

Infrared Spectra of Ethylene Adsorbed on Transition Metals at Low Temperatures and Hydrogenation of the Adsorbed Species

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Infrared spectra of ethylene adsorbed on Al_2O_3 -supported Pt, Pd, and Rh were measured at -78°C . π -Adsorbed ethylene was the main adsorbed species on these metals and a significant difference in the C=C stretching frequencies of π -adsorbed ethylene with metals was found. The dehydrogenated species of ethylene, MCHCHM, was also observed at -78°C . π -Adsorbed ethylene was rapidly hydrogenated by hydrogen at -78°C to form ethane. It was concluded that the stable σ -adsorbed ethylene was not formed in the course of hydrogenation of π -adsorbed ethylene.

INTRODUCTION

Hydrogenation of ethylene on transition metals is an important catalytic reaction and has been extensively studied, while the structure of the reactive surface species leaves many problems to be clarified. In infrared spectroscopic studies of ethylene adsorbed on transition metals, spectra have been measured mostly in the CH stretching frequency region at room temperature. The observed spectra are very complicated, and the presence of σ -adsorbed ethylene, partly dehydrogenated species or *n*-butyl groups on the surface has been reported (1).

As π -bonded olefins in transition metal complexes are reactive in hydrogenation or isomerization, hydrogenation of ethylene on metal surfaces has been considered to occur via π -adsorbed species. However, it is not until very recently that evidence for the existence of π -adsorbed ethylene on transition metal surfaces has been reported. So far the infrared work was mainly

concentrated in the CH stretching frequency region, where the distinction of π - and σ -adsorbed ethylene as regards CH stretching vibration is rather difficult. Moreover, π -adsorbed ethylene is very unstable on metal surfaces, which has hampered its detection. An infrared measurement more sensitive than the conventional method (2), or a low-temperature measurement (3), examining the C=C stretching region was required to demonstrate the existence of the π -adsorbed species.

In a previous report (3), it was shown that the main adsorbed species of ethylene on Pt- Al_2O_3 at -78°C was the π -adsorbed species. The observed bands at 1498, 1420, and 1199 cm^{-1} for C_2H_4 and 1319 cm^{-1} for C_2D_4 could be attributed to the bands of π -adsorbed ethylene from a comparison with the spectra of Zeise's salt.

In this report, infrared spectra of ethylene adsorbed on Al_2O_3 -supported Pt, Pd, Rh, and Ni have been measured at -78°C

in the C=C stretching frequency region in an attempt to clarify the behavior of π -adsorbed ethylene, and the difference in π -bonding of ethylene with the metals is discussed. The reaction between π -adsorbed ethylene and ir-active adsorbed hydrogen has been pursued by following the change in the ir spectra of the adsorbed species. The hydrogenation path of the dehydrogenated adsorbed species of ethylene is compared with that of π -adsorbed species.

EXPERIMENTAL METHODS

Alumina-supported metal catalysts were prepared by the impregnation method. Alumina (Degussa, $\text{Al}_2\text{O}_3\text{-C}$) was impregnated with an aqueous solution of nickel nitrate, palladium chloride, rhodium chloride, or chloroplatinic acid; the slurry was then dried and decomposed at 450°C for 20 hr in air. The content of each metal was about 9 wt%. For ir measurements the catalyst was pressed into a 20-mm diameter disk of weight about 100 mg. The disk was heated in an oxygen atmosphere at a pressure of 400 Torr (1 Torr = 133.3 N m^{-2}) for 1 hr at 380°C , evacuated for 1 hr, and then reduced in 400 Torr of hydrogen for 3 hr at the same temperature. Hydrogen was replenished after every 30 min, and after this treatment the disk was inserted in the ir cell. Before the measurement, the disk in the ir cell was reduced again in hydrogen at 300 Torr for 3 hr at 290°C , hydrogen being replenished after every 30 min, then evacuated for 2 hr at the same temperature to 10^{-6} Torr.

The cryogenic cell for the low-temperature measurement was similar to that used by Avery (4), except that the heating was effected by a nickel-chrome wire wound around the outside of the cell. The sample was cooled by dry ice with acetone or cold nitrogen gas.

