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# In situ infrared spectroscopy applied to catalytic reactions on metal single crystals

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## Abstract

Two reactions, the hydrogenation of buta-1,3-diene on a $Pd_8Ni_{92}$(1 1 1) alloy and the hydrogenation of benzene on Pt(1 1 1), have been investigated under catalytic conditions by reflection absorption infrared spectroscopy (RAIRS). The purpose of this study was to use infrared spectroscopy to observe both the consumption/production of the different reactants/products and the adsorbed species present during the reaction.

On $Pd_8Ni_{92}$(1 1 1), only butenes were produced during the buta-1,3-diene hydrogenation reaction up to the quasi-complete conversion of the diene, with a high rate of reaction. This alloy is therefore, active and very selective for such a reaction. In this case, no absorption bands corresponding to surface species were observed.

Ad-species were observed during the benzene hydrogenation reaction on Pt(1 1 1); they cannot be attributed to chemisorbed molecular benzene, but are more probably due to partially hydrogenated intermediates, such as cyclohexadiene and/or cyclohexene. © 2001 Published by Elsevier Science B.V.

*Keywords:* In situ reflexion absorption infrared spectroscopy; Hydrogenation reaction; Single crystals

## 1. Introduction

Over the last few decades, surface scientists have used various ultra-high vacuum (UHV) techniques in order to obtain more insight into the field of catalysis, namely through chemisorption studies on single crystal surfaces and through active site characterisation. The use of well-defined single crystal surfaces together with their characterisation in UHV remains important because it provides good references. But, with the classical tools of surface characterisation, monocrystalline samples can be analysed only before or after reaction but not during the reaction. Recent studies by sum frequency generation (SFG) allowing measurements of well controlled surfaces under gas pressure, demonstrated the necessity of extending the UHV surface studies to high pressure surface studies, bridging the pressure gap between surfaces and catalysis [1–5]. For example, it has been shown that the cyclohexene hydrogenation/dehydrogenation intermediates, and their respective concentrations, depend upon the temperature and the hydrogen pressure. Furthermore, the key intermediates of high pressure catalytic reactions may not be present under UHV conditions [4]. This is the case for ethylene which, in contact with Pt(1 1 1), only generates the formation of ethyl groups at very high hydrogen pressure [5]. The main difficulty lies in the fact that with monocrystalline samples, the surface on which the reaction takes place has a very low specific area, and that the surface species — intermediates, precursors or poisons — are formed at very low concentrations relative to the gas phase species during the reaction.

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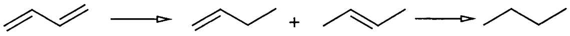
Optical spectroscopies such as reflection absorption infrared spectroscopy (RAIRS) and SFG, lend themselves well to such investigations during the catalytic reaction on well-defined surfaces. The surface sensitivity is inherent to the optical process in SFG, a second order process induced by a break of symmetry such as a gas or liquid surface interface. In order to be detected by SFG, a vibrational band has to be both infrared and Raman active [6–8]. Infrared spectroscopy at grazing incidence and using a p-polarised beam has also been shown to be surface sensitive with metallic substrates [9]; only molecular vibrations of the chemisorbed or interacting molecular species with a finite component of their dynamic dipole perpendicular to the surface are observable. By measuring spectra using both s- and p-polarisation, the gas phase which displays an isotropic distribution can be cancelled and thus the small signal issued from the species interacting with the surface can be obtained. At the same time, the products of the reaction can be measured in the gas phase through s-polarised spectra insensitive to the substrate.

The selective hydrogenation of alkynes and/or dienes is an important subject of industrial relevance, namely for highly pure $C_4$ unsaturated hydrocarbon production for the polymer industry [10]. In fact the technologies used for the production of unsaturated hydrocarbons (such as steam cracking or catalytic cracking) lead to the presence of traces of alkynes and/or dienes which have to be selectively transformed into alkenic compounds in order to avoid undesirable polymerisation reactions of these molecules. Buta-1,3-diene is the simplest conjugated hydrocarbon and can be used as a model to understand the mechanistic details of such a reaction for more complicated hydrocarbons.

