8%) on Rh/SiO_2 and Rh/MgO. Treatment of the surface with additional H_2 pulses produced CH_4 in decreasing quantities.

On elevation of the temperature to 623–673 K, CH_4 formation was still observed, particularly on Rh/TiO_2, which indicates that some of the carbon is less reactive toward H_2.

The activation energy of the hydrogenation of surface carbon was determined from the temperature dependence of the initial rate of CH_4 formation. After production of carbon the temperature of the catalyst was lowered to the reaction temperature and then the He stream was switched to H_2 flow. The amount of CH_4 formed was determined continuously with a flame ionization detector. The CH_4–time curves were extrapolated to zero time to obtain the initial rates. The amount of surface carbon produced was kept constant (~20 μmol/g catalyst) in each experiment. This corresponds to a coverage of about 0.6–0.9 of a Rh monolayer. The results for Rh/Al_2O_3 are

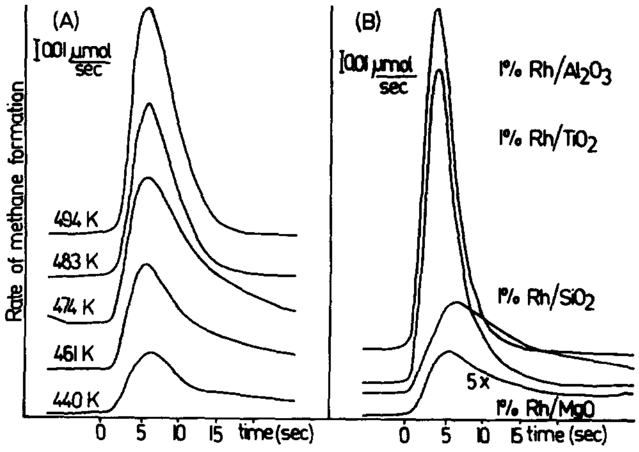

FIG. 5. (A) Rates of carbon hydrogenation over 1% Rh/Al_2O_3 at different temperatures. (B) Rates of carbon hydrogenation over different Rh samples at 513 K. The amount of Rh samples used was 0.33 g.

shown in Fig. 5. It appears that, depending on the temperature, about 10–24% of the surface carbon reacts with H_2 in a very fast process in the temperature range 440–513 K. The amount of surface carbon reacting in this stage increases with the rise of temperature.

Similar experiments were performed on other Rh samples. On Rh/TiO_2 the amount of carbon gasified in the initial fast reaction was almost the same as on Rh/Al_2O_3. On Rh/SiO_2, and particularly on Rh/MgO, the amount of carbon hydrogenated in this stage was much less, and the reaction occurred much more slowly (Fig. 5).

The activation energy determined from the temperature dependence of the initial rate of methane formation was 49 kJ/mol for Rh/TiO_2, 54 kJ/mol for Rh/Al_2O_3, and 64 kJ/mol for Rh/SiO_2. The Arrhenius plots are shown in Fig. 6.

The results of these measurements revealed the possibility that different forms of carbon exist on the surface. In order to confirm this assumption and to determine the reactivities of such different forms of carbon, the method of temperature-programmed reaction (TPR) spectroscopy was used. After the production of carbon and flushing of the surface with He at 548 K, the samples were cooled in a He flow to 303 K. The flow was then switched to H_2, the sample was heated at 40 K min^{-1}, and the hydrocarbons formed were analyzed.

Some characteristic TPR spectra are shown in Fig. 7. It appears that, from the point of reactivity, several forms of surface carbon can be distinguished. A very slight formation of CH_4 was found for every sample (the slightest on Rh/MgO) at 303–323 K: we shall designate this stage as α_1. The fur-

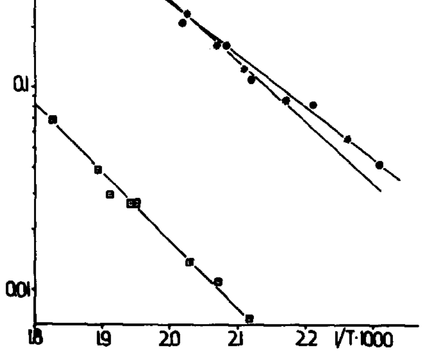

FIG. 6. Arrhenius plot for hydrogenation of carbon on different Rh samples. Due to appreciable scattering reliable data could not be obtained on Rh/MgO.