The experimental procedure to obtain the spectra of adsorbed ethylene was as follows. About 50 Torr of ethylene was

introduced into the cell at -78°C and was allowed to adsorb for 5 to 30 min. Then ethylene was condensed in a liquid nitrogen cold-trap, and about 20 Torr of argon was introduced into the cell to prevent the rise of the disk temperature by infrared irradiation during the measurement. When hydrogen was added to the cell to obtain the spectra of adsorbed hydrogen or the spectral changes of adsorbed ethylene after hydrogen addition, generally the pressure of hydrogen was kept below 10 Torr to prevent the rise of the cell temperature because of the good heat conductivity of hydrogen gas.

The ethylene was obtained from Takachiho Company and was of 99.9% purity, and deuterioethylene (C_2D_4) from MSD Company was of 99% deuterium purity. These were used after repeated vacuum distillation. Hydrogen was purified by passing through a heated Pd thimble. Deuterium obtained from Takachiho Company was of 99.5% purity and was used as such.

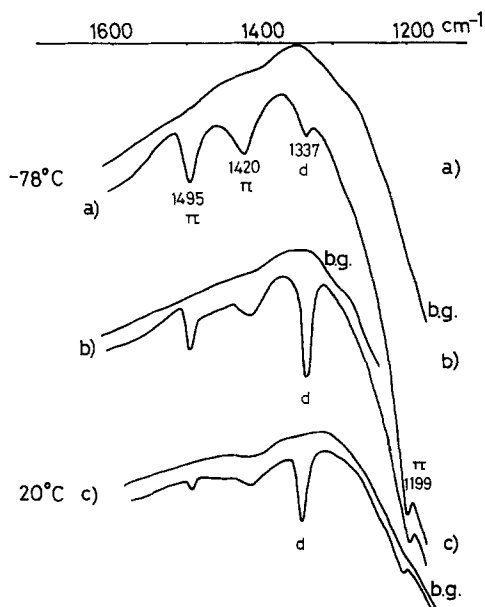


FIG. 1. Infrared spectra of C_2H_4 adsorbed on $\text{Pt-Al}_2\text{O}_3$. (a) At -78°C in Ar; (b) without Ar at -78°C ; (c) at room temperature.

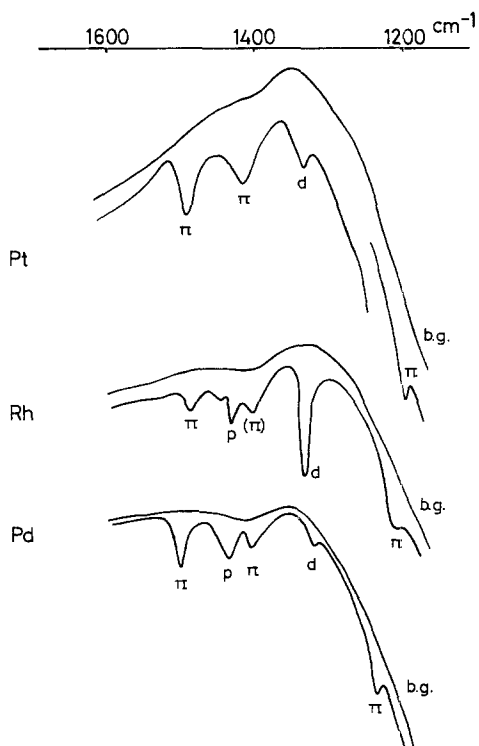


FIG. 2. Infrared spectra of C_2H_4 adsorbed on Pt, Rh, and Pd- Al_2O_3 at $-78^\circ C$. b.g., background; π , π -adsorbed ethylene; d, d-species; p, physically adsorbed ethylene.

RESULTS

Spectra of C_2H_4 Adsorbed on Pt, Pd, and Rh

As reported previously (3), π -adsorbed ethylene was the main adsorbed species when ethylene was adsorbed on Pt- Al_2O_3 at $-78^\circ C$ (Fig. 1a). In the frequency range between 1600 and 1200 cm^{-1} , the bands observed at 1495, 1420, and 1199 cm^{-1} were assigned to symmetric and asymmetric CH_2 scissors and C=C double bond stretching vibrations of π -adsorbed species, respectively, according to the vibrational analysis of Zeise's salt (5).