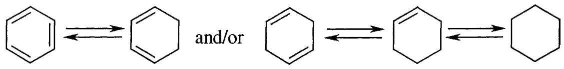
The activity and selectivity for the buta-1,3-diene hydrogenation reaction strongly depend on the metal used as a catalyst. Pd appears to be the best for selective hydrogenation into butenes up to very high butadiene conversion before butane formation, following



Furthermore, the Pd activity greatly depends on the surface crystalline orientation [11] and can be greatly enhanced by alloying effect [12–14]. From X-ray absorption near edge spectroscopy (XANES) of buta-1,3-diene and butene on Pd(1 1 1), the high selectivity of Pd(1 1 1) has been ascribed to the higher adsorption strength of buta-1,3-diene (di-π-bonded) relative to butene (π-bonded) [15]. Furthermore, it was shown that on the very active and selective Pd(1 1 1), Pd(1 1 0) and PdCu(1 1 0), the reactants (buta-1,3-diene and butene) were π-bonded [16], while they were σ-bonded on Pt(1 1 1) [15], a surface which displays a very low reactivity and less selectivity towards butenes in this reaction. Despite numerous surface studies on these systems, no similar studies have been done, to our knowledge, under catalytic conditions, i.e., in the presence of hydrogen.

The hydrogenation of buta-1,3-diene has been extensively studied using a variety of metal single crystals and metallic alloys as catalysts by Bertolini and co-workers [12–14]; the Pd based alloys can be more active than pure Pd in such a reaction. This is the case for $Pd_8Ni_{92}(1\,1\,1)$ which is about five times more active than Pd(1 1 1). A high level of palladium surface segregation has been shown on this sample, leading to a quasi-complete (∼80 at.%) layer of Pd in the topmost surface plane [12]. This reaction was used to test the in situ RAIRS reactor since the reaction rate is slow enough to allow infrared data to be obtained, but fast enough that the reaction progresses in a realistic time frame. Moreover, the use of an alloy avoids the formation of a hydride which would be obtained with a pure Pd single crystal under hydrogen pressures higher than 10 Torr, leading to the loss of its monocrystalline nature.

The hydrogenation of aromatics is also a very important reaction of practical use in elimination of these compounds in diesel oils [17]. Benzene is the simplest aromatic molecule and platinum is known to be one of the most effective catalysts to perform the total hydrogenation of such an aromatic molecule [18]. The study of benzene chemisorption on various transition metal single crystal surfaces has been the subject of many studies. The benzene molecule is generally found to chemisorb with its ring parallel to the surface plane. This is the case on Pt(1 1 1), as observed by high resolution electron energy loss spectroscopy (HREELS) [19,20] and RAIRS [21]. It is then tempting to assume that this ad-species is an intermediate species in the benzene hydrogenation reaction. But, it is known that above room temperature the reverse reaction cyclohexane → benzene can occur [3].



The reverse reaction has been observed under low pressure conditions without hydrogen [22]. In fact, in the presence of hydrogen the equilibrium will shift towards the hydrogenation or dehydrogenation reaction by changing the temperature and the hydrogen pressure. The determination of the nature of the surface species during the course of the reaction will help to draw probable conclusions on the intermediate species for these reactions.

In this work, the hydrogenation of buta-1,3-diene on $Pd_8Ni_{92}(1\,1\,1)$ and that of benzene on $Pt(1\,1\,1)$, have been investigated in a recently developed reactor attached to an infrared spectrometer.

## 2. Experimental

The experimental set-up consists of three main chambers separated by gate valves, with various probes to allow the sample to be transferred between all three chambers under vacuum. The first two UHV chambers have a base pressure of $4 \times 10^{-10}$ Torr and have been described previously [23]. One chamber is used for sample preparation and contains an ion gun and an infrared lamp for sputtering and annealing the sample, an X-ray photoelectron spectrometer (XPS) with a dual Al/Mg X-ray source and a quadrupole mass spectrometer. The second chamber, in which low energy electron diffraction (LEED) and HREELS are available, was not used in this study. The third chamber shown schematically in Fig. 1, consists of a small stainless steel reactor, equipped with two ZnSe IR windows, a leak valve to sample the reaction products by quadrupole mass spectrometry (QMS) during the reaction, a stainless steel UHV gas line, and a capacitive gauge. The total volume of the reactor is about 1 l and it can be evacuated through a turbomolecular pump. The reactor can be isolated from the pumping system and the other UHV chambers by two gate valves, allowing measurements to be carried out from UHV up to atmospheric pressure.

