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Infrared Spectra of Chemisorbed Molecules

IV. Hydrogenation of Some Small Alkenes on Silica-Supported Nickel

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The ir spectra of ethylene, propene, 1-butene and butadiene were monitored during hydrogenation on a silica-supported nickel catalyst using the flow-circulation method. A special cell was constructed for compensation of the spectrum of the gas phase. In the case of ethylene, a band at 3012 cm^{-1} was assigned to the NiCH═CHNi species. Other bands indicated the presence of surface groups containing saturated carbon atoms, presumably being the half-hydrogenated state, while polymerized material remained on the surface when the ethylene flow was stopped. The spectra of propene and 1-butene mainly consist of one intense band at about 2950 cm^{-1}, indicating chemisorbed secondary propyl and butyl groups, respectively. In the case of butadiene, a methylene-rich species dominated, and remained on the surface when the butadiene flow was stopped, thus obscuring the absorption bands of the reactive species present during the catalytic hydrogenation.

INTRODUCTION

To explain the hydrogenation of ethylene (*1*,*2*) and some other ethylenic hydrocarbons (*2*,*3*) on nickel catalysts, most authors suggest that adsorption of these hydrocarbons is caused by opening of their double bonds (associative adsorption). Addition of a hydrogen atom forms an adsorbed alkyl group, the so-called half-hydrogenated state first suggested by Polanyi and Horiuti (*4*). According to Twigg (*5*), this half-hydrogenated state is obtained via an Eley–Rideal mechanism in which adsorbed alkenes react with physically adsorbed hydrogen. The half-hydrogenated state may take up a second hydrogen atom, in which case hydrogenation has taken place or it dissociates to return to the adsorbed alkene. This mechanism has also been used to explain the distribution of deuterium in alkenes and saturated products during exchange experiments (*6*). A different mechanism for the hydrogenation of ethylene is suggested by Gardner and Hansen (*7*), where associatively adsorbed ethylene is supposed to react with ethylene from the gas phase:

$$\mathrm{MCH_2{-}CH_2M + C_2H_4(g) \rightarrow MCH{=}CHM + C_2H_6(g)} \quad (\mathrm{M} = \text{metal surface}),$$

while the dissociatively adsorbed species is hydrogenated on the surface:

$$\mathrm{MCH{=}CHM + 2HM \rightarrow MCH_2{-}CH_2M.}$$

Several mechanisms for the catalytic hydrogenation of ethylene have been derived from kinetic measurements and from deuterium exchange experiments, but ir studies (*8–10*) have been confined to the study of adsorbed ethylene in the absence of the gas phase. This paper deals with the monitoring of ir spectra of adsorbed species during catalytic hydrogenation of ethylene, propene, 1-butene and butadiene on a silica-supported nickel catalyst. Similar work was also initiated by Sheppard *et al.* (*11*), who studied the hydrogenation of ethylene on a platinum catalyst. However, interpretation of the spectra obtained was hampered due to difficulties caused by an insufficient compensation of the spectrum of the gas phase.

EXPERIMENTAL METHODS

Spectra were recorded on a Grubb-Parsons double-beam spectrometer equipped with an attenuator in the reference beam; the scanning speed was usually 1 μm/8 min. The cell was based on a design by Wagner and Hornig (*12*). The hydrogen flow was about 20 liters/hr and the alkene flow about 0.1 liters/hr.

To eliminate the contribution of the gas phase to the spectrum of the adsorbed species, a double-beam gas adsorption setup was used. However, small differences in optical path length may cause incomplete compensation, especially at higher pressures of the reactants. To overcome this difficulty we constructed a compensating gas cell with a variable optical path length (Fig. 1), mainly consisting of a high-vacuum metal extension bellows with a screw thread. An adjusting knob, also with a screw thread, is mounted on a stainless steel frame. By means of a keyway, the bellows can be prevented from rotating. The movable part of the cell and the vacuum system are connected by a spiraled steel capillary to prevent strain in the glass. The rock salt windows are stuck to the flanges with a mixture of Apiezon-Q sealing compound and T-grease. The cell should be adjusted at atmospheric pressure since, otherwise, movement of the bellows is hardly possible. Differences in gas composition in the compensating and measuring cells may be prevented by the flow-circulation method (*13,14*) based on the principle that part of the gas mixture is recycled by an all-glass circulation pump (*15*) (Fig. 2). The experiments were carried out at room temperature.