The band at 1337 cm^{-1} (denoted as d in the figures) whose stability differed from those of other bands was considered to be due to the CH deformation vibration of dehydrogenated species. The effect of irradiation of infrared light on the adsorbed species is shown in Figs. 1a and b. At

$-78^\circ C$ in the presence of argon, the main adsorbed species of ethylene on Pt- Al_2O_3 is of π -type (a). Without argon the disk temperature rose considerably and the intensity of band d increased while that of π -adsorbed ethylene diminished (Fig. 1b). Also at room temperature band d prevailed over that of the π -species as shown in Fig. 1c. In the frequency range between 4000 and 1200 cm^{-1} , only the CH stretching band at about 2900 cm^{-1} exhibited an intensity parallel to the band at 1337 cm^{-1} .

The weak absorption bands of ethylene adsorbed on the Al_2O_3 -support were observed at 2920, 2845, and 1440 cm^{-1} after 100 Torr of ethylene was admitted to Al_2O_3 at $-78^\circ C$ for 60 min.

Figure 2 shows the spectra of C_2H_4 adsorbed on Pt, Rh, and Pd- Al_2O_3 at $-78^\circ C$. Except for Pt, the spectra were recorded in the presence of a small amount

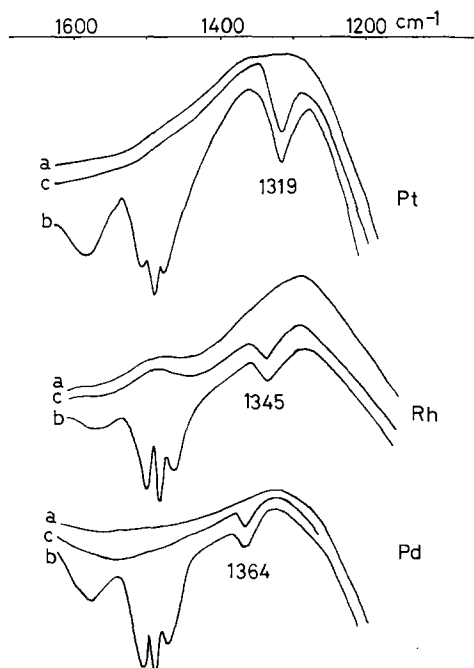


FIG. 3. Infrared spectra of C_2D_4 adsorbed on Pt, Rh, and Pd- Al_2O_3 at $-78^\circ C$. (a) Background; (b) in the presence of gaseous C_2D_4 , $P_{C_2D_4} = 60$ Torr; (c) after gaseous ethylene was removed by liq. N_2 cold trap and Ar was introduced.

TABLE 1
Observed Frequencies of C=C Stretching and CH₂ Scissors Vibrations of
 π -Adsorbed Ethylene on Transition Metals

	C ₂ H ₄				C ₂ D ₄	
	ν_2 (cm ⁻¹)	$\Delta\nu$ (%)	ν_3 (cm ⁻¹)	$\Delta\nu$ (%)	ν_2 (cm ⁻¹)	$\Delta\nu$ (%) ^a
Pt	1495	-125 (7.70)	1199	-143 (10.66)	1319	-196 (12.94)
Rh	1499	-124 (7.63)	1214	-128 (9.53)	1345	-170 (11.22)
Pd	1510	-113 (6.96)	1241	-101 (7.53)	1364	-152 (10.03)
Free	1623		1342		1515	

^a $\Delta\nu$ denotes a difference of the frequency from that in free ethylene, and the value in parentheses shows the percentage difference.

of gaseous ethylene; otherwise the intensities of the bands due to π -adsorbed species decreased. Additional absorption bands due to weakly, physically adsorbed species, denoted as p in the figures, are observed. The spectrum of adsorbed ethylene on Pd was similar to that on Pt-Al₂O₃. The bands at 1510, 1410, and 1241 cm⁻¹ are assigned to π -adsorbed ethylene. The band at 1444 cm⁻¹ is due to the CH₂ scissors vibration of physically adsorbed ethylene. The band at 1320 cm⁻¹ may be due to the CH deformation vibration which would be attributed to the same species as on Pt-Al₂O₃ (d-species).¹

More complicated spectra were obtained on Rh as shown in Fig. 2. The bands at 1499, 1410, and 1214 cm⁻¹ are assigned to π -adsorbed ethylene and a band at 1340 cm⁻¹ to the CH deformation band of d-species. The band near 1460 cm⁻¹ is considered to be due to CH₂ scissors vibration, which might show the existence of σ -adsorbed ethylene.

