JOURNAL OF CATALYSIS 8, 36–40 (1967)

Infrared Spectra of Chemisorbed Molecules

I. Ethylene on Silica-Supported Nickel

J. ERKELENS AND TH. J. LIEFKENS

From the Unilever Research Laboratory, Vlaardingen, The Netherlands

Received November 22, 1966, revised January 17, 1967

Spectra of ethylene adsorbed on a hydrogen-covered as well as on a hydrogen-free nickel surface have been obtained. Special attention has been paid to the change of the spectrum due to the reaction of the chemisorbed hydrocarbon species with hydrogen. The results obtained have been compared with literature data.

INTRODUCTION

The application of infrared spectra to solve problems concerning chemisorption has mainly been developed by Eischens and Pliskin (*1*, *2*). They studied spectra of various hydrocarbons such as ethylene, propylene, and hexene adsorbed on silica-supported nickel catalysts. The infrared spectrum of ethylene on various metal catalysts was also studied by Little, Sheppard, and Yates (*3*). However, they were not able to obtain a spectrum of the initially adsorbed species on nickel. Morrow and Sheppard (*4*) managed to overcome this difficulty and reported some results obtained with silica-supported nickel and platinum in a recent publication. Peri (*5*) also discussed the infrared spectrum of ethylene adsorbed on nickel catalysts; the spectrum he obtained closely resembles spectra obtained for butenes adsorbed on γ alumina. In addition to this work, some studies of the infrared spectra of ethylene adsorbed on platinum (*6*, *7*) and rhodium (*8*) should be mentioned here.

In this publication, infrared spectra of ethylene, chemisorbed on hydrogen-covered and hydrogen-free silica-supported nickel, have been reported on and compared with literature data. Publication seems useful at this stage, since there is no agreement between the various investigations mentioned. Special attention has been paid to the reactions of the initially formed surface species after addition, removal, and a second addition of hydrogen.

EXPERIMENTAL

The results described have been obtained with a disc (diameter 15 mm) of silica-supported nickel catalyst, pressed at 20 ton during 2 min. The weight of the disc was 31.2 mg and it contained 18.7% nickel. The transmission of the disc was 12% at 3000 cm^{-1}. Preliminary experiments had shown that discs containing about 10% or 30% nickel gave poorer results.

The catalyst was prepared as follows: An amount of Aerosil was mixed with the calculated amount of solid $Ni(NO_3)_2 \cdot 6H_2O$ and then ground in an agate ball mill during 4 hr. The mixture was then heated at 75°C during 24 hr. Due to the fact that the nickel nitrate dissolves in the crystallization water it contains, a homogeneous distribution of the nickel over the silica is achieved. The product obtained was again ground after which the nickel oxide was formed by careful heating. The oxide was reduced in the cell in a hydrogen current at 350°C during 16 hr.

The cell, provided with rock salt windows, which was used to obtain the spectrum of the adsorbed surface species, was based on the design by Clarke and Pullin (*9*). The

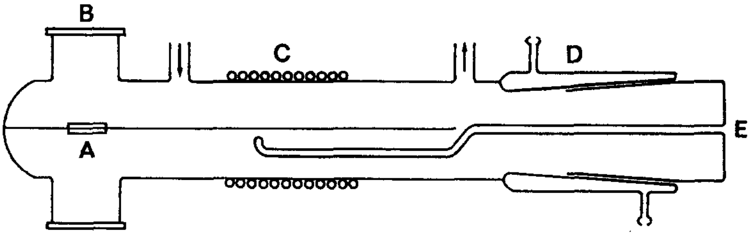

FIG. 1. Infrared measuring cell: A, disc; B, window; C, heating jacket; D, cooling jacket; E, thermocouple well.

windows were stuck to the glass by application of UHU plus (H.u.M. Fischer Bühl, Baden). As is shown in Fig. 1, the thermocouple well was constructed in the cooled ground joint, in order to prevent direct heating of the thermocouple wires by conduction through the glass.

The spectra were recorded on a "Grubb Parsons GS$_4$" double-beam spectrometer, the scanning speed being 1 μ in 64 min. The slit was manually adjusted at 0.6 mm.

