Hydrogenation of But-1-yne on Platinum/Silica Catalysts: An *in Situ* Dynamic Infrared Study

Ph. Maetz,* J. Saussey,† J. C. Lavalley,† and R. Touroude*,[1]

Laboratoire d'Etudes de la Réactivité Catalytique, des Surfaces et Interfaces, U.R.A. 1498 du CNRS, Institut Le Bel, 4 Rue Blaise Pascal, 67070 Strasbourg Cedex, France; and †Laboratoire de Catalyse et Spectrochimie, ISMRA, Université de Caen, 5 Avenue d'Edimbourg, 14032 Caen Cedex, France

Received May 5, 1993; revised October 4, 1993

In this study, an attempt is made to characterize the surface of the catalyst by infrared analysis during the hydrogenation of but-1-yne using an IR cell as the reactor. This cell operates in dynamic conditions under a hydrogen hydrocarbon flow and is online with a chromatograph apparatus which allows the extent of the reaction to be monitored. The results are analysed regarding the variation of the infrared bands as a function of the reaction selectivity. Two features are observed in the case of a selective catalyst: (i) the presence of H-bonded butyne species on the support and (ii) the presence, on platinum, of a species characterized by a broad absorption band at 1687 cm^{-1}, which could be assigned, by comparison with organometallic complexes, to an η^2-butyne species. The presence of this latter species leads to a selective catalyst by site blocking. On a nonselective catalyst the surface coverage and the nature of the adsorbed species are totally different, though the same conversions are obtained on both types of catalyst. An interpretation is made considering equilibria between adsorbed species and the virtual pressure of butyne.

INTRODUCTION

There has been a great deal of study concerning the selectivity for hydrogenation of acetylenic compounds. It has been noted that the formation of hydrocarbon deposits on the catalyst during the acetylene hydrogenation reaction has a marked influence on the selectivity for semihydrogenation. Various results and conclusions have appeared in the literature. Moses *et al.* (1) proposed that a polymeric hydrocarbon deposit, formed during the acetylene hydrogenation reaction, acts as a hydrogen transfer agent leading to a decrease in the selectivity. Den Hartog *et al.* (2) suggested that, on metals like Pd and Pt, the polymeric layer acts as a poison, increasing the selectivity of these metals for acetylene hydrogenation compared to the behaviour of other metals on which this layer would not be formed.

Carbonaceous layers have also been proposed as being the active sites for olefin hydrogenation. This idea was suggested first by Al Ammar and Webb (3) and, later, was fully described by Godbey *et al.* (4). These latter authors proposed that the hydrogenation reaction takes place on metal fully covered by ethylidyne-like species which act as a co-catalyst. Beebe and Yates (5) have shown, using *in situ* infrared analysis, that ethylidyne species have no influence on the hydrogenation rate of ethylene, and the formation of these species greatly depends on the hydrogen and/or olefin pressures. These species are also hydrogenated but with a rate which is several orders of magnitude lower than those involved in ethylene hydrogenation.

The selective hydrogenation of acetylene (1, 2) and butyne (6) gives rise mainly to ethylene and butene, respectively. However, small amounts of the fully hydrogenated products, i.e., ethane and butane, are also formed. It is thought that these species arise from the hydrogenation of ethylidyne and butylidyne intermediates. Using deductive reasoning it is proposed that the greater the ability of the catalyst to form this type of intermediate, the lower the selectivity for acetylenic hydrogenation. Some experimental results support this reasoning, but as yet no direct proof exists.

It is worthwhile to note that polymeric product or ethylidyne-like species are considered as totally or quasi-totally irreversibly adsorbed on the catalyst during the hydrogenation reaction.

In a previous publication (7), studying the hydrogenation of but-1-yne on alumina-supported platinum catalyst, we have shown that the formation of a *reversible* hydrocarbon deposit is necessary to obtain a selective semihydrogenation catalyst.

To investigate further the nature of the reversible hydrocarbon deposit which is formed during butyne hydrogenation, and its role in the selectivity of the reaction, *in situ* Fourier transform infrared (FTIR) spectroscopy combined with online measurements of activity and selectivity have been used. Other surface science methods

---

[1] To whom correspondence should be addressed.

0021-9517/94 $6.00

which operate in ultrahigh vacuum conditions could not be used.

IR spectroscopy is the predominant technique for *in situ* characterization of adsorbed species. On metal catalysts, this technique is most widely used monitoring CO spectra, when CO is employed either as a probe molecule relating changes in surface morphology (8), or as a reactant in CO hydrogenation (9). As far as hydrocarbons are concerned, in situ IR spectroscopy was only used to monitor the vibration bands characteristic of ethylidyne species formed during the hydrogenation of ethylene on alumina-supported palladium catalyst (5).

For C_3 and C_4 hydrocarbons, the IR spectra are much more complex. The interpretation of the spectra was reviewed recently by Chesters *et al.* (10). They were interpreted, taking into account the metal-surface selection rules (MSSR) (11), which are required for metal particles greater than 2 nm in diameter (12).

To our knowledge, the *in situ* FTIR method has never been used to study the selective hydrogenation reaction of acetylenic compounds.

In this paper we report on the hydrogenation of butyne on Pt/SiO_2 catalysts. The infrared spectra were recorded using a specific "cell reactor" which allowed us to work *in situ* and under dynamic conditions. For our studies, treatment under dynamic conditions was important since we have shown previously (7) that the hydrocarbon pressure in the gas phase is important to maintain the hydrocarbon deposition, thus leading to a selective catalyst. In this study, silica has been chosen as the support rather than alumina because the IR spectrum of butyne adsorbed on alumina is more complicated than that of butyne adsorbed on silica. For comparison from a kinetic viewpoint, the results obtained in a micropilot flow reactor are also presented.