Spectra of C₂D₄ Adsorbed on Pt, Pd, and Rh

When deuterioethylene (C₂D₄) is adsorbed on metals, the only absorption

¹ Hereafter we use d-species to describe adsorbed ethylene which shows a band near 1340 cm⁻¹ on these metals.

bands of the adsorbed species expected to be observed in the frequency range between 2000 and 1200 cm⁻¹ is the C=C double bond stretching vibration of π -adsorbed ethylene. We cannot expect to find other adsorbed species such as σ -adsorbed ethylene, as the C-C stretching and CD or CD₂ deformation vibrations appear in the frequency region lower than 1200 cm⁻¹.

Figure 3 shows the spectra of C₂D₄ adsorbed on Pt, Rh, and Pd at -78°C. The absorption bands corresponding to the C=C double bond stretching mode are observed at 1319, 1345, and 1364 cm⁻¹, respectively.² Also the frequencies of the symmetric CH₂ scissors and C=C stretching vibrations in π -adsorbed C₂H₄ are summarized in Table 1.

The measurement of the spectra of ethylene adsorbed on Ni-Al₂O₃ was attempted also at -78°C. The observed bands at 1522, and 1415 cm⁻¹ in C₂H₄ adsorption and at 1437 cm⁻¹ in C₂D₄ adsorption are considered to be due to the vibrations of π -adsorbed ethylene on Ni. But the spectrum of CO adsorbed on this

² The value for Pd is different from that reported in Ref. (3). The Pd sample in Ref. (3) was found to contain sodium carbonate, and the present value is more reliable.

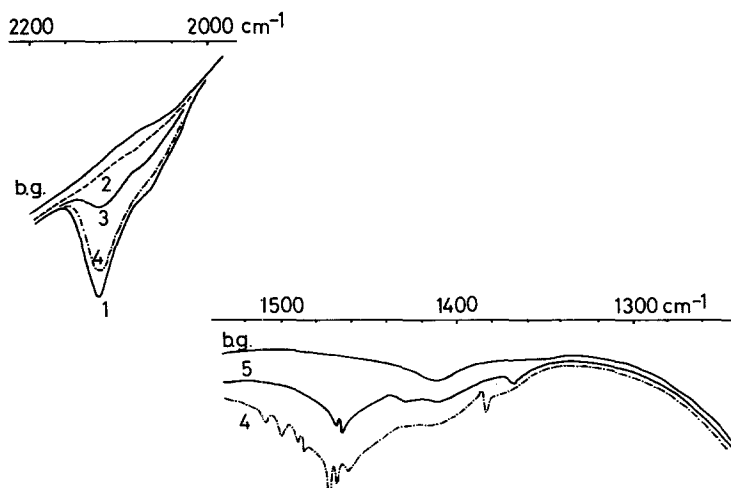


FIG. 4. Infrared spectra of adsorbed species found on Pt-Al₂O₃ at -78°C. (1) In the presence of hydrogen only, $P_{\text{H}_2} = 14.7$ Torr; (2) immediately after C₂H₄ was added, $P_{\text{C}_2\text{H}_4} = 11.2$ Torr; (3), (4) spectral changes during hydrogenation; (5) after removal of gaseous hydrocarbons.

sample showed that the reduction of Ni was not complete in this experimental condition and that oxide remained partially on the surface (6). Although the bands of π -adsorbed ethylene described above were not observed on nickel oxide at -78°C, the spectra might be somewhat different from those on completely reduced Ni samples.

Hydrogenation of π -Adsorbed Ethylene on Pt

When hydrogen was introduced in the cell at -78°C, the ir bands of π -adsorbed ethylene disappeared instantly and ethane appeared in the gas phase, but the band of the dehydrogenated d-species remained unchanged.

When hydrogen was adsorbed at -78°C, the PtH stretching bands were observed at 2125 and 2060 cm⁻¹ in H₂ adsorption and at 1525 and 1480 cm⁻¹ in D₂ adsorption. The lower-frequency bands, 2060 cm⁻¹ in H₂ adsorption and 1480 cm⁻¹ in D₂ adsorption, were weak when the pretreatment temperature of the catalyst was high (290°C).