The ethylene (Loos and Co.) was degassed by repeated freezing, pumping, and thawing. Hydrogen was purified over a column of B.T.S. catalyst (BASF) and dried over a column with molecular sieves (Linde 4A) and a liquid air trap.

The experimental procedure was as follows: After reduction of the catalyst (16 hr, 350°C) it was allowed to cool in hydrogen, which was removed by pumping during 5 min. After the background spectrum was registered, adsorption of ethylene occurred at a pressure of about 5 torr during 1½ hr at room temperature. The gas phase was removed by pumping down to 10^{-4} torr, measured by a McLeod manometer. Subsequently, the spectrum of the adsorbed molecules was registered.

RESULTS

The spectra obtained after ethylene was adsorbed on a hydrogen-covered, silica-supported nickel catalyst are shown in Fig. 2. No bands other than those reported here were observed in the ranges studied, namely 3080–2750 cm^{-1} and 2000–1330 cm^{-1}. Spectrum A shows ethylene adsorbed on a hydrogen-covered surface. Spectrum B was recorded 30 min after admission of 3 torr of hydrogen, spectrum C after 5 min pumping, and spectrum D after a second admission of hydrogen. The spectra B and D are almost identical. The frequencies of the various bands are collected in Table 1. After removal of the disc from the beam, no infrared bands due to hydrocarbons were found in the gas phase, not even after 5× ordinate expansion.

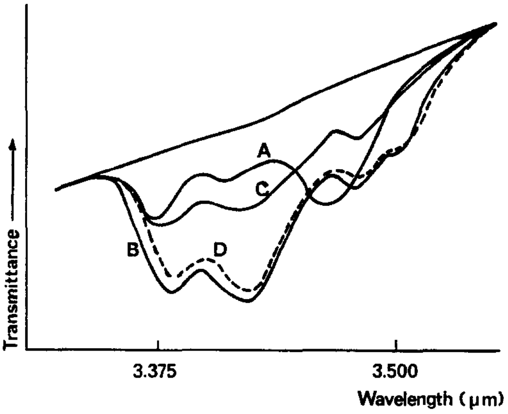

FIG. 2.

TABLE 1
WAVE NUMBERS (cm^{-1}) OF VARIOUS INFRARED BANDS OF ADSORBED ETHYLENE[a]

A	B	C	D
2963	2957	2963	2957
2931	2922	2922	2922
2887	—	—	—
	2874	2874	2874
	2857	—	2857

[a] A, ethylene adsorbed on a hydrogen-covered nickel surface, B, hydrogen admitted, C, hydrogen removed, D, hydrogen admitted.

When, prior to adsorption of ethylene, the surface was freed from hydrogen by pumping during 2 or 4½ hr at 350°C, spectra were obtained which did not differ from that obtained with a hydrogen-covered surface. Even when the catalyst was pumped at 450°C during 2 hr, the position of the bands had not changed, although the intensity was very low. The latter phenomenon may be due to the reduction of surface area of the metal by sintering.

The following quantitative data were derived from the spectra: The absorbance was calculated from the transmission spectra and plotted against wavelength. The integrated absorbance was then measured with a planimeter. The relative integrated absorbances are given in Table 2. The ratio of the absorbances of the bands at 2922 and 2957 cm^{-1} and of the corresponding bands in Table 1 was also determined. This ratio is a measure for the CH_2/CH_3 ratio in the adsorbed molecule. From the absence of any absorption bands in a blank experiment with an Aerosil disc, it followed that no physical adsorption of ethylene took place on the support.

TABLE 2

INTENSITY DATA OF THE SPECTRA[a]

Band	Relative integrated absorbance		Absorbance ratio bands at 2922 (2931) and 2957 (2963) cm^{-1} [b]	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2
Ethylene adsorbed	1.0	1.0	0.79	0.80
Hydrogen added	2.1	1.9	1.25	1.22
Hydrogen pumped	1.0	1.1	1.17	0.97
Hydrogen added	2.0	1.6	1.26	1.25

[a] Experiment 1, Hydrogen-covered surface, Experiment 2, catalyst pumped during 4½ hr at 350°C.