EXPERIMENTAL

1. Sample Preparation

The catalyst samples (Pt_I and Pt_{II}) were prepared by wet impregnation of silica (Degussa Aerosil 200) with an aqueous solution of H_2PtCl_6 (Johnson Matthey, pro analysis, >99%). The sample was oven dried at 393 K for 12 h and then reduced under hydrogen at 673 K for 2 h. The characteristics of the two catalysts used in this study, i.e., metal loadings and dispersions obtained by H_2 chemisorption, are given in Table 1.

2. In Situ Dynamic Infrared Cell and Operating Conditions

The infrared cell, installed on a Nicolet 5SX interferometer sample compartment, has been described elsewhere (13). The cell is coupled with a Delsi chromatograph allowing automatic gas sampling, thus facilitating the simultaneous observation of adsorbed species on the catalyst surface and the determination of activity and selectivity for the hydrogenation reaction. The catalyst sample, approx. 15 mg, was pressed into a self-supporting disc (16 mm in diameter, ca 0.2 mm thick). The reaction gas (H_2 or H_2–N_2 mixture) was introduced into the cell reactor at atmospheric pressure, and the gas flow rate was constant at 30 cm^3 NTP/min. The but-1-yne, at constant partial pressure (14 Torr, 1 Torr = 133.3 Pa), was carried over the catalyst sample by a flow of H_2 or H_2–N_2. The hydrogenation reaction was carried out at 298 K. Before each catalytic experiment, the catalyst was activated under H_2 at 573 K and atmospheric pressure for 1 h.

All the spectra were recorded at 298 K with 4 cm^{-1} resolution, by averaging 32 interferograms and subtracting the spectra of the sample activated under H_2. When a spectrum was recorded, a gas sample was simultaneously analysed by gas chromatography. It should be noted that minimising the dead volume in the cell was sufficient to totally suppress the IR bands due to gas phase species.

The activity and selectivity results obtained using the *in situ* IR cell reactor were compared with those obtained from the classical fixed bed flow reactor in order to ensure that the pressed pellet catalyst does not introduce heat and mass transfer limitations or channeling.

3. Fixed-Bed Flow Reactor and Operating Conditions

The fixed-bed flow reactor, operating under atmospheric pressure, is described elsewhere (7). The but-1-

TABLE 1

But-1-yne Hydrogenation: Activity and Selectivity of Pt/SiO_2 Catalysts (P_{H_2} = 38 Torr, P_{HC} = 14.2 Torr, Reaction Temperature = 273 K)

	Pt weight (%)	Dispersion (%)	Butyne flow rate (μmol/s)	Conversion (%)	r_A μmol/s · g_{cat}	TON (s^{-1})	Selectivity (%)
Pt_I	2.74	30	0.2	12.0	0.95	2.3	82
Pt_{II}	4.15	40	0.21	21.2	1.9	2.2	80

yne, at constant partial pressure (14 Torr), was carried over the catalyst sample by a flow of H_2/He (38/722). The hydrogenation reaction was performed at 273 K. Before each catalytic experiment the catalyst was activated under a H_2/He flow at 573 K and atmospheric pressure for 1 h. It is important to note that two catharometers were inserted upstream and downstream with respect to the reactor in order to record the hydrocarbon pressure. The comparison of both signals gives interesting information concerning adsorption and desorption phenomena occurring on the catalyst during the reaction. The reaction products were analyzed by gas–liquid chromatography.

The selectivity to but-1-ene (S) is defined as the ratio, but-1-ene/(but-1-ene + butane); but-2-enes were not observed. The conversion (Cv) is defined as the ratio, (but-1-ene+butane)/(but-1-ene + butane + but-1-yne). The specific activity, turnover number (TON), is defined as the number of reactant molecules converted per Pt surface atom (measured by H_2 chemisorption, Table 1) per second. The reaction rate has been calculated from the simplified formula $\alpha F/\omega$, α being the conversion, F the butyne flow rate, and ω the catalyst weight.

RESULTS

1. Results from Fixed-Bed Flow Reactor

To a sample of the catalyst being kept under H_2 flow, butyne was introduced at constant pressure during a certain time (rectangular pulse). The hydrocarbon pressure at the reactor outlet, recorded by the catharometer, shows that an adsorption phenomenon occurs at the beginning of the pulse and a corresponding desorption peak appears at the end, just after the butyne flow was stopped (Fig. 1, right side). Such characteristics were not observed when the same experiment was performed on the support material alone; the desorption peaks were found to contain only C_4 products, predominantly butane. Analysis of the reaction products shows that the conversion decreases and the selectivity increases before attaining a steady state at which stable conversion and selectivity (Fig. 1, left side) are observed. These results were qualitatively similar to those observed over alumina-supported Pt catalysts (7).

These observations were found to be dependent on experimental conditions. It has been observed that if the experimental conditions are changed, e.g., decreasing the hydrocarbon flow, increasing the temperature, or increasing the H_2 pressure, in order to increase the initial activity of the system, the adsorption/desorption phenomena described earlier are not observed. In addition, the selectivity of the system remains at a low value (Fig. 2) independently of the obtained conversion whilst, in the case described in Fig. 1, the conversion can attain 90% with keeping a high selectivity (7).

Table 1 shows the steady state activities and selectivities for two Pt/SiO_2 catalysts, reactions being performed at 273 K. The term steady state refers to the point at which both the conversion and selectivity of the system are stable. It can be seen from Table 1 that the TON and the selectivity for both catalysts are exactly the same.