Figure 4 shows the spectra when ethylene was introduced onto Pt-Al₂O₃ with pre-adsorbed hydrogen, the amount of ethylene

added being less than that of hydrogen introduced beforehand. The instant ethylene was added, adsorbed hydrogen disappeared from the surface, then the intensity of the PtH band gradually recovered together with the hydrogenation of ethylene to ethane. This would be explained if a part of adsorbed hydrogen was expelled from the surface by the adsorption of ethylene and the other part was used to hydrogenation. The residue of gaseous hydrogen was re-adsorbed after the total amount of ethylene was hydrogenated. After the hydrogenation was completed, the absorption band observed on the surface was a weak one due to methyl group deformation at 1375 cm⁻¹, except for the PtH stretching band. When the amount of ethylene added exceeded that of hydrogen introduced beforehand, addition of ethylene extinguished the PtH band completely, while π -adsorbed ethylene and the dehydrogenated d-species appeared on the surface.

Hydrogenation of d-Species on Pt

In a hydrogen atmosphere at -78°C the d-species was more stable than the π -adsorbed ethylene, and the band at

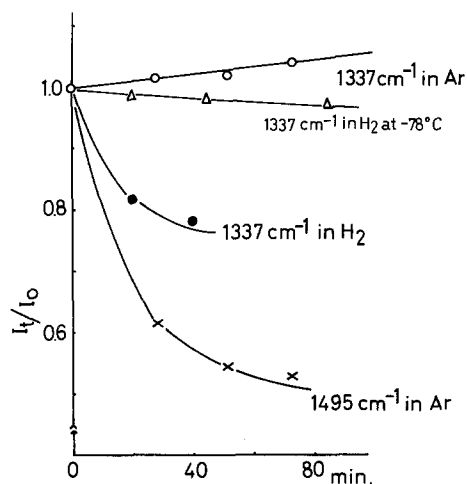


FIG. 5. Intensity changes of 1337- and 1495-cm⁻¹ bands of C₂H₄ adsorbed on Pt in Ar or H₂ atmosphere at -26 and -78°C. O, ●, X, at -26°C; Δ, at -78°C.

1337 cm⁻¹ scarcely changed its intensity. However, the band intensity decreased in the presence of hydrogen when the cell temperature was raised to -26°C as shown in Fig. 5, and ethane was produced in the gas phase. Figure 6 shows how the spectra of ethylene adsorbed on Pt changed after hydrogen addition. When ethylene was adsorbed as π -type as shown in Fig. 6a-1,

the hydrogenated species of π -adsorbed ethylene remaining on the surface was not observed after hydrogen addition. (6a-2) On the other hand, when hydrogen was introduced onto the d-species, the band at 1337 cm⁻¹ decreased in its intensity and the band due to CH₂ deformation appeared at 1450 cm⁻¹, as shown in Fig. 6b. The intensity of the latter band soon saturated, then the bands due to CH₃ deformation appeared at 1360 and 1475 cm⁻¹ and gradually increased their intensities. The band near 1420 cm⁻¹ was broad and variable with the composition of surface species or with hydrogen addition. When π -adsorbed ethylene and d-species coexist on the surface as shown in Fig. 6b-1, the observed band shifts to lower-frequency (1410 cm⁻¹) as compared with that in Fig. 6a-1. Hence a band of other surface species which has a -CH₂ group, such as CH₂MCH₂M or CH₂MCHM₂ might be overlapped. When ethylene was adsorbed again after the band at 1337 cm⁻¹ disappeared in hydrogen, the total amount of ethylene (π -species + d-species) adsorbed was the same as before. Hence it would be considered that all the d-species was