[b] See Table 1.

DISCUSSION

Infrared Bands

Eischens and Pliskin (*1*, *2*) assigned the band at 2887 cm^{-1} to the CH stretching vibration in associatively adsorbed ethylene, with configuration $NiCH_2–CH_2Ni$. In addition to this band, Morrow and Sheppard (*4*) also attribute a part of the band at 2931 cm^{-1} (in their spectrum on platinum at 2920 cm^{-1}) to this configuration. These bands do not occur in the spectrum of the ethylene-platinum complex studied by Sheppard and Powell (*10*). In this complex, ethylene is bonded to one platinum atom, so that the configuration suggested by Eischens *et al.* is not contradicted. The fact that π complexes—which may play a role in catalytic reactions (*11*, *12*)—are not found in infrared investigations of molecules adsorbed on metals has recently been discussed by Sheppard (*13*). Bond (*14*) suggested that π complexes would only exist under reaction conditions. It is , however, clear that this point deserves further investigation.

TABLE 3

ASSIGNMENT OF THE BANDS

Frequency of bands		Assignment
Found[a]	Literature[b]	
2957	2962	Asymm. CH_3
2922	2926	Asymm. CH_2
2874	2872	Symm. CH_3
2857	2853	Symm. CH_2

[a] See Table 1.

[b] Reference (*15*).

In Table 3, the other bands from Table 1 with the exception of that at 2887 cm^{-1} are compared with literature data (*15*). The structure of the adsorbed hydrocarbon may be derived from the ratio of the number of CH_2 and CH_3 groups present. This ratio can

TABLE 4

RATIO OF THE ABSORBANCE OF BANDS AT ABOUT 2920 AND 2960 cm^{-1} [a]

Compound	L	S (%)	Absorbance ratio	CH_2/CH_3
Ethyl iodide	+	13.5	0.57[b]	1
Ethyl bromide	+	13.5	0.72[b]	1
Propyl bromide	+	—	0.51	2
Butyl bromide		13	0.63	3
Pentyl bromide	+	—	0.94	4
Hexyl chloride	+	—	1.05	5
1-Hexene		0.3	1.06	3
1-Octene		0.3	1.88	5
Heptane		0.3	1.21	2½
Decane		1	1.88	4
Dodecane		1	2.21	5

[a] L, liquid; the solutions (S) are in CCl_4.

[b] Same ratio for liquid and solution.

be determined in principle by comparison with model compounds. In Table 4 the ratio of the absorbances of the bands at about 2920 and 2960 cm^{-1} are given for a number of model compounds. The existing differences between the various compounds, however, make a reliable estimation of the structure of the adsorbed molecule uncertain.

Surface Species

The band at 2887 cm^{-1}, characteristic of the presence of associatively adsorbed ethylene, was also found by Eischens and Pliskin (*1*, *2*). Contrary to this finding, Peri (*5*) reported the absence of associatively adsorbed ethylene. Morrow and Sheppard (*4*, *16*), however, reported that the $NiCH_2$–CH_2Ni species was present only after a short time of adsorption at −78°C. The results obtained by the various authors are obviously strongly dependent on the experimental conditions. The initial presence of a band at 2963 cm^{-1} in our spectra (due to CH_3 groups) points to the presence of partially hydrogenated species.

On addition of hydrogen, the band at 2887 cm^{-1} disappears and the bands formed are now at 2957, 2922, 2874, and 2857 cm^{-1}, the assignment of which is given in Table 3. The ratio of the absorbances of the bands at 2922 and 2957 cm^{-1} is now 1.25. On comparison with the data in Table 4, it may well be suggested that the greater part of the surface species have polymerized to products such as $Ni(CH_2)_3CH_3$. This is in agreement with experimental results obtained by other authors (*1*, *4*).

