JOURNAL OF CATALYSIS **91**, 327–337 (1985)

Decomposition of Formic Acid on Supported Rh Catalysts

FRIGYES SOLYMOSI AND ANDRÁS ERDÖHELYI

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

Received April 4, 1984; revised September 25, 1984

The decomposition of formic acid was studied on supported Rh catalysts in a flow reactor at 380–520 K. The dominant process in the decomposition was the dehydrogenation reaction which followed first-order kinetics. The values of activation energy of the reaction fell in the range 66–83 kJ mol^{-1}. The activity of the catalysts, based on the turnover frequencies, decreased in the order $Rh/TiO_2 > Rh/Al_2O_3 > Rh/MgO \approx Rh/SiO_2$. The presence of CO in the gas stream markedly inhibited the reaction. The effect of different treatments of the catalysts was also examined. *In situ* infrared spectroscopic measurements revealed that weakly held HCOOH, adsorbed CO, and formate species were present on the catalyst surfaces during the reaction. Evidence is presented to show that the surface formate is located not on the Rh, but rather on the support. The stability of this formate species was investigated by temperature-programmed desorption. It is assumed that the dissociative adsorption of HCOOH is the slowest step in the catalytic decomposition of formic acid. © 1985 Academic Press, Inc.

INTRODUCTION

The decomposition of formic acid has been a very widely used model reaction for testing the validity of different theories of heterogeneous catalysis. It was by means of this reaction that it was first shown that the catalytic performance of a metal is drastically influenced by the nature of the support (*1–6*). The activation energy of the dehydrogenation of HCOOH on alumina-supported Ni, Co, and Ag was claimed by Schwab *et al.* (*1*, *2*) to depend on the electrical conductivity properties of the Al_2O_3 support, which led them to assume that there was a strong electronic interaction between the metal and the support. However, the fact is that the electrical conduction of the insulator alumina depended hardly at all on the doping of the alumina with altervalent ions (variation within $2.5–7 \times 10^6$ ohm^{-1} cm^{-1}), and the activation energy of the dehydrogenation was similarly almost independent of doping (variation of ±10%). Accordingly, the catalytic results on this system could hardly be considered to be a proof of the role of an electronic interaction between the metals and Al_2O_3 (*6*). More convincing results of the support effect, however, were soon obtained using semiconductor oxides (TiO_2, Cr_2O_3, NiO) as support materials (*3–5*).

The increased interest in the support effect, particularly in TiO_2 as a support, during the past few years prompts us to recall three observations from the early studies which have seemed to escape the attention of most recent investigators:

(i) The doping of the TiO_2 support and the variation of the reduction temperature (673–773 K) of Ni/TiO_2 strongly influenced its catalytic performance, and the conclusion was drawn that electrons are transferred from TiO_2 to Ni in the electronic interaction between them (*5*).

(ii) NiO, a *p*-type semiconductor, exerted a marked influence on the catalytic properties of Ni (*3*, *4*). This effect, moreover, depended on the concentration of positive holes in the NiO, and therefore was attributed to a strong, catalytically effective electronic interaction between Ni and NiO (*3*, *4*).

(iii) Neglect of the effect of unreduced NiO leads to false conclusions as regards the role of supports for supported nickel catalysts (*4–6*).

Recent results indicate that the study of

0021-9517/85 $3.00

HCOOH decomposition is not only of academic interest, but also of strong relevance to some important industrial catalytic processes. It has emerged that the adsorbed formate ion is probably a surface intermediate in several reactions; it has been detected in the water-gas shift reaction (*7, 8*) in the synthesis and decomposition of CH_3OH (*9, 10*), and in the methanation of CO (*11, 12*) and CO_2 (*13–17*). Strong bands due to adsorbed formate ion are also produced in the low-temperature surface interaction of H_2 and CO_2 (*15, 18–21*).

Much work has been performed on supported Rh catalysts in order to elucidate the mechanism of selectivity in the reactions of CO and CO_2 with hydrogen. It seemed to us necessary to learn more about the behavior of formate on Rh. In this program we have recently investigated the interaction of HCOOH with Rh foil (*22*) and the single-crystal Rh(111) surface (*23*) by means of electron spectroscopic methods.

In the present paper we report on the catalytic decomposition of HCOOH over supported rhodium. We have found only very little reference in the literature to the catalytic decomposition of HCOOH on Rh (*24, 25*). In the early twenties, Hinshelwood and Topley (*25*) studied the decomposition of HCOOH on Rh foil. The reaction proceeded at measurable rates at 155–186°C, with an activation energy of 105 kJ mol^{-1}. Thus the reaction merits further study both from the standpoint of the support effect and the interest in formate as an intermediate in reactions in general.

EXPERIMENTAL

Materials. The catalysts were prepared by impregnating oxide supports with solutions of $RhCl_3 \cdot 3H_2O$ to yield a nominal 1 and 5% of metal. The powder supports used were: Al_2O_3 (Degussa P 110 Cl), SiO_2 (Aerosil 200), MgO (DAB 6), TiO_2 (Degussa P 25), and TiO_2 (BDH). The latter was precalcined at 1273 K. The impregnated powders were dried at 373 K. Before the measurements, the catalysts were oxidized and reduced at 673 K (in both cases for 30 min) *in situ* in a flow of O_2 or H_2 (~40 ml min^{-1}). After oxidation and reduction, the samples were flushed with He at 673 K for 15 min, and then cooled in flowing He to the reaction temperature. For catalytic studies, fragments of slightly compressed pellets were used; for ir spectroscopic studies, the samples were compressed at high pressure (~1600 atm) into transparent disks (15–20 mg cm^{-2}).