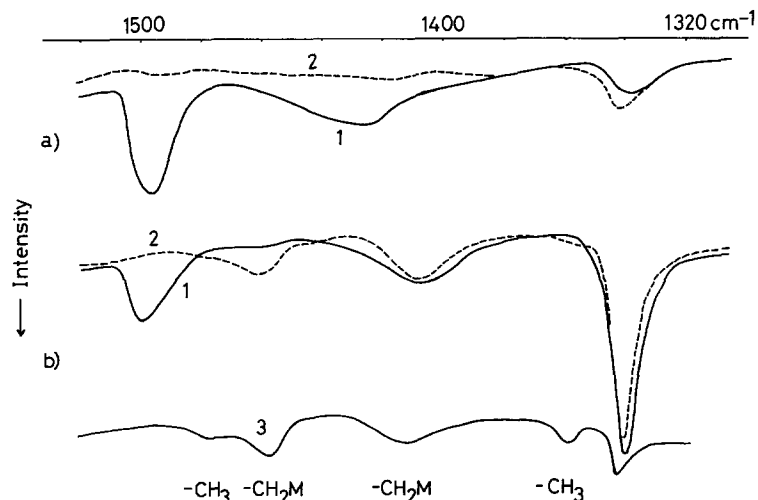


FIG. 6. Hydrogenation of ethylene adsorbed on Pt-Al₂O₃. (a) At -56°C: 1. adsorbed ethylene; 2. after hydrogen addition; (b) at -44°C: 1. adsorbed ethylene; 2. immediately after hydrogen was added, $P_{H_2} = 7.5$ Torr; 3. 200 min after hydrogen addition.

hydrogenated in hydrogen but was not dehydrogenated to carbide-like species.

The amounts of adsorbed hydrogen and ethylene at -78°C were measured. The result is shown in Table 2. A volumetric method was used for the hydrogen adsorption, while the amount of π -adsorbed ethylene was estimated from that of ethane produced at -78°C by introducing hydrogen on Pt where ethylene was preadsorbed. After π -adsorbed ethylene was removed, the temperature of the catalyst was raised to 0°C in hydrogen atmosphere. The subsequent formation of ethane was considered to be due to the hydrogenation of the d-species.

DISCUSSION

Adsorption of Ethylene on Transition Metals

First, the importance of the low-temperature measurement of the infrared spectra of adsorbed hydrocarbons should be emphasized. The present investigation has demonstrated that the low-temperature measurement in the C=C double bond stretching region makes the observation of π -adsorbed ethylene on transition metals easier. The band frequencies of the C=C stretching vibration of π -adsorbed ethylene are summarized in Table 1. Both in C_2H_4 and C_2D_4 the frequency is in decreasing order as follows: Pd > Rh > Pt.

π -Adsorbed ethylene on Pt was stable at -78°C in Ar, while that on Pd was unstable and was easily desorbed at the same temperature. On the other hand, π -adsorbed ethylene on all these metals was hydrogenated instantly by hydrogen addition at -78°C .

Vibrational analysis of Zeise's salt, $\text{K}[\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_3]$, showed that because of the strong interaction between the C=C stretching and symmetric CH_2 scissors vibrations, the higher-frequency band at 1515 cm^{-1} has the character of CH_2 scissors and the lower-frequency band at 1243 cm^{-1} has the character of C=C

TABLE 2
Adsorption of Hydrogen and Ethylene
on Pt- Al_2O_3 at -78°C^a

1. Adsorbed amount of H_2 (volumetric measurement), $P_{\text{H}_2} = 0.23$ Torr	7.89
2. Amount of C_2H_6 produced when C_2H_4 was introduced on 1.	7.66
3. Amount of C_2H_6 produced when H_2 was introduced on Pt where C_2H_4 was preadsorbed at -78°C (hydrogenation of π -adsorbed ethylene)	3.78
at 1°C (hydrogenation of d-species)	0.76

^a Values are ($\times 10^{19}$ molecules/g catalyst).

stretching vibration in the case of the C_2H_4 complex, while the band at 1353 cm^{-1} in the C_2D_4 complex represents mainly the C=C stretching character (5). Powell and co-workers (7) extended the above consideration to other olefin complexes and showed that the mixing of the C=C stretching and CH_2 scissors modes was especially large in C_2H_4 complexes. The extent of this mixing depends also on the strength of the interaction between ethylene and a metal. The mixing becomes small where the interaction is weak, and the higher-frequency band near 1500 cm^{-1} (ν_2 of C_2H_4 in Table 1) shows the character of C=C stretching vibration, while ν_3 of C_2H_4 shows that of symmetric CH_2 scissors vibration.