On removal of the hydrogen, the band at 2887 cm^{-1} does not reappear. This result might indicate that under the given conditions the half-hydrogenated state ($NiCH_2$–CH_3) is virtually absent on the surface, since it is plausible that from the half-hydrogenated state the associatively adsorbed ethylene could be re-formed. It is within reason to suggest that the decrease in CH_2/CH_3 absorbance ratio (Table 2) obtained on hydrogen removal is due to dissociation of C–H bonds of the polymerized surface species. After a second addition of hydrogen, the CH_2/CH_3 absorbance ratio increased again to the original value, due to a partial hydrogenation of the surface species. Since no hydrocarbons were found in the gas phase at this stage, the surface species were not removed on addition of hydrogen, and consequently play no role in the catalytic hydrogenation of ethylene. Similar results have also been reported by Eischens and Pliskin (*1*, *2*), by Morrow and Sheppard (*4*) for ethylene, and by Erkelens and Liefkens (*17*), who studied the reactions of adsorbed hexenes with hydrogen and deuterium. The fact that the hydrogenation reaction takes place on a part of the surface which is not covered by strongly adsorbed species has already been emphasized by Beeck (*18*).

In addition to the behavior of the CH_2/CH_3 absorbance ratio, Table 2 shows that the integrated absorbance increases after addition of hydrogen and decreases to the original value after removal of the hydrogen. This phenomenon also indicates a reaction in which the average number of hydrogen atoms per carbon atom increases on addition of hydrogen and decreases on removal of the hydrogen.

In contradiction with the work of Eischens and Pliskin (*1*), but in agreement with that of Morrow and Sheppard (*4*), the spectrum of ethylene, adsorbed on a bare nickel surface, does not differ from the spectrum obtained with a hydrogen-covered surface. It is possible that this fact is due to the difference in the preparation of the samples, or to (unknown) differences in the temperature of the samples due to the effect of the infrared beam (*19*). In this case, the existence of CH_3 groups in addition to associatively adsorbed ethylene points to the occurrence of self-hydrogenation since no hydrogen was initially present on the surface.

REFERENCES

1. EISCHENS, R. P., AND PLISKIN, W. A., *Advan. Catalysis* **10**, 1 (1958).
2. PLISKIN, W. A., AND EISCHENS, R. P., *J. Chem. Phys.* **24**, 482 (1956).
3. LITTLE, L. A., SHEPPARD, N., AND YATES, D. J. C., *Proc. Roy. Soc.* (*London*) **259**, 242 (1960).

4. Morrow, B. A., and Sheppard, N., *J. Phys. Chem.* **70,** 2406 (1966).

5. Peri, J. B., *Discussions Faraday Soc.* **41,** 121 (1966).

6. Lucchesi, P. J., Carter, J. L., and Sinfelt, J. H., *J. Am. Chem. Soc.* **86,** 1494 (1964).

7. Carter, J. L., Lucchesi, P. J., Sinfelt, J. H., and Yates, D. J. C., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 644 (1965).

8. Pickering, H. L., and Eckstrom, H. C., *J. Phys. Chem.* **63,** 512 (1959).

9. Clarke, J. K. A., and Pullin, A. D. E., *Trans. Faraday Soc.* **56,** 534 (1960).

10. Sheppard, N., and Powell, D. P., *Spectrochim. Acta* **13,** 69 (1958).

11. Erkelens, J., "Some Reactions of Cyclic Olefins on Evaporated Metal Films." Thesis, The Queen's University of Belfast, Northern Ireland, 1961.

12. Erkelens, J., to be published.

13. Sheppard, N., *Discussions Faraday Soc.* **41,** 254 (1966).

14. Bond, G. C., *Discussions Faraday Soc.* **41,** 255 (1966).

15. Bellamy, L. J., "The Infrared Spectra of Complex Molecules." Methuen, London, 1958.

16. Sheppard, N., *Discussions Faraday Soc.* **41,** 177 (1966).

17. Erkelens, J., and Liefkens, Th. J., *Discussions Faraday Soc.* **41,** 175 (1966).

18. Beeck, O., *Discussions Faraday Soc.* **8,** 118 (1950).

19. Eischens, R. P., private communication (1964).