The gases used were of commercial purity. The He was deoxygenated with an "Oxy-Trap" and an "Indicating Oxy-Trap" (Altech Co.). The other impurities were adsorbed with a molecular sieve (Linde 5A) cooled by liquid air.

HCOOH was a product of Merck, and was purified by distillation. The purity was measured by mass spectrometry.

Methods. The dispersion of Rh was determined via H_2 adsorption at 298 K with the use of a dynamic impulse method (*12*). The kinetic data were obtained in a flow reactor made from a 15-mm-i.d. Pyrex glass tube. The dead volume was filled with glass beads. The HCOOH introduced into the reactor was that resulting after bubbling He or H_2 or a mixture of He + CO through concentrated HCOOH. The concentration of HCOOH was usually about 10%. The weight of the catalyst sample was 0.3–0.5 g. The space velocity was 20.000 hr^{-1}. Unreacted HCOOH and any water formed in the reaction were condensed in a trap cooled to 255 K. Gases were analyzed with a Hewlett–Packard 5750 gas chromatograph. A Poropak QS column was used for the separation of reactants and products. Temperature-programmed desorption (TPD) measurements were carried out in the catalytic reactor. After injection of 1 μl (21.6 μmol) HCOOH onto the catalyst, the reactor was flushed with He at room temperature, and then heated at 40 K min^{-1} in a He stream. The effluent gas was analyzed with a gas chromatograph using a thermal conductivity or flame ionization detector.

Infrared spectra were recorded with a

Specord 75 IR double-beam spectrometer. In the high-temperature cell, the spectra were taken at the reaction temperature, either *in vacuo* or in the gas flow (*26*). The sample holder of the cell was made from glass. The sample was brought to the required temperature by electrically heating kanthal wires inserted into the sample holder. To prevent damage to the NaCl windows due to the high temperature, the cell was cooled externally with circulating water. The measurement and regulation of temperature were performed with iron–constantan thermocouples.

RESULTS

HCOOH Decomposition in He Flow

The decomposition of HCOOH on supported Rh (1 wt%) occurred at a measurable rate above 380 K. The activities of the catalysts were very constant with time. A slight decrease in the activity with time was observed on Rh/TiO_2. The rate of reaction depended sensitively on the support. The selectivity factor ($CO_2/CO_2 + CO$) was 0.6–1, with the exception of Rh/TiO_2 (Degussa), on which it was 0.34–0.4. No alteration in the selectivity of the catalysts was experienced with variation of reaction temperature. The dependence of the rate of catalytic decomposition on the partial pressure of HCOOH was determined on Rh/SiO_2 (Fig. 1). In the conversion range where the activation energy of the decomposition was determined, the reaction order was 0.8. We obtained a similar result on Rh/Al_2O_3. In this case the order of reaction was ~1.0 at the conversion of ~13%.

It is important to mention that, with the exception of Degussa TiO_2, no decomposition of HCOOH occurred on the supports alone up to 550 K. On the Degussa TiO_2 in the temperature range 413–513 K, only the dehydration reaction occurred, with an activation energy of 77.5 kJ mol^{-1}. The contribution of the catalytic effect of the TiO_2 support was avoided when TiO_2 (BDH) sintered at 1273 K was used as support. The Arrhenius plots for different samples are shown in Fig. 2. The activation energy (E_{CO_2}) value of 75.4–83.7 kJ mol^{-1} was practically the same for Rh supported on MgO, Al_2O_3, and SiO_2. On Rh/TiO_2, however, we obtained the lower value of 66.2 kJ mol^{-1}. The activation energy for the dehydration reaction was determined only for Rh/TiO_2 and Rh/Al_2O_3 (Table 1).

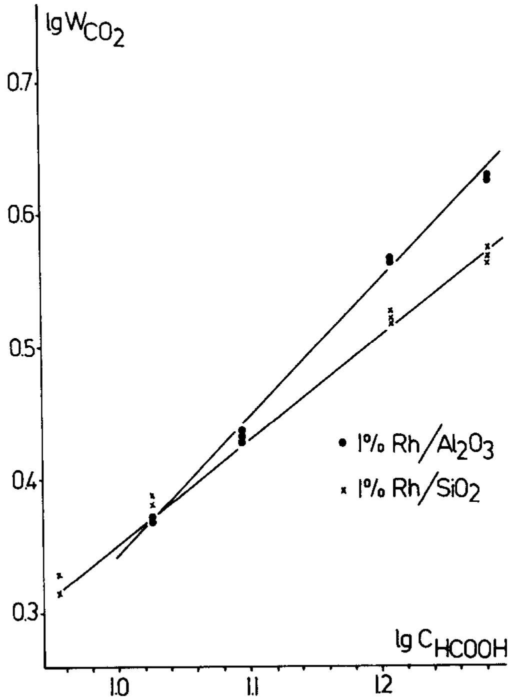

FIG. 1. Dependence of the rate of HCOOH dehydrogenation on the concentration of HCOOH in He stream on Rh/SiO_2 and on Rh/Al_2O_3 catalysts at 483 K. W_{CO_2} = rate of CO_2 formation, μmol/g · s.