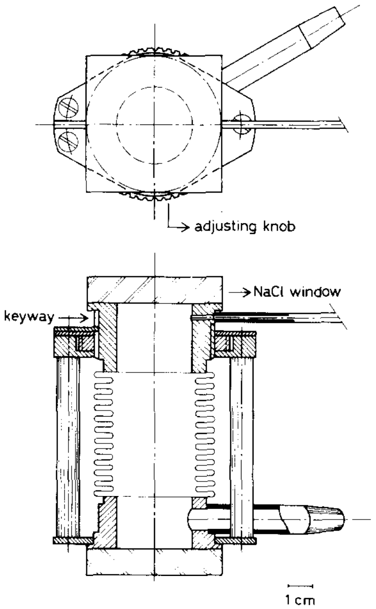

FIG. 1. Compensating gas cell with variable optical path length.

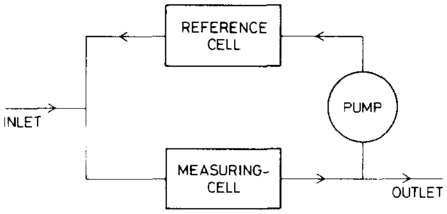

FIG. 2. Flow diagram of the flow-circulation method using an all-glass circulation pump.

Ethylene (99.8%, ex Phillips Petroleum Co.), propene (99.0%), 1-butene (99.0%) and butadiene (99.5, ex Baker) were used without further purification. Hydrogen was purified over BTS catalyst and dried over molecular sieves. This treatment proved to be insufficient to remove traces of carbon monoxide since an ir absorption band gradually appeared near 2040 cm^{-1}, obviously due to chemisorbed carbon monoxide. This band was not present when ultra-pure hydrogen (ex Baker) was used. The silica-supported nickel impregnation catalyst was prepared according to Linsen (*16*) and contained 10% nickel by weight. Reduction was carried out at 300°C for 1.5 hr. The latter process has also been studied by ir spectroscopy and described elsewhere (*17*). The progress of the reaction was checked by glc analysis, using a column (length 4.5 m) packed with Porapak-Q at 155°C. In all cases, the saturated hydrocarbons were the only reaction products formed.

RESULTS

Ethylene

The intensity of the spectrum of ethylene adsorbed onto the nickel catalyst surface during hydrogenation (Fig. 3) somewhat increased as a function of time. An almost perfect compensation of the contribution of the gas phase was observed after removal of the catalyst disk from the beam (Fig. 3a).

The band at about 3012 cm^{-1} was not present in the spectrum of ethylene adsorbed on the hydrogen-covered surface before the reaction was started and disappeared after the ethylene flow had been stopped. This was accompanied by a decrease in the intensity of the total spectrum. Other bands were present at about 2952, 2924, 2890 and 2857 cm^{-1}. These bands, extensively discussed by Morrow and Sheppard (*10*), are assigned to CH_3 and CH_2 groups. We could not reproduce the band at 2758 cm^{-1} we observed in a preliminary experiment (*18*). No ir absorption bands were observed in a blank experiment using an Aerosil disk.

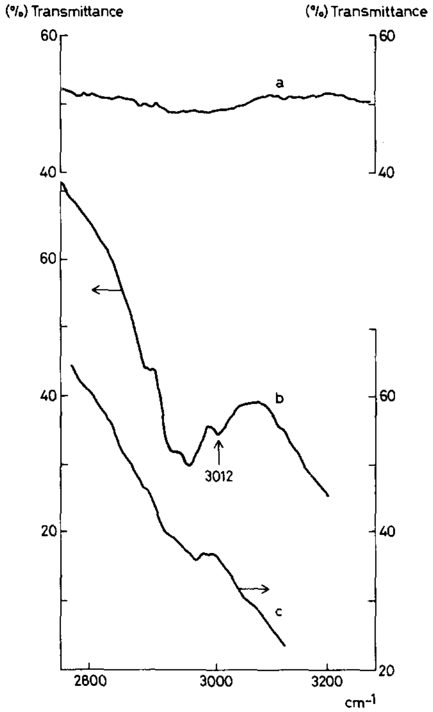

FIG. 3. Infrared spectrum of ethylene: (a) no catalyst disk in ir beam; (b) during reaction; (c) in the absence of gaseous ethylene.