The sample is fixed onto a copper or stainless steel plate which can be transferred onto an X, Y, Z sample manipulator. The sample single crystal (on its support) is placed onto a stainless steel or copper block which can be resistively heated up to 700 K. In addition, a chromel–alumel thermocouple is used to measure the temperature of the block close to the sample. With such a set-up, the temperature of the sample is not measured directly but there is no wiring inside the reactor able to react with the gases.

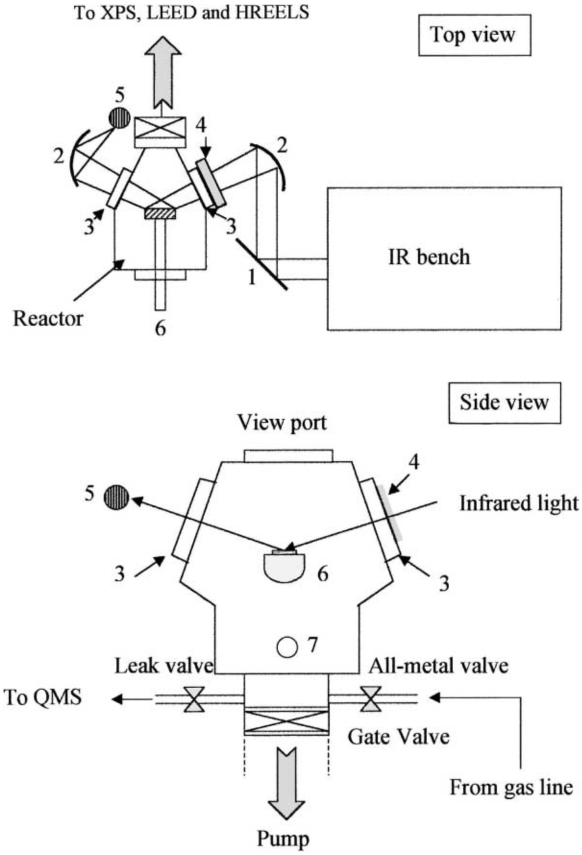


Fig. 1. Schematic view of the reactor and of the attached RAIRS experiment. (1) Planar mirror; (2) parabolic mirrors; (3) ZnSe IR windows; (4) ZnSe polariser; (5) MCT detector; (6) sample manipulator; (7) capacitive gauge.

The reactor is interfaced through external optics to a Magna IR 560 FTIR spectrometer from Nicolet. The external beam is focused on the sample inside the reactor off a parabolic mirror at a grazing incidence angle of 82°. After specular reflection on the sample, the beam is then focused by another parabolic mirror onto a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. A polariser (ZnSe) is inserted in the incoming IR beam, to allow the selection of either the p-polarised (light polarised in the plane of incidence) or the s-polarised (light polarised perpendicular to the plane of incidence) component of the light. With such an arrangement only polarised beam can be used, even for transmission measurements. By measuring successive spectra with p- and s-polarisation ($I_p$ and $I_s$), and by rationing $\Delta R/R = (I_p - I_s)/(I_p + I_s)$, the contribution of the gas phase, which is isotropic and insensitive to polarisation effect is cancelled out from the spectra. All FTIR spectra were collected using s- and p-polarised light with a spectral resolution of 4 $cm^{-1}$, with 512 or 1024 scans co-added and infrared radiation detected over the spectral range 4000–600 $cm^{-1}$.

The $Pd_8Ni_{92}(1\,1\,1)$ and Pt(1 1 1) single crystals, with a surface area of 0.86 and 0.5 $cm^2$, respectively, were cleaned under UHV in the preparation chamber by repeated cycles of argon ion bombardment and vacuum annealing at 1000 K (for 10 min) and 920 K, respectively. Oxidation treatment ($2 \times 10^{-8}$ Torr $O_2$, 600–1000 K) was performed periodically on Pt(1 1 1) before sputtering and annealing in order to remove carbon. The temperature of the single crystals was measured using a chromel–alumel thermocouple. The surface segregation and cleanliness of the crystals before the reactions were checked by XPS.

For the hydrogenation reactions, a mixture of the hydrocarbon and hydrogen was prepared in a stainless steel container and introduced into the isolated reactor via an all metal valve. Ratios of approximately 1/40 Torr of buta-1,3-diene/hydrogen and 1/200 Torr of benzene/hydrogen were used. Reactions were carried out at 295 K or above. The gas mixture was introduced into the isolated reactor at pressures of 10–40 Torr. Spectra were recorded using both p- and s-polarised light as the reaction progressed.