The specific activities of supported Rh samples in terms of turnover frequencies ($N_{formate}$ and N_{CO_2}, rates per unit surface area of metal) were calculated. The values obtained at 448 K are shown in Table 1.

It appears that the most effective catalyst for HCOOH decomposition is Rh/TiO_2. A higher efficiency was exhibited in both dehydrogenation and dehydration. This was followed in turn by Rh/Al_2O_3, Rh/MgO, and Rh/SiO_2.

The catalytic decomposition of HCOOH was also examined on Rh foil, and in the

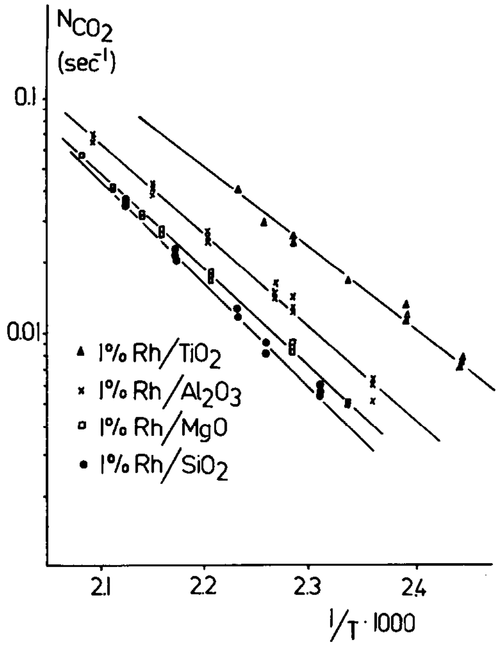

FIG. 2. Arrhenius plots for dehydrogenation of HCOOH on different Rh catalysts. N_{CO_2} = turnover number, i.e., (molecules formed)/(metal site · s).

same temperature range as on supported Rh. The reaction occurred almost exclusively in the direction of dehydrogenation. No decay in activity was experienced. The activation energy was 76.7 kJ mol^{-1}.

On examining the Rh samples after the catalytic reaction (after 1–2 hr use), we found chemisorbed CO, formate, and various carbonates (see later). Following elimination of these surface species in a He flow at 548 K, no or only very slight methane formation was observed upon admitting H_2 pulses to the sample. Since surface carbon formed on Rh samples below 573 K shows a high reactivity toward H_2 (*27*), we may conclude that no carbon was formed during the decomposition of HCOOH on Rh catalysts.

In subsequent measurements we examined *the effects of different pretreatments* on the catalytic efficiency of Rh samples, with special emphasis on Rh/TiO$_2$. No change in catalytic behavior was found for the sample reduced at 473 K. When the reduction was performed at 773 K, the activity of the catalyst (on a weight basis) increased by 20–30%. The selectivity and the activation energy remained unchanged (Table 1). The turnover frequencies cannot be compared, as there was no hydrogen uptake by Rh/TiO$_2$ reduced at 773 K.

TABLE 1

Kinetic Data for the Decomposition of HCOOH on Supported Rh Catalysts

Sample	Surface area of the supports (m^2 g^{-1})	Rh dispersion (%)	W_{CO_2} (μmol/g · s) at 448 K	N_{CO_2} (s^{-1} × 10^3) at 448 K	S_{CO_2} (%)	E_{CO_2} (kJ mol^{-1})
		He + 10% HCOOH				
1% Rh/Al$_2$O$_3$[a]	100	32.6	0.625	19.3	86.2	75.0 ± 3
1% Rh/MgO[a]	170	15.1	0.206	13.7	89.5	78.1 ± 1.2
1% Rh/SiO$_2$[a]	240	33.0	0.393	11.8	95.4	83.7 ± 2.5
1% Rh/TiO$_2$[a]	25	30.0	1.18	41.2	63.3	66.2 ± 4
1% Rh/TiO$_2$[b]	25	—	1.58	—	71.1	69.8 ± 3.2
1% Rh/TiO$_2$[c]	25	—	3.0	—	69.7	65.5 ± 2.5
		H_2 + 10% HCOOH				
1% Rh/Al$_2$O$_3$[a]	100	32.6	0.27	8.3	61.3	69.1 ± 1.4
1% Rh/TiO$_2$[a]	25	30.0	0.48	16.5	46.0	74.5 ± 2.1

Note. N_{CO_2} = Turnover number, molecules formed/(metal site · s). S_{CO_2} = Selectivity factor, $CO_2/(CO_2 + CO)$. W_{CO_2} = rate of CO_2 formation, μmol/g · s.

[a] The catalyst was reduced at 673 K.

[b] The catalyst was reduced at 773 K.

[c] The catalyst was oxidized at 673 K.

A threefold increase in decomposition rate was experienced on the *oxidized samples* (oxidation at 673 K in an O_2 flow for 60 min, and cooling in a He flow to the reaction temperature), without any alteration in the selectivity and activation energy. As a result of the reducing effect of HCOOH after long use of the oxidized catalyst (~20 hr), the rate of HCOOH decomposition on the oxidized sample slowly decreased.