The band at about 3012 cm^{-1} was also observed by Morrow and Sheppard (*10*) in their study of the adsorption of ethylene on platinum and assigned to the surface species MCH=CHM. A band may be expected for C=CH groups at this position, for the frequency is too low to assign it to $C=CH_2$ groups (*19*) or to ethylene molecules π-bonded to single surface metal atoms (*20*). The latter two groups would be expected to absorb also near 3080 cm^{-1} but a band in this region was not observed. The band at 3012 cm^{-1} is not due to a physically adsorbed species since Sheppard and Yates (*21*) observed that, in this case, at least an intense band near 3100 cm^{-1} should be present. Our work shows that during the hydrogenation of ethylene on a nickel catalyst, the dissociatively adsorbed species NiCH=CHNi is present. Other ir absorption bands are due to the reacting species, e.g., in the half-hydrogenated state, since a decrease in intensity of the total spectrum occurs after stopping ethylene flow (Fig. 3c).

Propene and 1-Butene

During catalytic hydrogenation, the spectrum of propene mainly consists of one intense band at about 2950 cm^{-1} with a shoulder at 2878 cm^{-1}; both bands are assigned to CH_3-stretching vibrations (Fig. 4). The absence of an absorption minimum between these bands indicates the presence of other absorptions, possibly due to surface CH vibrations (*10*). During

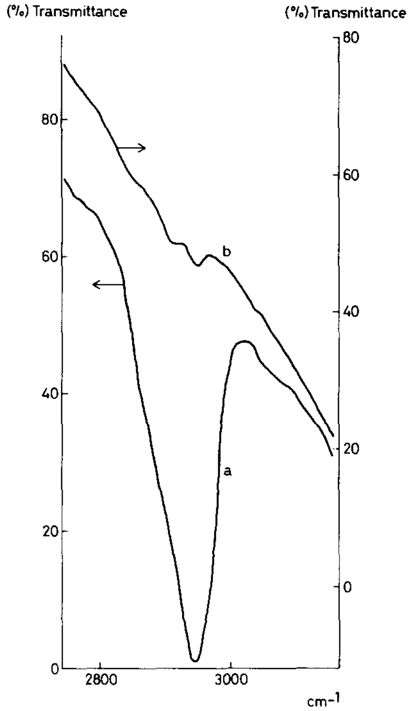

FIG. 4. Infrared spectrum of propene: (a) during reaction; (b) in the absence of gaseous propene.

the propene flow smaller bands are also present at roughly 3080, 1680, 1456 cm^{-1}; these may be assigned to $\nu{=}CH_2$, $\nu C{=}C$ and δ_{as} CH_3, respectively. All the bands mentioned also occur in the spectrum of the gas phase. The smaller bands will be assigned to propene physically adsorbed on the support, rather than to an incomplete compensation of the gas phase (a remaining weak absorption was indeed observed at 2963 cm^{-1}) or to the chemisorbed reacting species. The band at about 3080 cm^{-1}, for instance, is very small with respect to the one at 2950 cm^{-1}, while in the spectrum of the gas phase the first band has roughly half the intensity of the second one. Obviously the bands do not belong to the same species, unless there is a strong decrease in the specific intensity of the 3080 cm^{-1} band upon adsorption. However, this is improbable because such a decrease was not observed in the adsorption of 1-butene on Vycor silica glass (*22*).

Another argument supporting this view is the increase in intensity of the 2950 cm^{-1} band as a function of time, not accompanied by an increase in intensity of the 3080 cm^{-1} band. We interpret the intensity enhancement of the 2950 cm^{-1} band as an increase in the concentration of a methyl-rich reactive species on the catalyst surface and suggest that mainly the chemisorbed secondary propyl group will be present on the surface. However, in deuteration experiments (using a completely different propene/D_2 ratio), a reactive species adsorbed at the primary carbon atom was preferred (*23*). Because of the absence of bands due to CH_2 vibrations we do not think that the methyl-rich species can be identified with the reaction product physically adsorbed on the support.