Buta-1,3-diene was purchased from air liquide (purity >99.5%) and benzene from Prolabo (normapur quality). Several freeze-pump-thaw cycles were carried out on benzene before use.

## 3. Results and discussion

### 3.1. Buta-1,3-diene hydrogenation

An example of the s-polarised IR spectra showing the gas phase species obtained during a reaction on $Pd_8Ni_{92}(1\,1\,1)$ is shown in Fig. 2. The first infrared spectrum (Fig. 2a) shows exclusively buta-1,3-diene, but as the reaction progresses, the intensity of the bands associated with buta-1,3-diene is reduced and other bands appear in the spectra. The strongest bands in the C–H stretching region of the spectra appear at lower wavenumbers as the reaction progresses, indicating the formation of $sp^3$ carbons. For ease of identification, gas phase spectra of buta-1,3-diene, but-1-ene, but-2-ene (4% *cis*- + 55% *trans*- + He) and butane are reported in Fig. 3. A complete assignment of the bands can be found in the literature [24–28]. After 197 min, the spectrum is dominated by a broad band at 2975 $cm^{-1}$. Along with the band at 1658 $cm^{-1}$, this provides a fingerprint of but-1-ene. Then, after 476 min a new band starts to develop at 963 $cm^{-1}$, characteristic of but-2-ene. In fact, as previously observed [12–14], but-1-ene undergoes isomerisation to

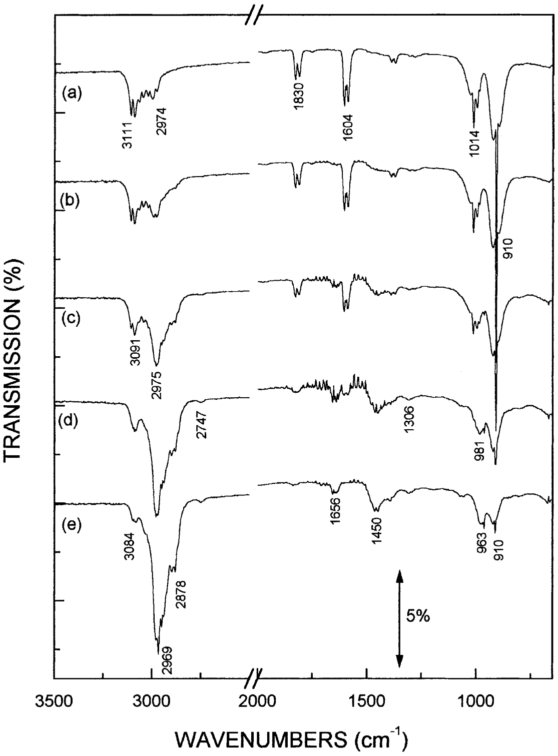


Fig. 2. RAIR spectra obtained during $C_4H_6/H_2$ reaction over a $Pd_8Ni_{92}(1\,1\,1)$ sample at 295 K (0.6 Torr $C_4H_6$ + 21 Torr $H_2$) as a function of increasing reaction time: (a) $t = 0$ min; (b) 52 min; (c) 197 min; (d) 476 min; (e) 1344 min. These spectra have been obtained with s-polarisation, a resolution of 4 $cm^{-1}$ and with 512 scans co-added.