Decomposition of HCOOH in the Presence of CO and H_2

The rate of decomposition of HCOOH was drastically decreased when CO was introduced into the gas stream containing HCOOH. Detailed data are presented in Fig. 3. It can be seen that even a small amount of CO inhibits the reaction: the rate of decomposition decreased almost to zero in the presence of 20% CO. This behavior was observed on all catalyst samples (Fig. 3). When CO was adsorbed on the catalyst just before the catalytic reaction, the inhibitory effect was exhibited only in the first 5–8 min.

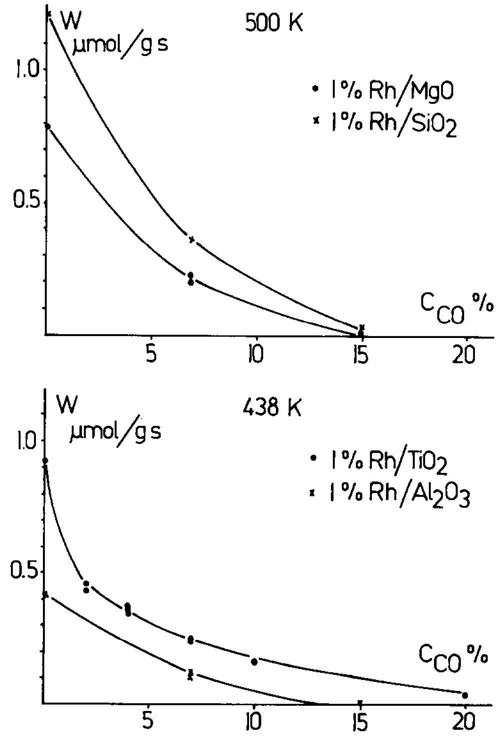

FIG. 3. The effect of CO concentration on the rate of dehydrogenation of HCOOH decomposition on supported Rh catalysts.

The decomposition of HCOOH was also investigated under similar conditions, but in the presence of a large amount of H_2. In this case, instead of He, H_2 was passed through the HCOOH solution and was led to the catalyst bed. The presence of H_2 decreased the rate of decomposition of HCOOH by 40–50%. The selectivity toward CO_2 formation was lower and the dehydration assumed much greater importance. At the same time the formation of CH_4 was detected, particularly on Rh/Al_2O_3. Methane formation, however, did not account for more than ~1–3% of the decomposed HCOOH. This value was a factor of 3–4 higher when the HCOOH residence time was increased from 0.16 to 0.48 sec. The activation energy for the dehydrogenation was somewhat higher than in the previous cases. The kinetic data are listed in Table 1.

TPD Measurements

In the subsequent measurements the surface reactions of adsorbed HCOOH were investigated by TPD spectroscopy. Reduced Rh samples cooled in a He stream were exposed to 1 µl (26.1 µmol) HCOOH at 300 K. The samples were kept in a He stream for 15 min, and then heated in a He flow. TPD spectra are shown in Fig. 4. HCOOH desorption was observed only from Rh/SiO_2, with a peak temperature of T_p = 415 K. Surface reaction took place first on Rh/TiO_2, as indicated by the formation of CO, CO_2, and CH_4 above 400 K (Fig. 4). Desorption occurred in three stages, at 436, 488, and 600 K.

The desorption of these products from the other samples proceeded at higher temperatures (Fig. 4). No significant differences were observed in the product distributions. The results of quantitative analysis of the gases desorbed are shown in Table 2.

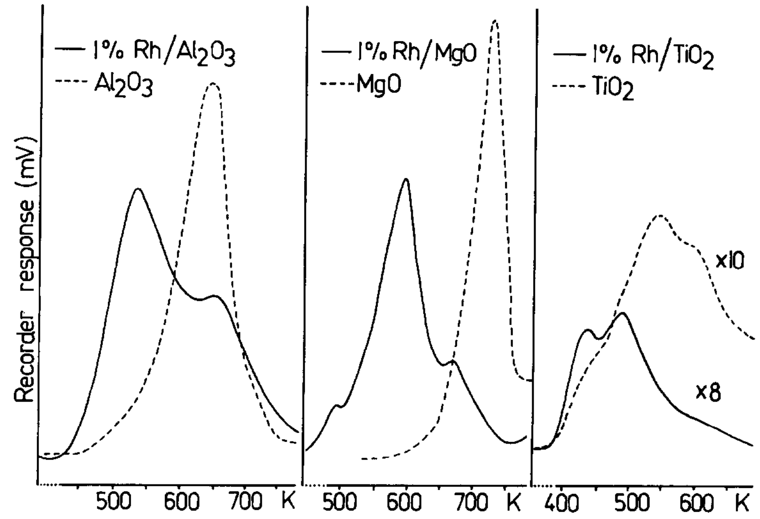

FIG. 4. Temperature-programmed desorption spectra after injection of 1 μl (21.6 μmol) of HCOOH on different samples at 300 K, showing the effect of the metal. The product distribution of carbon-containing compounds is given in Table 2.

With the exception of Rh/TiO_2, practically the total amount of HCOOH injected onto the samples at 300 K remained adsorbed, and then desorbed and decomposed at higher temperatures.

As HCOOH adsorbs strongly on oxidic supports, for evaluation of the role of Rh similar TPD measurements were performed *with the supports alone*. TPD spectra are also shown in Fig. 4 and the results of gas analysis in Table 2. Although, as will be shown later, the formate locates not on the Rh, but rather on the support, the TPD results clearly show that the presence of Rh can accelerate the decomposition of this surface compound. This feature can be accounted for by an occurrence of a surface migration of formate species to the Rh.