2. Results from Infrared Cell Reactor

2.1. SiO_2 support. But-1-yne (14 Torr) and hydrogen (150 Torr) were exposed to the support material at 298 K; the support had itself been treated at 573 K under H_2 pressure. Analysis of the effluent gas stream by gas chromatography showed that only the reactant but-1-yne was observed. The IR spectrum of the SiO_2 surface shows two bands at 3310 and 2115 cm^{-1} (Fig. 3a), corresponding to $\nu(\equiv C\text{–}H)$ and $\nu(C\equiv C)$, respectively. The spectrum is similar to that recorded for but-1-yne in CCl_4 solution

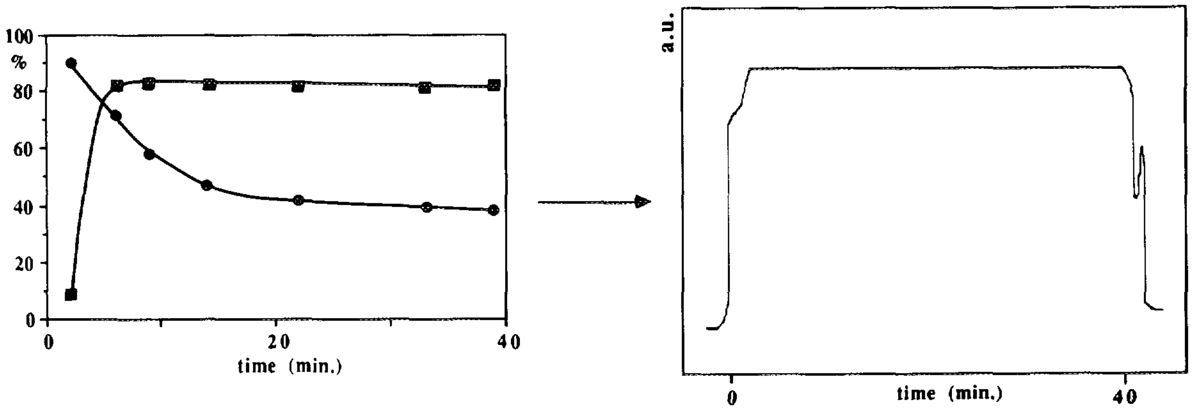


FIG. 1. On Pt_1 catalyst (P_{H_2} = 38 Torr; P_{HC} = 14.2 Torr; hydrocarbon flow = 0.16 μmol/s; T = 293 K). Left side: But-1-yne conversion (●) and but-1-ene selectivity (■) as a function of time-on-stream. Right side: Catharometer signals: hydrocarbon pressure (arbitrary units) as a function of time-on-stream.

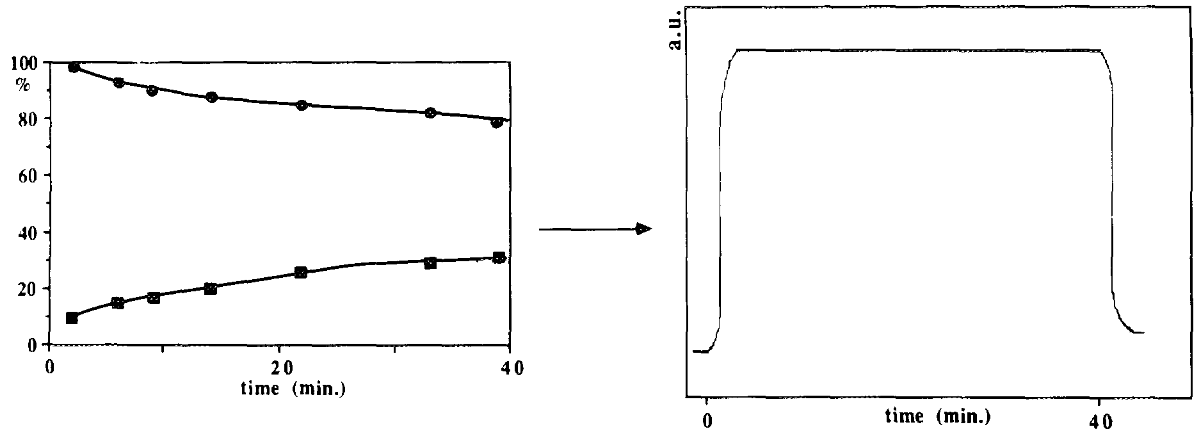


FIG. 2. On Pt$_l$ catalyst (P_{H_2} = 760 Torr; P_{HC} = 14.2 Torr; hydrocarbon flow = 0.31 μmol/s, T = 293 K). Left side: But-1-yne conversion (●) and but-1-ene selectivity (■) as a function of time-on-stream. Right side: Catharometer signals: hydrocarbon pressure (arbitrary units) as a function of time-on-stream.

(14), ν(C≡C) and ν(≡C–H) being observed at 2116 and 3305 cm^{-1}, respectively. On silica, the butyne species is adsorbed on silanol groups by hydrogen bonding (Fig. 4) as indicated by the perturbation of the SiO–H IR band, which shifts from 3745 to 3574 cm^{-1}. After the butyne flow has been stopped, the bands characteristic of butyne instantaneously disappear, and the SiO–H vibration band recovers its initial position.

2.2. Pt/SiO$_2$ catalysts. A spectrum of but-1-yne exposed to Pt/SiO$_2$ without hydrogen was first recorded (Fig. 3b). It is similar to the one recorded on SiO$_2$ (Fig. 3a). The ν(≡C–H) is slightly displaced to lower wavenumbers while ν(C≡C) is not affected. A weak band appears at 2158 cm^{-1} attributed to Pt butylide species (Table 2).

But-1-yne hydrogenation was studied on both catalysts at 298 K under 38 Torr hydrogen pressure (Figs. 5–7).

The spectra of the activated samples which were used in a subtraction operation to obtain the shown spectra, present a weak band at 2045 cm^{-1} due to traces of CO resulting from the activation process. This phenomenon has already been observed by other authors studying platinum catalysts (15, 16). This band disappeared under butyne flow, explaining the negative peak observed when subtracting spectra. Water is also present in the background at 1620 cm^{-1}, due to cooling down the sample after the activation process.