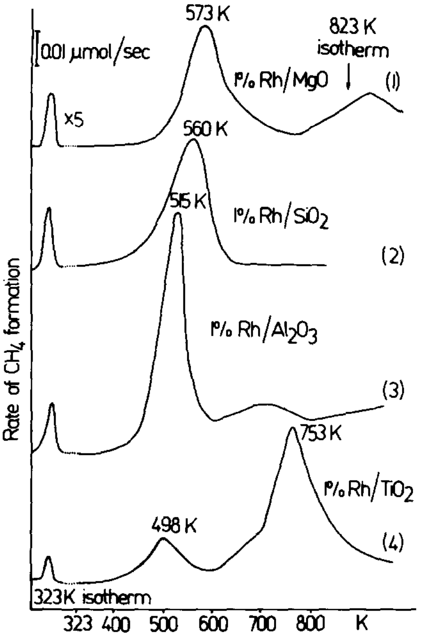

FIG. 7. TPR spectra with H_2 following carbon deposition by exposure of Rh samples to CO pulses at 548 K. The amount of Rh samples was 0.33 g.

ther parts of the TPR spectra differ from sample to sample. The formation of CH_4 occurs at the lowest temperature ($T_{max} \approx$ 498 K) on Rh/TiO_2 (α_2). This is followed by a stage at 663 K (α_3). However, the majority of the surface carbon reacted above 673 K ($T_{max} \approx 753$ K) (β). On Rh/MgO the main stage of formation of CH_4 begins above 473 K (T_{max} = 573 K), and on Rh/SiO_2 above 400 K ($T_{max} \approx 560$ K). On Rh/Al_2O_3 the main stage (α_2) was observed at 423–593 K (T_{max} = 515 K) with a small peak at 690 K (β). On repetition of the measurement on the same sample, the amount of CH_4 formed in the high-temperature stage (β) increased somewhat.

When Rh samples were exposed to CO at 603 K, the reactivity of the surface carbon formed was much less. In these cases the α_2 peaks became very small, and the majority of the carbon reacted in the β stage (Fig. 8). Similar changes in the reactivity of surface carbon were experienced when the carbon was produced at 548 K and kept at the same temperature in He flow for a longer time. However, no change in the TPR curve occurred by keeping the sample at 523 K for 60 min after production of surface carbon at 548 K.

From the comparison of aging of surface carbon on different Rh samples it appeared that the aging occurs more rapidly on Rh/TiO_2, and less rapidly on Rh/SiO_2. When the production of surface carbon on Rh/TiO_2 was performed at 503 K the greater portion was hydrogenated in the α_2 stage (T_{max} = 498 K) and only a small amount in the high-temperature stages (Fig. 8).

DISCUSSION

General Characteristics of the Hydrogenation of CO_2 and CO over Rh

Supported Rh is a very effective catalyst in the hydrogenation of CO_2. In a flow system at atmospheric pressure the main prod-

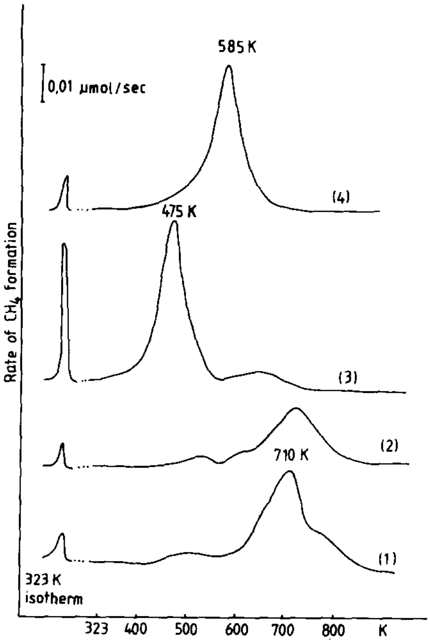

FIG. 8. The effect of the temperature of the carbon production and the heat treatment on the reactivity of surface carbon. The carbon was produced by CO disproportionation (1) on Rh/Al_2O_3 at 603 K, (2) on Rh/Al_2O_3 at 548 K and kept in He stream at 548 K for 60 min, (3) on Rh/TiO_2 at 503 K, and (4) on Rh/SiO_2 at 573 K.