TABLE 2

Characteristics of Temperature-Programmed Desorption after Adsorption of 1 μl HCOOH

Samples	T_p[a] (K)	Relative amount of carbon compounds formed during desorption (%)		
		CO	CH_4	CO_2
1% Rh/TiO_2	436, 488, 600	16	9	75
TiO_2	— 542, 600	19	—	81
1% Rh/Al_2O_3	532, 648	17	8	75
Al_2O_3	— 643	18	—	82
1% Rh/MgO	492, 595, 668	10	7	83
MgO	— 728	70	—	30

[a] Temperatures where the rate of desorption of the products exhibits maxima (see Fig. 4).

Infrared Spectroscopic Measurements

Adsorption of HCOOH on reduced supported Rh samples (except Rh/SiO_2) produced intense absorption bands at 1585, 1395, and 1373 cm^{-1}. A very weak band was also detected at 2914–2921 cm^{-1}. These bands were stable against evacuation at 300 K. On Rh/SiO_2, only one band appeared, at 1720 cm^{-1}, and this was eliminated by evacuation at 300 K.

The above bands had high intensities in the ir spectra taken during the catalytic decomposition of HCOOH (Fig. 5). In addition, however, new bands developed at 2030–2050 and 1860 cm^{-1} due to the chemisorbed CO formed in the decomposition of HCOOH. The intensity of these bands slightly increased with the reaction time up

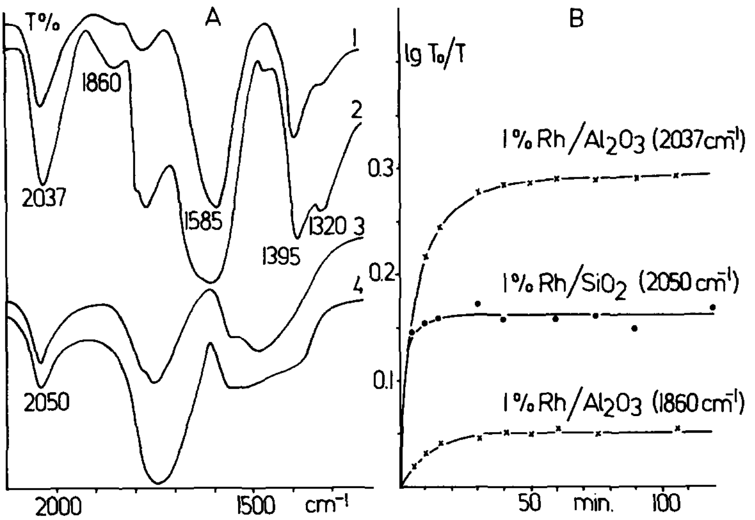

FIG. 5. (A) Infrared spectra taken during the decomposition of HCOOH at different times on 1% Rh/Al_2O_3: (1) after 5 min, (2) after 120 min; and 1% Rh/SiO_2: (3) after 5 min, (4) after 120 min at 473 K. (B) Changes in the intensities of CO bands during the decomposition of HCOOH at 473 K. The concentration of HCOOH in the stream was ~10%, and the flow rate was 30 ml min^{-1}. The sample weight was 60 mg.

to 25–50 min (Fig. 5). In addition, a broad band peaking at about 1780 cm^{-1} due to gaseous or weakly held HCOOH appeared in the spectra. Evacuation of the cell at room temperature eliminated this band, but resulted in no change in the intensities of the bands due to adsorbed formate and CO.

DISCUSSION

Although the metal-catalyzed decomposition of HCOOH has been the subject of very many investigations, the bulk of the work has been concerned with the study of this reaction over Cu, Ni, and Cu–Ni alloys (*24, 28, 29*). Recent papers provide useful surveys of the kinetic results (*30*). While it was assumed earlier that the slowest step in the decomposition is the chemisorption of HCOOH, which involves an electron transfer from HCOOH to the metal (*1, 2, 24, 28, 29*) or to semiconductor catalysts (*3, 31, 32*), the identification of a stable formate species on the surface of Ni (*33–35*) and also on many oxides (*29*) led to the decomposition of adsorbed formate being regarded as the rate-limiting step.

The catalytic behavior of Pt metals in this reaction has received much less attention, and particularly few data are available as regards the adsorption of HCOOH, and the formation and stability of formate species on these metals. As pointed out previously (*18, 19*), there are many misreferences and unchecked statements in the literature relating to this question. As concerns ir studies on formic acid chemisorbed on SiO_2-supported Ni, Pd, Pt, Rh, Cu, Ag, and Au, Bond (*24*) refers to seven papers, but only one of these deals with the adsorption of formic acid on Pt, and even in this work the authors found *no evidence of surface formate ion* (*35*). Mars *et al.* (*28*) also refer to two of these papers (*36, 37*), stating that formate ion is present on Pt, Pd, and Rh surfaces. These misreferences very probably originated from the paper of Hirota *et al.* (*33*), which deals with ir studies of HCOOH on Ni and Cu. In this paper Hirota *et al.* write that negative formate ion ($HCOO^-$) is produced, among others, on Pd, Pt, and Rh during the adsorption of formic acid; however, the references given (*36, 37*) do not contain any such data concerning these metals.