(a) Catalyst Pt$_l$. Figure 5a shows the IR spectra recorded during the hydrogenation reaction on Pt$_l$ catalyst; the wavenumbers of the absorption bands are listed in Table 2. The conversion, selectivity, and time-on-stream corresponding to each spectrum are also given in Fig. 5a. When but-1-yne is introduced into the reactor, there is a progressive increase in the intensities of the absorption bands at 3574, 3302, and 2115 cm^{-1}. According to the

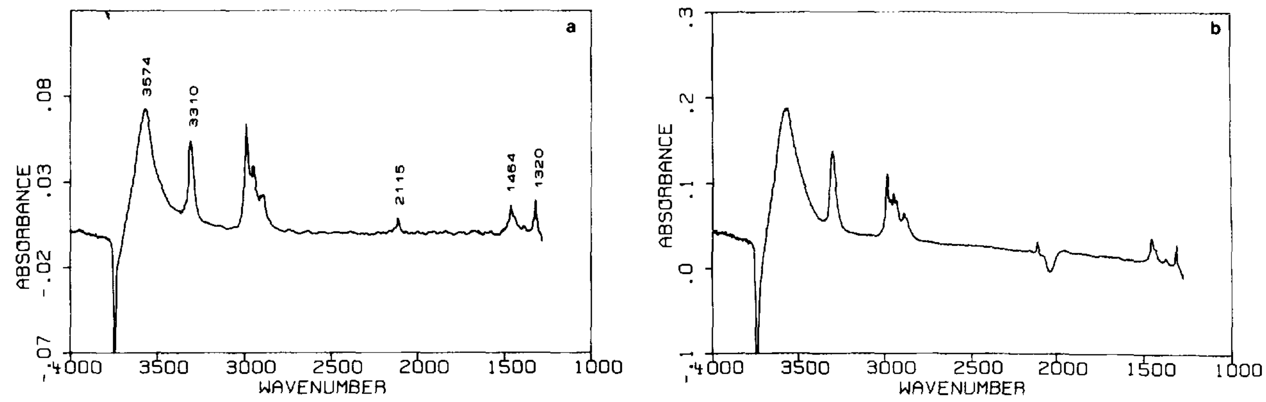


FIG. 3. (a) IR spectrum recorded when butyne (14 Torr) and H$_2$ (150 Torr) are carried on SiO$_2$. (b) IR spectrum recorded when butyne (14 Torr) without H$_2$ is carried on Pt/SiO$_2$.

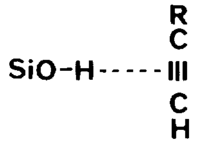


FIG. 4. Adsorbed butyne species on SiO_2.

spectrum recorded for but-1-yne adsorption on SiO_2, these three bands are assigned to a but-1-yne species π-adsorbed on the OH silica group. The intensities of these three bands increase from spectra A to D, and remain constant afterwards.

In the $\nu CH_2/\nu CH_3$ region (2700–2900 cm^{-1}) the spectra change very rapidly at the beginning of the experiment. On spectrum A in Fig. 5a, the relative intensities of the major absorption bands are totally different with respect to the other spectra (B to F).

Chromatographic results show a decrease in the butyne conversion and a corresponding increase in the selectivity to but-1-ene up to 79%. Selectivity afterwards remains stable and activity is nearly constant, while a small activity decrease is observed after a long time-on-stream. The calculated activity when the selectivity attains the highest value (79%) is 9.2 μmol/s · g_{cat}. Together with the increase of the selectivity, a broad absorption band appears at 1687 cm^{-1}; this band is well resolved when the selectivity reaches a high value, 79%. In the region below 1500 cm^{-1}, one can note a weak absorption band at 1340 cm^{-1} (Fig. 6) in addition to the bands already observed on the support at 1463, 1380, and 1320 cm^{-1}.

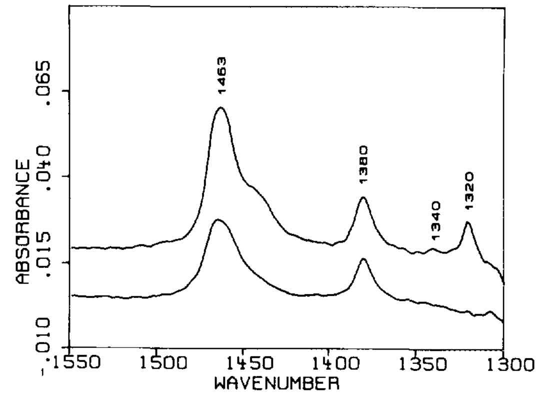


FIG. 6. IR spectra in the 1350–1500 cm^{-1} region. Upper spectrum: Pt_I catalyst (selectivity: 79%); lower spectrum: Pt_{II} catalyst (selectivity: 50%).

When the hydrocarbon flow is stopped, the but-1-yne species adsorbed on the support immediately disappears, as indicated by the spectra (Fig. 5b). The disappearance of this peak corresponds to a dramatic decrease in the selectivity of the system and a rapid increase in the butane conversion (reaching 100%). The intensity of the band at 1687 cm^{-1} is also seen to decrease, disappearing totally