During hydrogenation, the spectrum of 1-butene shows bands at 2950 and 2874 cm^{-1} (Fig. 5). Here, the intensity of the bands strongly increased as a function of time. Referring to the arguments used for

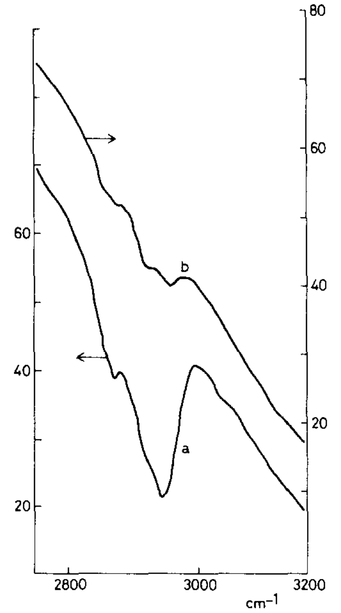

FIG. 5. Infrared spectrum of 1-butene: (a) during reaction; (b) in the absence of gaseous 1-butene.

propene, we believe that also in this case, a methyl-rich species (secondary butyl group) prevails on the surface during the catalytic reaction.

After the propene and 1-butene admission had been stopped, a strong decrease in intensity of the spectra occurred but bands at 2963 and 2924 cm^{-1} remained (Figs. 4b, 5b). These spectra resemble that of adsorbed ethylene after stopping the hydrocarbon flow.

Butadiene

The strong absorption bands at 2911 and 2853 cm^{-1} in the spectrum of butadiene observed during hydrogenation (Fig. 6) are certainly not caused by the methyl groups (*10*), since, in this case, bands near 2958 and 2870 cm^{-1} may be expected. An unstrained methylene group would be expected to give absorption near 2920 and 2855 cm^{-1}. Eischens and Pliskin (*24*) as well as Morrow and Sheppard (*10,25*) assigned a band in the 2880 to 2870 cm^{-1} region to the $-CH_2Ni$ group in a four-membered strained ring, as is the case with the associatively adsorbed ethylene species, while a band in the region 2920–2895 cm^{-1} was assigned to the unstrained $-CH_2M$ group (*26,27*). The spectrum obviously points to the presence of a methyl-deficient species on the surface, containing various types of methylene groups.

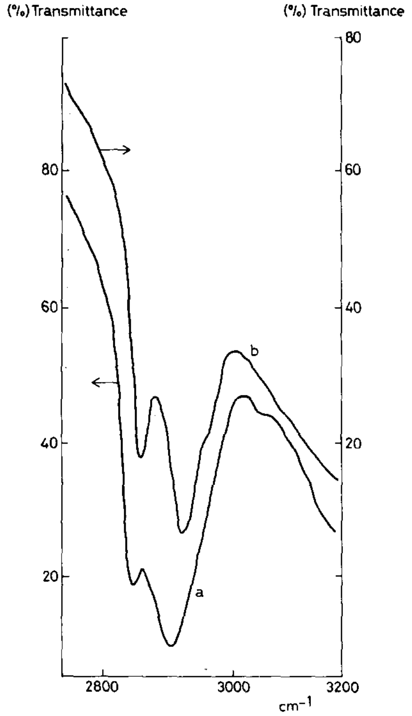

FIG. 6. Infrared spectrum of butadiene: (a) during reaction; (b) in the absence of gaseous butadiene.

In addition to the strong bands mentioned above, bands are also present at for instance 3070, 1764, 1560, 1395 and 1371 cm^{-1}, which also occur approximately at the same position in the spectrum of the gas phase. They must be ascribed to butadiene physically adsorbed on the support, since at least the strongest of these bands were also observed in a blank experiment using a pressed Aerosil disk.