Characteristics of the Decomposition of HCOOH on Supported Rh

The present study shows that the supported Rh samples are very effective in the decomposition of HCOOH. The reaction occurs at measurable rates on 1% Rh-containing catalyst even at 380–420 K, which is a considerably lower temperature range than that required to attain the same rate on supported Ni and Cu catalysts. The predominant reaction in the decomposition is dehydrogenation, but the dehydration of HCOOH also occurred, particularly on Rh/TiO_2 and Rh/Al_2O_3.

In harmony with this behavior, a relatively strong absorption band due to linear CO appeared at 2030–2050 cm^{-1} in the ir spectra of Rh samples in the course of the catalytic reaction (Fig. 5). The band is formed, in general, at the beginning of the reaction, its intensity subsequently increasing only slightly. However, this CO spectrum differs basically from that observed following direct CO adsorption on the same reduced Rh samples (*18, 19, 38, 39*). In the case of CO adsorption on reduced Rh, the linear CO band occurs at a higher frequency (ca. 2060 cm^{-1}) and there is also the production of a twin-CO band. Similar characteristics were experienced in the low-temperature interaction of $H_2 + CO_2$ (*18, 19*) and in the hydrogenation of CO and CO_2 (*12–14*). We believe that the shift to lower frequency (red shift) of the linear CO band in these cases is primarily caused by the formation of Rh-carbonyl-hydride, and the "coverage effect" on the position of the linear CO band plays only a minor role. We have proposed that this species plays an important role in the methanation of CO and CO_2 (*12–14*), as the presence of H on the same Rh may promote the dissociation of CO. The existence of this surface species and its assumed role were recently confirmed by Worley *et al.* (*40*).

In contrast to the findings on Cu, Ni, and their alloys, the decomposition of HCOOH on Rh is not a zero-order process, but is nearly first-order. This holds for Rh foil and supported Rh samples. It may be noted that Hinshelwood and Topley (*25*) also found a first-order dependence. This result makes it very unlikely that the decomposition of formate species is the rate-determining step in the catalytic reaction of HCOOH on rhodium.

The ir spectra obtained following the adsorption of HCOOH at 300 K and during the catalytic reaction are apparently in contradiction with the above statement, for (with the exception of Rh/SiO_2) a strong and stable formate species has been identified on supported Rh samples. As we have detected the formation of formate species in the $H_2 + CO_2$ interaction and reaction on Rh catalysts (*13, 14, 18, 19*), a great effort was made to establish the possible sites of formate species on these samples. We now present strong arguments which indicate that the formate species is located not on the Rh, but almost exclusively on the supports. These arguments are

(i) The adsorption of HCOOH on Al_2O_3, MgO, and TiO_2 in the absence of Rh produces identical ir spectra (*18, 19*).

(ii) The number of formate species produced by surface reactions (such as $H_2 + CO_2$ interaction, HCOOH adsorption, etc.) is 5–8 times higher than that of surface Rh atoms (*18, 19*).

(iii) The intensities of the absorption bands due to CO chemisorbed on Rh are not influenced if HCOOH is adsorbed on Rh samples before or after CO adsorption, yielding intense formate bands (*41*).

(iv) No formate bands are detected in the ir spectra of Rh/SiO_2 at 300–500 K following HCOOH adsorption and during the catalytic decomposition of HCOOH (Fig. 5) (we may recall that no formate is formed on the silica surface). This observation, which is in harmony with our previous results (*18, 19*), is particularly decisive.

These collected results suggest that, under our conditions, formate is unstable on Rh and, if it is formed, decomposes rapidly. This behavior is in contrast with that on silica-supported Ni and Cu catalysts, where stable formate is present on the surface during the catalytic reaction at 300–550 K (*33–37*).

The high instability of formate species is confirmed by our recent studies on Rh foil (*22*) and the Rh(111) surface (*23*) under UHV conditions. By means of thermal desorption and electron energy loss spectroscopic measurements, we distinguished molecularly and dissociatively adsorbed HCOOH. The molecularly adsorbed HCOOH desorbs with peak temperatures of $T_p = 153$ and 172 K. The formate species starts to decompose at around 200 K, yielding H_2 and CO_2 as primary products. The decomposition goes to completion by 300 K.

Taking all these results into account, we propose the following steps for the decomposition of HCOOH:

$$HCOOH_{(g)} = HCOOH_{(ads)} \quad (1a)$$

$$HCOOH_{(ads)} = H_{(ads)} + HCOO_{(ads)} \quad (1b)$$

or $$HCOOH_{(g)} = H_{(ads)} + HCOO_{(ads)} \quad (2)$$

$$HCOO_{(ads)} = H_{(ads)} + CO_{2(ads)} \quad (3)$$

$$CO_{2(ads)} = CO_{2(g)} \quad (4)$$

$$H_{(ads)} + H_{(ads)} = H_{2(g)} \quad (5)$$

As the desorption of CO_2 from Rh occurs below 300 K, with $T_p = 244$ and 177 K (*42*), whereas H_2 desorbs slightly above 300 K, with $T_p = 275$–330 K (*43*), it is not possible for the desorption of either compound to be the slowest step in the decomposition. We also have to assume that the decomposition of formate on Rh is fast enough not to be the rate-limiting process. In light of this, it appears most likely that *the dissociative chemisorption of HCOOH is the slowest step in the above reaction scheme.*

The fact that the decomposition is almost completely suppressed by the presence of *carbon monoxide* in the He carrier gas is in harmony with this picture. The CO adsorbs strongly to the Rh and thereby reduces the number of free Rh sites, decreasing the probability of the dissociative adsorption of HCOOH. It is noteworthy that the presence of CO in the reacting gas mixture, or the preadsorption of CO on Rh, did not influence the development and intensities of the formate bands, again suggesting that these bands are due to formate located on the supports, its occurrence there having hardly any effect on the reactions on the Rh.