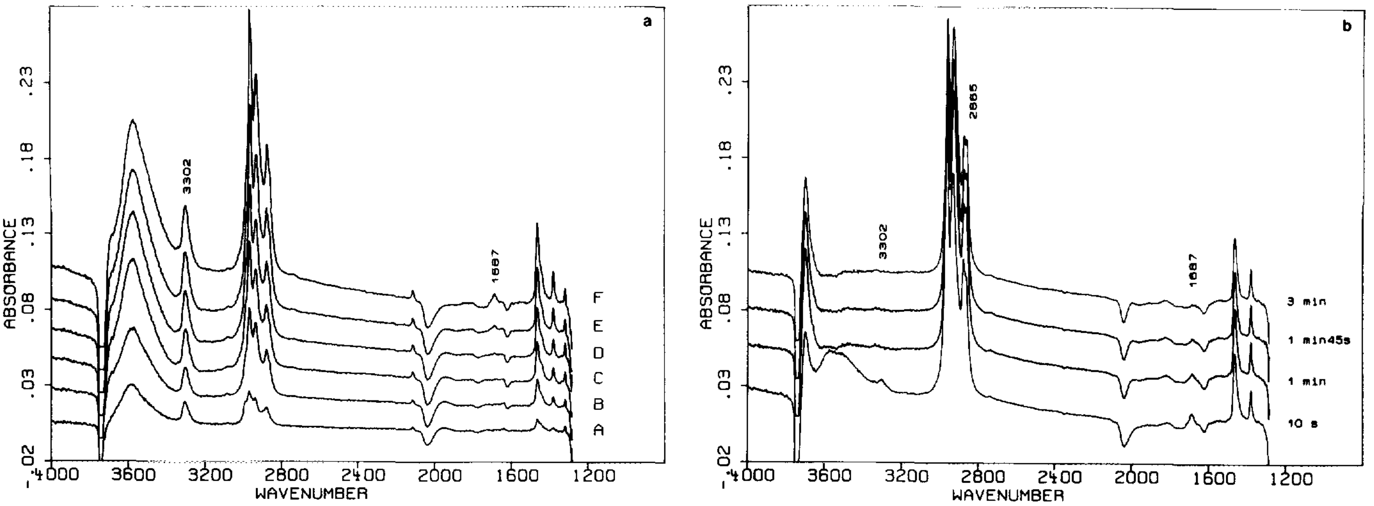


FIG. 5. Butyne hydrogenation on Pt_I catalyst (butyne = 14 Torr; H_2 = 38 Torr; T = 298 K). (a) IR spectra and product analyses as a function of time-on-stream. (b) IR spectra as a function of time on H_2/N_2 flow after stopping butyne flow.

	A	B	C	D	E	F
Time-on-stream (min)	0.5	3	13	35	70	240
Conversion (%)	—	63	49	41	33	27
Selectivity (%)	—	55	60	75	79	79

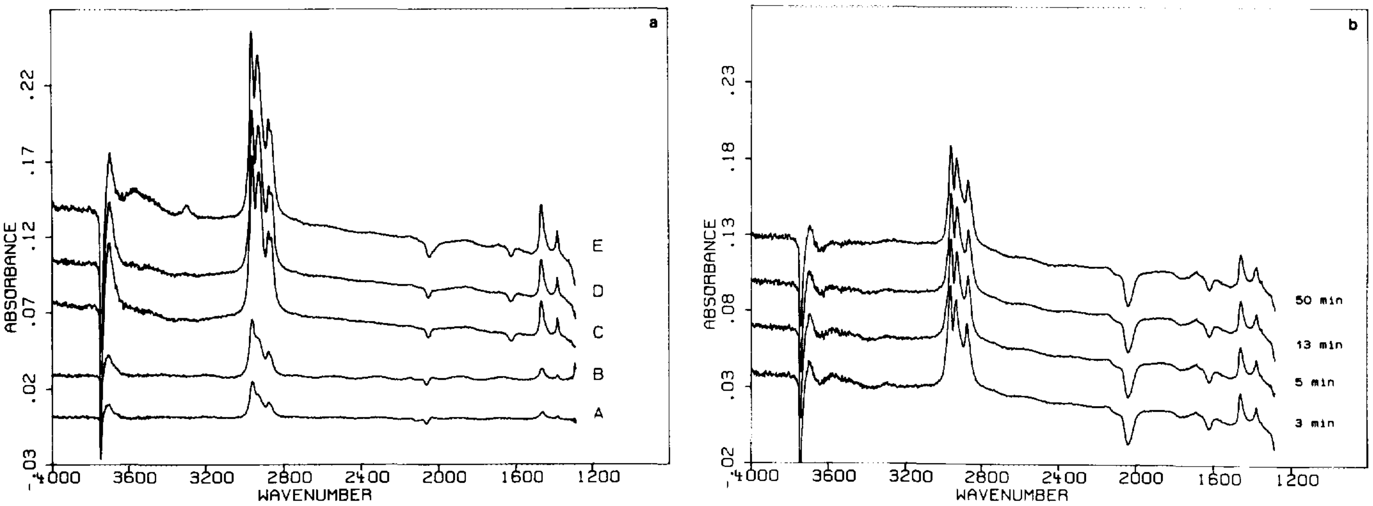


FIG. 7. Butyne hydrogenation on Pt$_{II}$ catalyst (butyne = 14 Torr; H_2 = 38 Torr; T = 298 K). (a) IR spectra and product analyses during time on stream. (b) IR spectra as a function of time on H_2/N_2 flow after stopping butyne flow.