uct of the reaction was CH_4 (*1–3*). The support exerted a dramatic influence on the specific rate of the methanation reaction; the turnover number was 14 times larger on Rh/TiO_2 than on Rh/Al_2O_3, and 45 times larger than on Rh/SiO_2 at 548 K (*3*). We found the same activity order for the hydrogenation of CO; again the Rh/TiO_2 reduced at 673 K showed an outstanding activity (*2, 4*). In this case other hydrocarbons were also produced in smaller concentrations (*2, 4*). Other workers have found that at higher pressures (*25, 26*), or using Rh-carbonyls as catalysts (*27–29*), alcohols and other oxygenated products are also formed in the H_2 + CO reaction. On Rh/TiO_2, small amounts of methanol and ethanol were detected below atmospheric pressure (*4, 30*). Preoxidation of either unsupported (*31*) or supported Rh (*32*) increased the rate of methanation and changed the product distribution of the reaction considerably. An interesting feature of the reactions is that the specific rate of methanation was more than 1 order of magnitude higher for the hydrogenation of CO_2 than for that of CO (*1–4*). This difference was not restricted to supported Rh, as it was also observed on Rh foil (*33*).

During the course of this work and the preparation of this paper several new publications have appeared on the catalytic behavior of supported Rh in the hydrogenation of CO_2 and CO (*34–40*). A marked influence of the support was experienced in each of these studies. Iizuka *et al.* (*36*) observed an exceptionally high activity of Rh/ThO_2 for both reactions. Katzer *et al.* (*34*) found that the selectivity of hydrogenation of CO to alcohols varies with the basicity of the support. The role of an electronic interaction between the metal and the TiO_2 support, proposed first by Szabó and Solymosi (*9*) and applied to Rh/TiO_2 in the cases of the hydrogenation of CO_2 (*2, 3*) and of CO (*2, 4*), was considered and used in explaining the effect of the support, particularly for Rh/TiO_2 (*34–40*).

In situ ir spectroscopic measurements during the hydrogenation of CO_2 and CO indicated the presence of both linearly and bridge-bonded CO and formate ion (*3, 4*). Evidence was presented, however, showing that the formate ion is located not on the Rh, but rather on the support (*41, 42*). These studies did not reveal any significant differences between Rh supported on alumina, magnesia, titania, and silica, or at least no differences which might help to explain the differences in the catalytic activities and particularly the high activity of Rh/TiO_2. One difference which may be pointed out was that on Rh/SiO_2 there was no indication of the presence of formate ion either during low-temperature interaction (298–425 K) or during the methanation reactions (425–573 K), and the stability of the formate species on Rh/TiO_2 was comparatively low.

Although these two samples have the highest and the lowest activities for the supported Rh catalysts investigated, we do not think that these features are the reasons for their observed catalytic performances.

Adsorption and Desorption of CO

Let us investigate more closely the results of the present study and the conclusions drawn therefrom. Table 1 contains the data obtained for the adsorption of CO at 298 K on four different Rh samples. It shows no significant differences between the samples reduced at 673 K, and even Rh/TiO_2 adsorbs significant amounts of hydrogen and CO. This means that the reaction between metal and TiO_2, observed by Tauster *et al.* (*17, 18*) following the reduction (ca. 773 K) and resulting in suppression of the adsorption of both H_2 and CO, either did not occur at all or only occurred to a small extent in this case. The results also indicate the relatively low dispersion of Rh on all samples.

The dominant feature of the ir spectra of adsorbed CO is the appearance of the twin absorption at 2101 and 2034 cm^{-1}. If an electronic interaction operates between the

Rh and the support, we would expect some differences in the positions of the CO bands, particularly in the case of Rh/TiO_2 (see below); however, this was not the case. The location of the twin bands was practically the same on all Rh samples. The linearly bonded CO was identified only on Rh/SiO_2, peaking at around 2065 cm^{-1}. There was no indication of the presence of bridged CO on any samples.