Adapting this assignment to π -adsorbed ethylene, it is concluded that ν_2 in C_2D_4 in Table 1 has essentially a C=C stretching character. The frequency of the C=C stretching can be regarded as a measure of the strength of the π -interaction between metal and ethylene because the stronger the interaction the weaker the C=C bond becomes. The observed frequency of ν_2 depends on the metal and decreases in the order Pd > Rh > Pt. Accordingly the reverse order, Pd < Rh < Pt, in the stability of the π -adsorbed ethylene is concluded. It is interesting that this trend parallels the stability of chemisorbed ethylene which Bond and his co-workers (8) deduced

from the rate analysis of ethylene hydrogenation. Sato (9) showed that the relative rate of ethylene desorption increases in the order Ni > Pd > Rh > Pt, indicating that the trend of stability is consistent with the present results.

The vibrational bands of the adsorbed species other than π -adsorbed ethylene were observed around 1340 cm^{-1} on all the metals. This species was stable in hydrogen at -78°C in contrast with π -adsorbed ethylene. The bands at 1337 and 2900 cm^{-1} on Pt are attributable to the same species, because of their consistent behavior. Sheppard (1) assigned the band at 2907 cm^{-1} to M_2CHCHM_2 type which was observed on Pt-SiO₂ at -145°C . The band at 1337 cm^{-1} is assigned to the CH deformation vibration of MCH= or M_2CH -group. It would be appropriate to assign M_2CHCHM_2 or MCHCHM structure to this species. From a UPS investigation (10), a dehydrogenated species which had olefinic character was observed on Pd, Pt, and W when ethylene was adsorbed, but not on Ni. The above species giving the 1337-cm^{-1} band is possibly the same as the dehydrogenated species observed by UPS. Recently Ibach and his co-workers (14) observed the vibrations of chemisorbed ethylene on Pt(111) employing electron energy loss spectroscopy. The chemisorbed species of ethylene below 260 K was observed to convert into a new stable species above 260 K. This conversion appeared to be similar to the fact that the amount of d-species on Pt-Al₂O₃ increased above 230 K, but the correspondence is not clear.

Hydrogenation of Ethylene Adsorbed on Pt at Low-Temperature

The following conclusions are deduced from the infrared study of ethylene and hydrogen adsorption:

(1) π -Adsorbed ethylene is hydrogenated instantly by hydrogen at -78°C ;

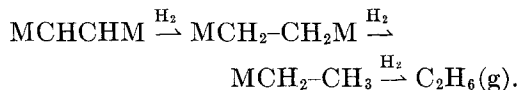
(2) the dehydrogenated MCHCHM species is more stable than π -adsorbed ethylene against hydrogen at -78°C ;

(3) the MCHCHM species is not formed as long as hydrogen exists on the surface.

More than 80% of the ethylene adsorbed on Pt at -78°C was π -adsorbed ethylene, and the amount of ethylene at full coverage was about half of that of adsorbed hydrogen as seen in Table 2. If it is assumed that one hydrogen molecule occupies two platinum atoms, one adsorbed ethylene molecule is considered to occupy four Pt atoms. Nearly 100% of the hydrogen adsorbed on Pt reacted with ethylene to form ethane as shown in Table 2. Basset *et al.* (11) observed that adsorbed hydrogen showing the band at 2120 cm^{-1} was necessary to hydrogenate benzene on Pt-Al₂O₃.

The γ type of chemisorbed hydrogen on Pt which was detected by temperature programmed desorption is considered to correspond to hydrogen showing the band at 2120 cm^{-1} from the consistency of the activation energy of desorption (12). Tsuchiya *et al.* (13) observed that β - and γ -hydrogen reacted with ethylene to form ethane on Pt black.

π -Adsorbed ethylene and the MCHCHM species were both hydrogenated to ethane, but their hydrogenated spectra were different, as shown in Fig. 6. Although π -adsorbed ethylene was easily hydrogenated at low temperatures, no hydrogenated species remained on the surface after hydrogen addition. On the other hand, σ -adsorbed ethylene and ethyl compounds appeared when the MCHCHM species were hydrogenated.



This MCHCHM species was completely hydrogenated to ethane at -20°C in a hydrogen atmosphere. Consequently it is suggested that the reaction path of hydrogenation of the π -adsorbed ethylene and

MCHCHM species are different, and the stable σ -adsorbed ethylene as observed by ir measurement at room temperature (1) is not formed in the course of hydrogenation of π -adsorbed ethylene.

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