The lower inhibiting effect of H_2 can also be explained in this way, since the Rh–H bond is weaker than the Rh–CO bond (*43*). The slight inhibitory effect of hydrogen makes it very unlikely that the reaction

$$H_{(ads)} + HCOOH_{(g)} = H_{2(g)} + HCOO_{(ads)} \quad (6)$$

plays any important role in the decomposition of HCOOH on Rh catalysts.

The introduction of CO_2 into the He flow exerted no observable influence on the reaction. This is not surprising, as CO_2 adsorbs very weakly on the Rh surface at the temperature of the catalytic reaction (*42*).

Besides the products of dehydrogenation and dehydration, traces of CH_4 were also detected. In the presence of a larger amount of H_2 in the He carrier gas, particularly at lower flow rates, an increase in CH_4 formation was clearly observed. The production of CH_4 could at first sight be explained by hydrogenation of the decomposition products CO_2 and CO. However, CH_4 was also produced in the reaction between the formate adsorbed on the support and the hydrogen activated on the Rh (*46*), at 425 K, i.e., below the methanation temperatures of CO and CO_2. We believe that CH_4 is formed in the same reaction also in the present case of formic acid decomposition. This finding may be important in an evaluation of the possible routes of the methanation reaction, and it indicates that the formate bonded to the support cannot be considered a totally inactive surface species. For further details of this reaction we refer to our previous work (*46*).

The Effect of the Support

Let us now examine the effect of the support on the catalytic performance of the Rh. On the basis of the specific activity (N_{CO_2}, the frequency of CO_2 formation per surface Rh site), Rh/TiO_2 is the most effective catalyst, followed in turn by Rh/Al_2O_3, Rh/MgO, and Rh/SiO_2. The differences in the specific activities of the last three samples, however, are very slight, if any.

The Rh/TiO_2 sample also exhibited the highest specific activity in the dissociation of CO (*27*), and in the hydrogenation of CO (*12*) and CO_2 (*13, 14*). Its activity was only slightly higher when it was reduced at 773 K, which means that the "SMSI effect" does not play any role in its catalytic performance. One may assume that the electronic interaction between Rh and TiO_2 is responsible for the high catalytic activity of Rh/TiO_2, just as was proposed more than 2 decades ago for Ni/TiO_2 (*5*).

We believe that this electronic interaction has a dominant role in the hydrogenation of CO and CO_2, where the specific activity of Rh/TiO_2 was about two orders of magnitude higher than those of Rh/MgO and Rh/SiO_2 (*12–14*). Although the electronic interaction between Rh and TiO_2, i.e., the electron transfer from TiO_2 to Rh, can promote the formation of formate anion on the Rh, we cannot absolutely rule out that in this case part of the decomposition also proceeds on the TiO_2 support.

TiO_2 was found to be an effective catalyst for the decomposition of formic acid (*29, 31*). It catalyzed both the dehydrogenation and the dehydration. The selectivity of TiO_2 depended on the mode of preparation and on the pretreatment; in general, the higher the sintering temperature, the higher was the CO_2/CO ratio. It is true that the decomposition of HCOOH on the TiO_2 sample (BDH, sintered at 1273 K) used as support in the present study was negligible, actually less than 1% conversion at the highest reaction temperature, 450 K, but the possibility cannot be excluded that, due to the presence of Rh, the TiO_2 surface became more active. In this case, N_{CO_2} must be regarded as an upper limit. One possible means for this activation is that the hydrogen formed and activated on the Rh migrates onto the TiO_2, creating new active sites for the decomposition of HCOOH. The occurrence of this process on Rh/TiO_2, i.e., the formation of additional Ti^{3+} centers, was demonstrated by the ESR, NMR, and ir measurements of Conesa *et al.* (*44*).

The fact that the activity of TiO_2 can be enhanced in this way was shown by Burch and Flambard (*45*). They found that the addition of Ni to TiO_2 significantly increased the adsorption capacity of the latter. As TiO_2 catalyzes the decomposition of HCOOH in both directions, the occurrence of HCOOH dehydration on Rh/TiO_2 may be a result of the reaction on the support.