If the behavior of the absorption bands reported by various authors (*5, 41–44*) to be due to twin CO is examined very thoroughly, it appears that the location of the twin bands hardly depends on the coverage, which is basically different from the situation for linearly bonded CO. It may be concluded that the factors responsible for the shift of the CO band with the coverage do not operate in this case, or at least not to a detectable extent. This means that, although the appearance of the twin CO ir absorption is very sensitive to the method of preparation of the Rh samples and their pretreatment (*43, 44*), the electronic interaction, if any, between the Rh and the support does not result in any shift in position of the twin CO bands. Another important factor is that the twin CO is produced on partially oxidized Rh, very probably on Rh(I), while the terminal CO is bonded to Rh metal (*43, 44*).

No significant differences between the four samples were found in the thermal desorption of CO. The desorption temperature of CO, T_{max}, lay in the range 463–473 K. During the desorption of CO, however, CO_2 was also formed, but its formation temperature varied with the support (Fig. 2). We may assume that the formation of CO_2 is the result of disproportionation of CO on Rh

$$2CO_{(g)} = C_{(s)} + CO_{2(g)}.$$

As the CO and the carrier gas were very carefully purified and dried, and any water remaining in the reactor or on the samples after reduction was also eliminated, we can safely state that no significant contribution to the high-temperature formation of CO_2 is made by the water–gas shift reaction

$$CO + H_2O = CO_2 + H_2.$$

The occurrence of this process was observed during the desorption of CO from alumina- and silica-supported Rh and Ru when the system contained water vapor (*45*). Nevertheless, no reliable conclusion concerning the effect of the support on the disproportionation of CO can be drawn from the different temperatures of CO_2 formation on the Rh samples, as CO_2 formed in the above process will not be desorbed immediately, but will be bonded to the support material, and its desorption temperature then varies with the support. This is well illustrated by the results obtained on Rh/SiO_2 and Rh/MgO. In the first case, CO_2 was desorbed in only one stage simultaneously with the CO, while in the case of Rh/MgO all the CO_2 was desorbed in one stage at much higher temperatures, in harmony with the weak bonding of CO_2 to SiO_2 and with the strong bonding of CO_2 to MgO.

Dissociation of CO

There is some controversy in the literature as regards the dissociation of CO on Rh surfaces (*46–54*). In a survey of the CO chemisorption properties of transition metal surfaces, Brodén *et al.* (*46*) have pointed out that the tendency to dissociative CO chemisorption increases the further an element is above and to the left of Pt in the Periodic Table, i.e., the more electropositive the metal. In their scheme, the chemisorption of CO on Rh is expected to be molecular at room temperature, a behavior which was confirmed experimentally.

Discrepancies mainly arise from the high-temperature behavior of chemisorbed CO. Somorjai and co-workers (*33, 48, 49*) have reported that adsorbed CO undergoes dissociation on Rh foil and on Rh(331) and Rh(755) surfaces. Other authors, however, using different methods, found no evidence for the dissociation of CO on Rh(111) and

Rh tips, even up to 1000 K, and argued that the same is true for polycrystalline and stepped surfaces on Rh (*50–53*).

In our first contribution to this dispute we reported that the dissociation of CO proceeds on Rh/Al_2O_3 above 473 K (*54*). This observation was recently confirmed by Niwa and Lunsford (*39*). In the present work this reaction was investigated in more detail, including the effect of the support on the process.

If we assume that a similar electronic interaction occurs between Rh and the support as in the case of Ni/TiO_2 catalyst (*9, 12*), i.e., electrons flow from the support to the metal, we might expect that the dissociation of CO will be influenced by the nature of the support. This assumption is based on the bonding characteristics of CO in the carbonyl complexes of transition metals (*55, 56*). Two bonds, dative and π, exist between the metal and the CO in these complexes. The σ bond results from electron transfer from the filled σ orbital of the ligand to an unfilled *d* orbital on the metal. The π bond forms by back-donation of electrons from the *d* orbitals of the metal into the antibonding π^* orbital of the ligand. Formation of the σ and π bonds leads to a cooperative strengthening of the metal–ligand bond. The back-donation, however, results in weakening of the C–O bond.

Considering the high electron concentration of *n*-type TiO_2 as compared to those of the other supports used in this study, which exhibit no, or only a very limited electronic conductivity, we may assume an enhanced electron transfer from TiO_2 to Rh. As a result, the electron donation from Rh into an antibonding π-orbital of the CO will be larger, which strengthens the Rh–C bond and weakens the C–O bond.