	A	B	C	D	E
Time-on-stream (min)	1	3	15	45	80
Conversion (%)	—	95	60	54	30
Selectivity (%)	—	11	52	51	53

TABLE 2

Observed Wavenumbers (cm^{-1}) and Assignments

SiO$_2$ (H_2: 150 Torr)	Pt/SiO$_2$	Pt$_I$ selectivity: 79% (H_2: 38 Torr)	Pt$_{II}$ selectivity: 50% (H_2: 38 Torr)	Vibration	Species
3574	3576	3574	3714	ν(SiO-H)	Silanol
3310	3303	3302		$\nu(\equiv C—H)$	C
		3080		$\nu_a(=CH_2)$	D
		3020?		$\nu_s(=CH_2)$	D
2991	2989	2990		ν_a, $\nu'_s(CH_3)$	C
	2967	2966	2963	$\nu(CH_3)$	P
2962				$\nu(CH_3)$	?
2950	2949			$\nu_s(CH_3)$	C
	2934	2934	2928	ν_a, $\nu_s(CH_2)$	P
2905				$\delta(CH_2) + \delta'_s(CH_3)$	C
2888	2891			$2\delta_a(CH_3)$	C
	2873	2879	2878		P
		2860	2863		P
	2158			$\nu(C\equiv C)$	E
2115	2115	2115		$\nu(C\equiv C)$	C
		1687		$\nu(C=C)$	A
			1465	δ_a, $\delta'_s(CH_3)$	P
1462	1463	1463		δ_a, $\delta'_s(CH_3)$	C
1440	1440	1440		$\delta(CH_2)$	C
1384	1381			$\delta_s(CH_3)$	C
		1380	1380	$\delta_s(CH_3)$	P
		1340			F
1330					?
1321	1321	1320		$\omega(CH_2)$	C

Note. A, η^2 but-1-yne species; C, but-1-yne/SiO$_2$ species; D, but-1-ene/SiO$_2$ species; E, Pt butylide species; F, diσ-π species?; P, polymeric species.

TABLE 3

Observed Wavenumbers (cm^{-1}) of IR Spectra Bands on Pt/SiO_2 Catalyts after Cutting off the Total Flow

Catalyst Pt_I	Catalyst Pt_{II}
2966	2963
2934	2928
2879	2878
2865	
1464	1465
1380	1380

after some minutes under H_2 flow. The final IR spectrum shows that four absorption bands remain in the C–H stretching region of the spectrum at 2966, 2934, 2879, and 2865 cm^{-1} (Table 3) with corresponding C–H bending modes in the 1300–1500-cm^{-1} region and some perturbation of the SiO–H band still exists. From the spectra it is impossible to deduce the chemical structure of the polymeric species.

(b) Catalyst Pt_{II}. Figure 7a shows the IR spectra recorded during the hydrogenation reaction on the Pt_{II} catalyst; the wavenumbers of the absorption bands are listed in Table 2. As in Fig. 5a, the conversion, selectivity, and time-on-stream are indicated.

Initially, when but-1-yne and hydrogen are introduced into the reactor, the spectrum (spectrum A, Fig. 7a) is similar in the $\nu CH_2/\nu CH_3$ region to that recorded on the Pt_I catalyst (spectrum A, Fig. 5a). Afterwards, the spectra change, but it is worth noting that the three characteristic bands of the SiOH-bonded but-1-yne species are not observed until the last spectrum (spectrum E), where they become visible but are very weak. In another experiment, the surface of the catalyst was first saturated with but-1-yne π-adsorbed on SiOH group; when hydrogen (76 Torr) was introduced to the catalyst this species instantaneously disappeared.

Similarly, as in the Pt_I catalyst, the conversion decreases with time-on-stream, and the selectivity increases, but only to 50%. Compared to the spectra recorded on Pt_I, the spectra recorded on Pt_{II} are of remarkable simplicity. There is no detectable absorption band near 1687 cm^{-1} (Fig. 7a) or 1340 cm^{-1} (Fig. 6).

When the hydrocarbon flow is stopped, there is no appreciable change in the spectra. In the $\nu CH_2/\nu CH_3$ region, three bands at 2963, 2928, and 2878 cm^{-1} remain (Fig. 7b, Table 3), their intensities being approximately half that recorded for the Pt_I.

DISCUSSION

It was found that, for the Pt_I catalyst, the activities and selectivities observed in the IR cell reactor, either under transient or steady state conditions, were analogous to those observed in the micropilot flow reactor. The steady state activity observed in the IR apparatus was found to be 10 times higher than that observed in the micropilot system; this is due to the fact that different reaction temperatures were used, 298 and 273 K, respectively. If we consider the apparent activation energy of this reaction (15 kcal/mol (17)), it can be seen that the activities of both systems are the same. Thus the IR cell is considered to be operating without diffusion limitation, since mass and heat transfer were checked not to control the kinetics in micropilot experiments.

The results for Pt_{II} are apparently different in both reactors; a selectivity greater than 50% was not obtained in the IR cell working at 293 K, whilst in the micropilot reactor, at 273 K, a selectivity as high as 80% was obtained; this apparent contradiction will be discussed later.

The IR spectra of the Pt_I catalyst showed the presence of a H—bonded but-1-yne species on the support, a broad absorption band near 1687 cm^{-1}, and another at 1340 cm^{-1}. Neither of these phenomena were observed for the Pt_{II} catalyst. The discussion will be mainly concerned with the interpretation of these results, but first we will attempt to assign some of the observed IR absorption bands.

In the 2800–3000-cm^{-1} region of the IR spectra recorded for both catalysts at the beginning of the reaction (Fig. 5a, spectrum A and Fig. 7a, spectrum A), the position and the relative intensities of the three major bands (2966, 2933, and 2837 cm^{-1}) are the same (the additional bands observed in spectrum A of Fig. 5a, in this region, are due to the presence of butyne adsorbed on OH silica group). They are also similar to those recorded by Morrow and Sheppard (18) when they studied the chemisorption of but-1-ene on Pt/silica, at 298 K, reacting under hydrogen. The absorption bands are slightly displaced to higher wavenumbers but the relative intensities of the three major absorption bands are the same. According to these authors, these peaks indicate the formation of butane which is adsorbed on the surface of the support, indicated by the slight perturbation in the OH vibration frequency of the silica.

We have observed the variation of an absorption band near 1687 cm^{-1}. This band was present when high selectivity for butyne hydrogenation on Pt_I was obtained, and it disappeared very quickly when the hydrocarbon flow was stopped. It was not observed on Pt_{II} where the selectivity remained low.