REFERENCES

1. Schwab, G. M., Block, J., and Schultze, D., *Angew. Chem.* **71,** 101 (1958).
2. Schwab, G. M., Block, J., Müller, W., and Schultze, D., *Naturwissenschaften* **44,** 582 (1957).
3. Szabó, Z. G., Solymosi, F., and Batta, I., *Z. Phys. Chem. N.F.* **17,** 125 (1958).
4. Szabó, Z. G., Solymosi, F., and Batta, I., *Z. Phys. Chem. N.F.* **23,** 56 (1960).
5. Szabó, Z. G., and Solymosi, F., "Proceedings, of 2nd International Congress on Catalysis," p. 1627. Editions Technip, Paris, 1961.
6. Solymosi, F., *Catal. Rev.* **1,** 233 (1967).
7. Grenoble, D. C., Estadt, M. M., and Ollis, D. F., *J. Catal.* **67,** 90 (1981).
8. Amenomiya, Y., *J. Catal.* **57,** 64 (1979).
9. Deluzarche, A., Kieffer, R., and Muth, A., *Tetrahedron Lett.,* 3357 (1977).
10. Kagel, R. O., and Greenler, R. G., *J. Chem. Phys.* **49,** 1638 (1968).
11. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **49,** 383 (1977).
12. Solymosi, F., Tombácz, I., and Kocsis, M., *J. Catal.* **75,** 78 (1982).
13. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Catal.* **68,** 371 (1981).
14. Solymosi, F., and Erdöhelyi, A., "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980," p. 1448. Kodansha/Elsevier, Tokyo/Amsterdam, 1981.
15. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Chem. Soc. Faraday Trans. 1* **77,** 1003 (1981).

16. Ramarson, E., Kieffer, R., and Kiennemann, A., *J. Chem. Soc. Chem. Commun.*, 645 (1982).
17. Deluzarche, A., Cressely, J., and Kieffer, R., *J. Chem. Res.* 136(S), 1656(M) (1979).
18. Solymosi, F., Erdöhelyi, A., and Bánsági, T., *J. Chem. Soc. Faraday Trans. 1* **77,** 2645 (1981).
19. Solymosi, F., Erdöhelyi, A., and Kocsis, M., *J. Catal.* **65,** 428 (1980).
20. Kadinov, G., Palazov, A., and Shopov, D., "Proceedings, 4th International Symposium on Heterogeneous Catalysis, Várna, 1979," p. 325. Bulgarian Acad. Sci., Sofia, 1980.
21. Erdöhelyi, A., Lancz, M., and Solymosi, F., "Proceedings, 5th International Symposium on Heterogeneous Catalysis, Varna, 1983," p. 115. Bulgarian Acad. Sci., Sofia, 1984.
22. Solymosi, F., and Kiss, J., *J. Catal.* **81,** 95 (1983).
23. Kiss, J., and Solymosi, F., to be published.
24. Bond, G. C., "Catalysis by Metals." Academic Press, New York/London, 1962.
25. Hinshelwood, C. N., and Topley, B., *J. Chem. Soc.* **123,** 1014 (1923).
26. Bánsági, T., Raskó, J., and Solymosi, F., in "Proceedings, International Symposium on Spillover of Adsorbed Species" (G. M. Pajonk, S. J. Teichner, and J. E. Germain, Eds.), p. 109. Elsevier, Amsterdam, 1983.
27. Erdöhelyi, A., and Solymosi, F., *J. Catal.* **84,** 446 (1983).
28. Mars, P., Scholten, J. J. F., and Zwietering, P., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 14, p. 35. Academic Press, New York, 1963.
29. Trillo, J. M., Munuera, G., and Criado, J. M., *Catal. Rev.* **7,** 51 (1972).
30. Iglesia, E., and Boudart, M., *J. Catal.* **81,** 214 and 224 (1983).
31. Szabó, Z. G., and Solymosi, F., *Acta Chim. Hung.* **25,** 145 and 161 (1960).
32. Szabó, Z. G., and Solymosi, F., *Z. Elektrochem.* **63,** 1177 (1959).
33. Hirota, K., Kuwata, K., Otaki, T., and Asai, S., "Proceedings, 2nd International Congress on Catalysis, Paris, 1960," p. 809. Editions Technip, Paris, 1961.
34. Sachtler, W. M. H., and Fahrenfort, J., "Proceedings, 2nd International Congress on Catalysis, Paris, 1960," p. 831. Editions Technip, Paris, 1961.
35. Eischens, R. P., and Pliskin, W. A., "Proceedings, 2nd International Congress on Catalysis, Paris, 1960," p. 789. Editions Technip, Paris, 1961.
36. Hirota, K., Kuwata, K., and Nakai, Y., *Bull. Chem. Soc. Jpn.* **31,** 861 (1958).
37. Hirota, K., Otaki, T., and Asai, S., *Z. Phys. Chem. N.F.* **21,** 438 (1959).
38. 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).
39. 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).
40. Worley, S. D., Mattson, G. A., and Caudill, R., *J. Phys. Chem.* **87,** 1671 (1983).
41. Kocsis, M., thesis, University of Szeged, 1982.
42. Solymosi, F., and Kiss, J., *Chem. Phys. Lett.* **110,** 639 (1984).
43. Yates, J. T., Thiel, P. A., and Weinberg, W. H., *Surf. Sci.* **84,** 472 (1979).
44. Conesa, J. C., Munuera, G., Munoz, A., Rives, V., Sanz, J., and Soria, J., *in* "Proceedings, International Symposium on Spillover of Adsorbed Species" (G. M. Pajonk, S. J. Teichner, and J. E. Germain, Eds.), p. 149. Elsevier, Amsterdam, 1983.
45. Burch, R., and Flambard, A. R., *J. Chem. Soc. Chem. Commun.*, 965 (1981).
46. Solymosi, F., Bánsági, T., and Erdöhelyi, A., *J. Catal.* **72,** 166 (1981).