This effect, however, should be exhibited in the infrared spectrum of adsorbed CO, as the CO band should shift to lower frequencies as a consequence of increased back-donation from the Rh. As pointed out before, this can be observed in the position of the terminal CO band. In this respect it is more useful to compare the spectra obtained *in situ*, during the disproportionation and hydrogenation of CO. These spectra are basically different from those obtained on room-temperature CO adsorption: the twin CO band was completely missing, and the terminal CO band appeared at 2045–2055 cm^{-1}. There was some indication of a shift of terminal CO to lower frequency on Rh/TiO_2 compared to other samples.

Although the results obtained in the present study (Table 3) seem to be in harmony with the above expectation, as the efficiency of the supports in promoting the dissociation of CO over Rh decreased in the order $TiO_2 > Al_2O_3 > SiO_2 > MgO$, the effect of TiO_2 was far from being as large as expected on the basis of its semiconductive properties and its high activity in the methanation reaction.

It is important to mention, however, that under these reaction conditions, i.e., in the presence of hydrogen, much more profound differences in the extent of CO dissociation, or carbon deposition, are observed between the various supported Rh samples. We found that at 548 K the total carbon deposit was 126 μmol/g catalyst on Rh/TiO_2, 11 μmol/g on Rh/Al_2O_3, 3.37 μmol/g on Rh/SiO_2, and 0.37 μmol/g on Rh/MgO (*4*). Surface carbon was deposited on Rh/TiO_2 even at 473 K.

This means that either the dissociation of H_2 occurs to a greater extent on Rh/TiO_2 than on other samples or *the C–O bond is already weakened to such an extent that, with the interaction of adsorbed hydrogen,* possibly through the formation of Rh-carbonyl-hydride species, *it is more easily ruptured than on other Rh samples.*

As there was no indication of the presence of the twin CO band during the disproportionation of CO and the $H_2 + CO$ reaction, we can exclude the possibility that the dissociation of CO should occur in the twin form, as suggested by Tamaru (*57*) and Bossi *et al.* (*58*) in the case of Ru catalyst. It is more probable that the C–O bond is ruptured in both cases in the bridge-bonded CO and then in the terminal CO. It seems very plausible that the surface irregularities are the active sites for this process, as proposed by Somorjai *et al.* (*33*, *49*).

In the case of Rh/Al_2O_3 we determined the activation energy for the carbon deposition and obtained an average value of 50 kJ/mol. This value is comparable with that determined by Van Ho and Harriott (*59*) under the same conditions on Ni/SiO_2. The other authors found much higher values on Ni and other supported metals, but followed the reaction at much larger carbon deposition (*60*).

Hydrogenation of Surface Carbon

Study of the gasification of surface carbon by various methods revealed that from the point of view of reactivity different kinds of surface carbon exist on all Rh samples. Neglecting the highly reactive carbon (~1–2% of the total surface carbon) which can be hydrogenated even at 300 K, the hydrogenation of carbon on supported Rh occurs only above 420 K. Rh/TiO_2 differed from the other samples in that it contains more active surface carbon (T_{max} for the α_2 stage is 498 K).

Since the hydrogenation of surface carbon requires the activation of H_2, we cannot exclude the possibility that this process occurs more easily on Rh/TiO_2 than on other Rh samples. To check this idea, a comparative study is in progress in our laboratory on the adsorption and desorption of H_2 on and from Rh supported by different oxides.

The Rh/TiO_2 also contains the less reactive form of carbon (T_{max} for the β stage is 753 K). This may indicate that the surface carbon is more mobile on this catalyst and some of the carbon migrates farther from the active sites (edge and corners of Rh clusters) than on other catalysts, and is perhaps partly located on the TiO_2. This is very probably the case during the hydrogenation of CO at 548 K, when a large amount of surface carbon accumulates on Rh/TiO_2 (*4*). As a result the activity of Rh decreased to some extent, but it was still ca. 2 orders of magnitude higher than that of Rh/SiO_2; the surface carbon content on Rh/TiO_2 was 10 times that on Rh/SiO_2 (*4*).