Although a weak band observed near 1453 cm^{-1} could possibly be due to the asymmetric CH_3-deformation frequency, we would rather assign this band to a deformation vibration of the strained nickel-bound CH_2 group, in view of the abovementioned absence of the stronger CH_3-stretching vibration. After the butadiene flow had been stopped, the intensity of the spectrum decreased somewhat although the change in intensity was much smaller than in the case of the other molecules studied. A considerable amount of the methylene-rich surface species remained. A shoulder at about 2952 cm^{-1} appeared, due to the ν_{as} CH_3 vibration, while the valley between the bands at 2911 and 2853 cm^{-1} increased, possibly because of the disappearance of the strained nickel-bound CH_2 group. This group is probably due to the reactive intermediate, the spectrum of which cannot be properly observed due the presence of the methylene-rich species. The ir technique is obviously not suitable for studying the reactive species during butadiene hydrogenation.

DISCUSSION

By monitoring the ir spectrum during the hydrogenation reaction, unique information may be obtained on the nature of the reacting system on the catalyst surface. We showed that at least in the case of ethylene, dissociative adsorption occurred, notwithstanding the fact that the experiments were carried out at an extremely high hydrogen/ethylene ratio. The question arises whether this dissociatively adsorbed species is a reaction intermediate or whether it could exist during reaction in an inert state due to hydrogen deficiency on part of the surface and consequently be readily hydrogenated when the ethylene flow is stopped. We are of the opinion that the species plays some part in the reaction since it is only present during the hydrogenation. Moreover, if it could only exist in an inert state there seems to be no reason why it should not be formed during chemisorption of ethylene on a bare nickel surface (*9*). Jenkins and Rideal (*28*) showed that dissociatively adsorbed species cannot be hydrogenated to ethane easily and therefore this factor was considered by these authors to be of secondary importance for the hydrogenation reaction. However, this does not prove that the dissociatively adsorbed species may not be active as an intermediate in the reaction as suggested by Gardner and Hansen (*7*). One is inclined to believe that the main reason for the discussions on the reaction mechanism of the catalytic ethylene hydrogenation, which started as early as 1934 (*29*), is the fact that this reaction is not one process but a combination of associative and dissociative mechanisms operating simultaneously. This view is supported by the presence of ir bands due to saturated species during the hydrogenation reaction. The situation for ethylene resembles that for cyclohexene hydrogenated on an iron catalyst (*30*). From the change in the deuterium exchange pattern on heat treatment of the catalyst it was concluded that an associative as well as a dissociative adsorption must have taken place during the catalytic deuteration (or hydrogenation). However, there is a driving force in the direction of benzene formation.

Dissociative adsorption was not observed for propene and 1-butene; although it may not be impossible that a band due to the dissociatively adsorbed species is overlapped by the main absorption band of the spectrum, it may well be that the mechanism of the ethylene hydrogenation differs from that of the higher terms of the homologous series.

Kemball (*31*) pointed out that the amounts of the adsorbed radicals responsible for the reaction mechanisms may be quite small, provided that both the formation and desorption to stable molecules proceed rapidly. The spectrum which remained after the alkene flow had been stopped and which is usually ascribed to "polymerized" material (*9,10*) indeed showed that the actual reaction only takes place on that part of the surface not covered with saturated hydrocarbon species. It is possible that this polymerized material plays a part in the hydrogen transfer during hydrogenation. The results of Thomson and Wishlade (*32*), who observed that only a small fraction of preadsorbed ^{14}C-labeled ethylene was removed during ethylene hydrogenation, were explained by Gardner and Hansen (*7*) along the same lines. Experiments made by Erkelens and Liefkens (*33*), however, suggest that in the case of 1-hexene adsorbed on nickel, the exchange reaction is slow in the presence of gaseous deuterium, contradicting the view that hydrogen transfer would give rise to a major contribution to the hydrogenation reaction.

A more detailed conclusion concerning the reaction mechanism could possibly be obtained by carrying out a spectrokinetic investigation, in which the behavior of the ir bands could be studied as a function of pressure, temperature and time. Then, it would also be possible to obtain more detailed information on the "steady state," usually presumed to be established in kinetic considerations dealing with hydrogenation or deuteration reactions.

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