The band at 1687 cm^{-1} cannot be assigned to any adsorbed butene species. The free ν(C═C) mode of but-1-

ene is lower (1645 cm^{-1} (19)) and the formation of but-2-ene has never been detected in our experiments. In fact, concerning the adsorption of but-1-ene, but-2-ene *cis* and *trans*, the ν(C=C) mode of the π-complex adsorbed on the OH group of silica was found respectiverly at 1636, 1654 and 1668 cm^{-1}. Thus the band at 1687 cm^{-1} must arise from the adsorption of but-1-yne, or from the formation of an intermediate of the hydrogenation reaction adsorbed on platinum.

It is possible that diσ-π species (MHC=CRM) or vinylidene species (M=C=CHR) are formed. For example, there could exist an interaction between the π C=C bond and the metallic site, as proposed in the case of methylacetylene (20). However, the presence of a peak in the IR spectrum in the range 1600–1700 cm^{-1}, corresponding to π-adsorption on the metal, has never been detected, neither by IR (21, 22) nor by electron-loss spectroscopy (20). The presence of a C=C vibration band is often observed near 1300–1350 cm^{-1} (21, 22). In our spectra, the low absorption band at 1340 cm^{-1} could indicate the presence of diσ-π species. By comparison with organometallic compounds (23), we could attribute the peak at 1687 cm^{-1} to an η^2-but-1-yne species. However, for such organometallic compounds, i.e., with an η^2-alkyne ligand, the ν(C=C) mode of a π-complex is generally found between 1750 and 1900 cm^{-1}. The lower value that we have observed could be explained by a greater back-donation of the *d* metallic orbitals to the π antibonding orbital of the ligand, but-1-yne being coordinated with more than one platinum atom.

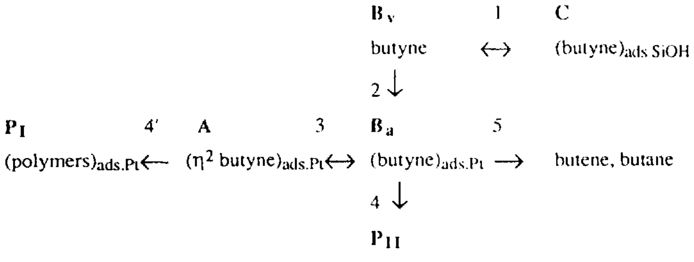
A better characterisation of this species cannot be drawn from this study, since the spectra in the ν(C—H) region are complex due to the superposition of several kinds of hydrocarbon surface species (H-bonded to support and poisoning species); also, the carbon–metal absorption bands, below 1000 cm^{-1}, are obscured by the strong absorption bands of the support. Therefore, in the absence of more information, the formation of a η^2-butyne species is assumed. The π-adsorption of but-1-yne on the metal particles could lead to the formation of such η^2-but-1-yne species, which could then lead to the formation of some vinylidene species, as described in the case of organometallic complexes (24). In our study, however, we have no direct evidence concerning the presence of π-adsorbed species on the metal particles. The C=C stretching vibration mode in such species is parallel to the metallic surface and therefore expected to exhibit a very low intensity, taking into account the metal-surface selection rules (11).

Comparing the catalytic behaviour of the Pt$_{\rm I}$ and Pt$_{\rm II}$ catalysts and their corresponding IR spectra, it appears that the degree of surface coverage is the key factor governing the activity and the selectivity of the reaction. It is to be noted that the surface coverage is not in equilibrium with the gas phase pressure since, for the same conversion (about 30%), the presence of π-adsorbed but-1-yne on the OH of the support is observed on Pt$_{\rm I}$, whereas it is quasi-inexistent on Pt$_{\rm II}$.

This surprising result can be related to the features observed in the micropilot reactor when the initial activity was very high. Such a case is described in Fig. 2. When the initial activity was very high, adsorption and desorption phenomena were not observed and high selectivity was not obtained, independently of the conversion; the conversion could be more or less high depending on the irreversible poisoning. The changes of behaviour observed in Fig. 2 with respect to Fig. 1 are due to H$_2$ pressure increase. Increasing the reaction temperature or decreasing the flow rate would have led to similar changes (17). In the IR cell reactor, operating at 298 K, Pt$_{\rm II}$ initially converts a very large amount of the butyne, larger in fact than was obtained in the experiment, reported in Table 1, performing in the micropilot reactor operating at a lower temperature, 273 K, and larger also than Pt$_{\rm I}$ because it contains twice as many surface Pt atoms (loading and dispersion are higher).

Thus, it is clear that the selectivity is related to the initial period of the reaction in such a way that a high initial conversion does not lead to a high surface coverage of butyne, as shown in the IR spectra. In this case, an equilibrium between adsorbed surface species and gas phase species is not established. These observations can be rationalised by the following reaction scheme (Scheme 1), which uses the concept of virtual pressure, an idea which is well established in catalysis (25–27). This reaction scheme is presented without a detailed description of all possible hydrogenated intermediates. Such detail, being out of the scope of this paper, is presented elsewhere (6, 17).

In the reaction scheme, the virtual pressure of butyne, B$_{\rm v}$, is directly related to the coverage of the adsorbed butyne species, B$_{\rm a}$, but not to the true butyne pressure. When B$_{\rm a}$ is rapidly hydrogenated to butene, butane (step 5), B$_{\rm a}$ and B$_{\rm v}$ concentrations are so low that the equilibria leading to the formation of η^2-butyne (A) and H-bonded butyne (C), respectively (steps 3 and 1), are not estab-



SCHEME 1

lished. Conversely, when B_v and B_a are high, H-bonded butyne species and η^2-butyne exist. Therefore, although the pressure of butyne in the reactor was the same (30% butyne conversion) for both catalysts Pt_I and Pt_{II}, the virtual butyne pressures were very different and could explain the observed differences in the degree of surface coverage and hydrogenation selectivities. The formation of η^2-butyne species would prevent butene readsorption and its further hydrogenation, explaining the high selectivity of a catalyst covered by these species.