We have determined the activation energy of the hydrogenation of surface carbon, which increased in the order $Rh/TiO_2 < Rh/Al_2O_3 < Rh/SiO_2$. As the determination of these values was based on the initial rate measurements, they certainly refer to the reaction of the more active (α_2) carbon. Although we do not know the structure of the surface carbon, from the earlier results on Ni catalysts (*61*) and on the effect of Rh metal on the reactivity of carbon (*62*) we may assume that this reactive carbon is carbidic, while the less reactive form is amorphous. Tomita *et al.* (*62*) found that graphitic carbon can be hydrogenated in the presence of Rh only at 1000 K, and thus it appears that we were not dealing with a reaction of this type.

A marked decrease in the reactivity of surface carbon was observed on Rh/Al_2O_3 and Rh/TiO_2 when the samples containing carbon were kept at 548 K for a longer time or when the carbon was produced at higher temperature, 573–603 K. In this case a significant portion of the more reactive carbon (carbidic form, α_2) has been transformed into the less reactive β form (amorphous). It is very likely that the appearance of the high-temperature (β) stage on the TPR spectra of surface carbon (Fig. 7) is already a result of the aging of carbon, i.e., the transformation of the carbidic form into the amorphous form during the production and reaction of surface carbon. It appears that this process occurs more rapidly on Rh/TiO_2 than on the other Rh samples and contributes greatly to the observed loss in the catalytic activities of Rh/TiO_2 and Rh/Al_2O_3 in the hydrogenation of CO (*4*).

REFERENCES

1. Solymosi, F., and Erdöhelyi, A., *J. Mol. Catal.* **8**, 471 (1980).
2. Solymosi, F., and Erdöhelyi, A., "Proceedings International Congress on Catalysis," 7th (Tokyo, 1980), p. 1448. Elsevier, Amsterdam, 1981.

3. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981).
4. Solymosi, F., Tombácz, I., and Kocsis, M., *J. Catal.* **75,** 78 (1982).
5. Solymosi, F., and Sárkány, J., *Appl. Surf. Sci.* **3,** 68 (1979).
6. Solymosi, F., Völgyesi, L., and Raskó, J., *Z. Phys. Chem. N. F.* **120,** 79 (1980).
7. Rives-Arnau, V., and Munuera, G., *Appl. Surf. Sci.* **6,** 122 (1980).
8. Nakamura, R., Nakai, S., Sugiyama, K., and Echigoya, E., *Bull. Chem. Soc. Jpn.* **54,** 1950 (1981).
9. Szabó, Z. G., and Solymosi, F., "Proceedings, International Congress on Catalysis," 2nd (Paris 1960), p. 1627. Technip, Paris, 1961.
10. Szabó, Z. G., Solymosi, F., and Batta, I., *Z. Phys. Chem. N. F.* **17,** 125 (1958).
11. Szabó, Z. G., Solymosi, F., and Batta, I., *Z. Phys. Chem. N. F.* **23,** 56 (1960).
12. Solymosi, F., *Catal. Rev.* **1,** 233 (1967).
13. Schwab, G. M., Block, J., and Schultze, D., *Angew. Chem.* **71,** 101 (1958); Schwab, G. M., Block, J., Müller, W., and Schultze, D., *Naturwissenschaften* **44,** 582 (1957).
14. Schwab, G. M., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 27, p. 1. Academic Press, New York, 1978.
15. Kao, C. C., Tsai, S. C., Bahl, M. K., and Chung, Y. W., *Surf. Sci.* **95,** 1 (1980).
16. Kao, C. C., Tsai, S. C., and Chung, Y. W., *J. Catal.* **73,** 136 (1982).
17. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
18. Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
19. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).
20. Vannice, M. A., and Garten, R. L., *J. Catal.* **66,** 242 (1980).
21. Vannice, M. A., *J. Catal.* **74,** 199 (1982).
22. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).
23. Mustard, D. G., and Bartholomew, C. H., *J. Catal.* **67,** 186 (1981).
24. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).
25. Bhasin, M. M., Bartley, W. J., Ellgen, P. C., and Wilson, T. P., *J. Catal.* **54,** 1201 (1978).
26. Ellgen, P. C., Bartley, W. J., Bhasin, M. M., and Wilson, T. P., *Advan. Chem.* **178,** 147 (1979).
27. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51,** 2268 (1978).
28. Ichikawa, M., *Bull. Chem. Soc. Jpn.* **51,** 2273 (1978).
29. Ichikawa, M., and Shikakura, K., "Proceedings, International Congress on Catalysis." 7th (Tokyo 1980), p. 925. Elsevier, Amsterdam, 1981.
30. Takeuchi, A., and Katzer, J. R., *J. Chem. Phys.* **85,** 937 (1981).
31. Castner, D. G., Blackard, R. L., and Somorjai, G. A., *J. Catal.* **66,** 257 (1980).
32. Tombácz, I., and Solymosi, F., unpublished results.
33. Sexton, B. A., and Somorjai, G. A. *J. Catal.* **46,** 167 (1977).
34. Katzer, J. R., Sleight, A. W., Gajardo, P., Michel, J. B., Gleason, E. F., and McMillan, S., *Faraday Discuss. Chem. Soc.* **72,** 121 (1981).
35. Iizuka, T., Tanaka, Y., and Tanabe, K., *J. Mol. Catal.* **17,** 381 (1982).
36. Iizuka, T., Tanaka, Y., and Tanabe, K., *J. Catal.* **76,** 1 (1982).
37. Tanaka, Y., Iizuka, T., and Tanabe, K., *J. Chem. Soc. Faraday Trans. 1* 78, 2215 (1982).
38. Meriaudeau, P., Ellestad, H., and Naccache, C., *J. Mol. Catal.* **17,** 219 (1982).
39. Niwa, M., and Lunsford, J. H., *J. Catal.* **75,** 302 (1982).
40. Conesa, J. C., Sainz, M. T., Soria, J., Munuera, G., Rives-Arnau, V., and Munoz, A., *J. Mol. Catal.* **17,** 231 (1982).
41. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Catal.* **65,** 428 (1980).
42. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Chem. Soc. Faraday Trans. 1* **77,** 2645 (1981).
43. Worley, S. D., Rice, C. A., Mattson, G. A., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Chem. Phys.* **76,** 20 (1982); Worley, S. D., Rice, C. A., Mattson, G. A., Curtis, C. W., Guin, J. A., and Tarrer, A. R., *J. Phys. Chem.* **86,** 2714 (1982).
44. Primet, M., *J. Chem. Soc. Faraday Trans. 1* **74,** 2570 (1978).
45. Fujimoto, K., Kameyama, M., and Kunugi, T., *J. Catal.* **61,** 7 (1980).
46. Brodén, G., Rhodin, T. N., Brucker, C., Bendow, R., and Hurych, Z., *Surf. Sci.* **59,** 593 (1976).
47. Marbrow, R. A., and Lambert, R. M., *Surf. Sci.* **67,** 489 (1977).
48. Castner, D. G., and Somorjai, G. A., *Surf. Sci.* **83,** 60 (1979).
49. Castner, D. G., Dubois, L. H., Sexton, B. A., and Somorjai, G. A., *Surf. Sci.* **103,** L134 (1981).
50. Thiel, P. A., Williams, E. D., Yates, J. T., and Weinberg, W. H., *Surf. Sci.* **84,** 54 (1979).
51. Yates, J. T., Williams, E. D., and Weinberg, W. H., *Surf. Sci.* **91,** 562 (1981).
52. Gorodetskii, V. V., and Nieuwenhuys, B. E., *Surf. Sci.* **105,** 299 (1981).
53. Yates, J. T., Williams, E. D., and Weinberg, W. H., *Surf. Sci.* **115,** L93 (1982).
54. Solymosi, F., and Erdöhelyi, A., *Surf. Sci.* **110,** L630 (1981).
55. Blyholder, G., *J. Phys. Chem.* **68,** 2772 (1964).
56. Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry." Interscience, New York, 1972.

57. Tamaru, K., "Proceedings, International Congress on Catalysis," 7th (Tokyo 1980), p. 47. Elsevier, Amsterdam, 1981.
58. Bossi, A., Carnisio, G., Garbassi, F., Giunchi, G., Petrini, G., and Zanderighi, L., *J. Catal.* **65,** 16 (1980).
59. Van Ho, S., and Harriott, P., *J. Catal.* **64,** 272 (1980).
60. Tøttrup, P. B., *J. Catal.* **42,** 29 (1976).
61. McCarty, J. G., and Wise, H., *J. Catal.* **57,** 406 (1979).
62. Tomita, A., Sato, N., and Tamai, Y., *Carbon* **12,** 143 (1974).