The decrease in the conversion with time-on-stream (i.e., catalytic deactivation) is attributed to the decrease in the number of active sites which are gradually covered by A species and also polymeric products (P) which are irreversibly adsorbed on the catalysts. It is worth noting that the irreversible hydrocarbon deposit is different on both catalysts. On Pt_{II}, it is present in a smaller quantity, and there is no band at 2865 cm^{-1}, whereas the absorption near 1380 cm^{-1} is more complex in the final IR spectrum. It is thought that, on Pt_I, polymeric products are formed from η^2-butyne species (step 4′), in addition to those formed on both catalysts, from the reactive species B_a (step 4). The small perturbation of the surface OH groups also indicate that these polymers have some methyl or ethyl terminal groups which interact with the silica support.

CONCLUSIONS

Our results show clearly that two features are specially observed in the case of a selective catalyst:

(i) the presence of H-bonded butyne species on the support,

(ii) the presence, on platinum, of a species characterized by a broad IR absorption band at 1687 cm^{-1}, assigned to an η^2-butyne species.

Under reaction conditions, these species are in equilibrium with a virtual pressure of butyne and lead to a selective catalyst by site blocking. The equilibria are becoming established during the initial phase of the reaction. When the reactivity of the catalyst is initially very high, the surface coverage is so low that the equilibria are not established and a poor selectivity for hydrogenation is observed.

In addition to this reversible coverage of the surface, an irreversible deposit consisting of polymeric species is formed during the reaction. These polymeric species are also formed on the support.

Further investigations must be carried out in order to define more precisely the structure of these deposits and to follow their behaviour as an entire kinetic study. As we have shown, the combined *in situ* on-line FTIR and activity measurements can contribute substantially to a better understanding of the selective hydrogenation reaction.

ACKNOWLEDGMENT

We are grateful to Dr. D. Yu. Murzin of the Karpov Institute of Physical Chemistry of Moscow (Russia) for helpful discussions and a critical reading of a draft of this paper.

REFERENCES

1. Moses, J. M., Weiss, A. H., Matusek, K., and Guczi, L., *J. Catal.* **86,** 417 (1984).
2. Den Hartog, A. J., Deng, M., Jongerius, F., and Ponec, V., *J. Mol. Catal.* **60,** 99 (1990).
3. Al Ammar, A. S., and Webb, G., *J. Chem. Soc., Faraday Trans. I* **74,** 195, 657 (1978); *J. Chem. Soc., Faraday Trans. I* **75,** 1900 (1979).
4. Godbey, D., Zaera, F., Yates, R., and Somorjai, G. A., *Surf. Sci.* **167,** 150 (1986).
5. Beebe, T. B., Jr., and Yates, J. T., *J. Am. Chem. Soc.* **106,** 663 (1986).
6. Hub, S., and Touroude, R., *J. Catal.* **114,** 411 (1988).
7. Maetz, Ph., and Touroude, R., *Catal. Lett.* **4,** 37 (1990).
8. Anderson, J. A., McQuire, M. W., Rochester, C. H., and Sweeney, T., *Catal. Today* **9,** 23 (1991).
9. Browne, V. M., Fox, S. G., and Hollins, P., *Catal. Today* **9,** 1 (1991).
10. Chesters, M. A., de la Cruz, C., Gardner, P., McCash, E. M., Pudney, P., Shahid, G., and Sheppard, N., *J. Chem. Soc., Faraday Trans.* **86,** 2757 (1990).
11. Pearce, H. A., and Sheppard, N., *Surf. Sci.* **59,** 205 (1976).
12. Greenler, R. G., Snider, D. R., Witt, D., and Sorbello, R. S., *Surf. Sci.* **118,** 415 (1982).
13. Joly, J. F., Zanier-Szydlowski, N., Colin, S., Raatz, F., Saussey, J., and Lavalley, J. C., *Catal. Today* **9,** 31 (1991).
14. Saussey, J., Lamotte, J., and Lavalley, J. C., *Spectrochim. Acta, Part A* **32,** 763 (1976).
15. Eley, D. D., Moran, D. M., and Rochester, C. H., *Trans. Faraday Soc.* **64,** 2168 (1968).
16. Primet, M., Basset, J. M., Mathieu, M. V., and Prettre, M., *J. Catal.* **28,** 368 (1973).
17. Maetz, Ph., *Thesis.* Strasbourg, 1992.
18. Morrow, B. A., and Sheppard, N., *Proc. R. Soc. London, A* **311,** 415 (1969).
19. Sheppard, N., *J. Chem. Phys.* **17,** 74 (1949).
20. Koestner, R. J., Frost, J. C., Stair, P. C., van Hove, M. A., and Somorjai, G. A., *Surf. Sci.* **116,** 85 (1982).
21. Anson, C. E., Keiller, B. T., Oxton, I. A., Powell, D. B., and Sheppard, N., *J. Chem. Soc., Chem. Commun.,* **470** (1983).
22. Evans, J., and McNulty, G. S., *J. Chem Soc., Dalton Trans.,* 683 (1983).
23. Boag, M., Green, M., Grove, D. M., Howard, J. A. K., Spencer, J. L., and Stone, F. G. A., *J. Chem. Soc., Dalton Trans.,* 2170 (1980).
24. Bullock, R. M., *J. Chem. Soc., Chem. Comm.* 165 (1989).
25. Temkin, M., and Pyzhev, V., *Z. Fiz. Khim.* **13,** 851 (1939).
26. Kemball, C., *Discuss. Faraday Soc.* **41,** 190 (1966).
27. Boudart, M., *Catal. Lett.* **3,** 111 (1989).