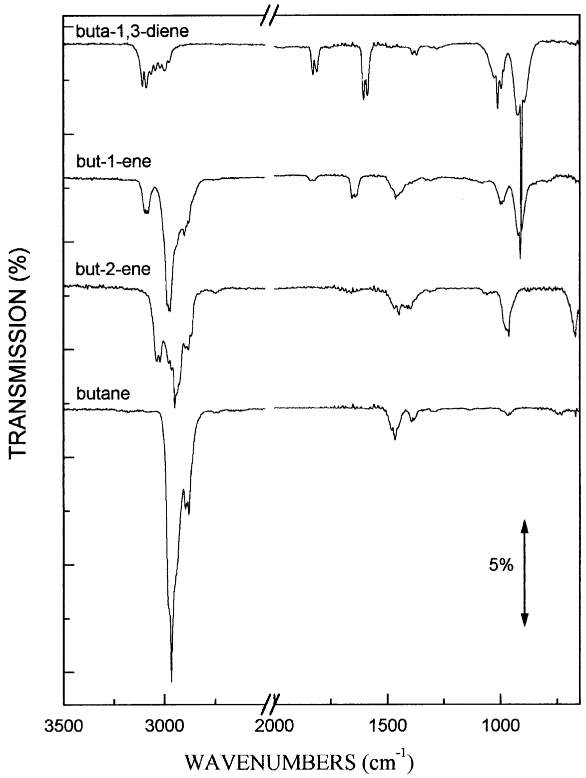


Fig. 3. Infrared spectra of buta-1,3-diene, but-1-ene, a mixture of *cis*- and *trans*-but-2-ene, and butane in their gas phase at 0.5 Torr and 300 K. These spectra have been obtained with s-polarisation, a resolution of 4 cm$^{-1}$ and an accumulation of 256 scans.

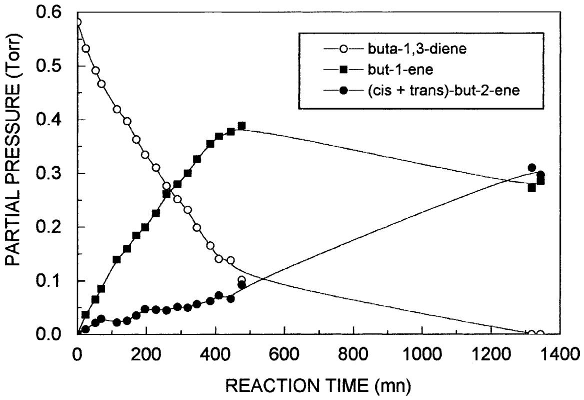


Fig. 4. Evolution of the partial pressures of buta-1,3-diene, but-1-ene and (*cis*+*trans*) but-2-ene as a function of reaction time in the reaction of buta-1,3-diene hydrogenation on $Pd_8Ni_{92}$(1 1 1) at 300 K. These pressures have been determined from the intensity of the characteristic 1605 and 1658 cm$^{-1}$ bands for buta-1,3-diene and for but-1-ene, respectively, normalised to the gas phase spectra of each molecule. For but-2-ene, the concentration was obtained by subtraction of the buta-1,3-diene and but-1-ene partial pressures from the total hydrocarbon pressure.

but-2-ene and after 1344 min, the infrared spectrum shows that but-2-ene is the predominant species.

A plot of partial pressure versus reaction time for buta-1,3-diene, but-1-ene and (*cis*+*trans*) but-2-ene is shown in Fig. 4. The partial pressures were calculated with reference to gas phase spectra of each molecule measured at a given pressure. This curve is in agreement with previous results obtained by QMS [12], at least for low conversion. However, the infrared spectra appear to be more sensitive to small quantities of the gases as the mass spectrometry data shows complete consumption of buta-1,3-diene while it is still present in the infrared spectrum. Furthermore, isomers but-1-ene and but-2-ene can be separated from IR spectra which was not possible from standard QMS.

The initial reaction rate (determined at 110 min and 21 Torr $H_2$) is about $1.1 \times 10^{15}$ mol/cm$^2$/s, which then decreases. The formation of the fully saturated product, the *n*-butane, was not observed in the time scale used for the measurements of the reaction. At a first sight, this is surprising if one compares the present data with the results obtained previously on the $Pd_8Ni_{92}$(1 1 1) surface [12]. However, in previous experiments, the volume of the reactor was very small (84 cm$^3$) compared to the present one (1000 cm$^3$), i.e., the number of hydrocarbon molecules to be transformed for complete conversion on the same surface area is more than one order of magnitude higher. There is also the possibility that the surface species undergo some cracking with the formation of some unreactive carbon which blocks the active sites. This has been confirmed by recent experiments performed on the same sample in a very large reactor (2000 cm$^3$) with various different partial pressures of butadiene: the rate of deactivation was found to be dependant on the buta-1,3-diene pressure. Varying the hydrogen pressure did not influence markedly the deactivation process. Auger spectra recorded after the reactions under such experimental conditions showed clearly the presence of carbon left on deactivated surfaces.

Treatment of the spectra recorded after reflection on the alloy surface with s- and p-polarised light to obtain the differential reflectance spectrum Δ*R*/*R* was carried out in order to observe the adsorbed species present during the reaction. The gas phase contributions were eliminated from the spectrum but, unfortunately, the absorption bands corresponding to the surface species were too weak in intensity to be observed above the noise level.

### 3.2. Benzene hydrogenation

The hydrogenation of benzene on Pt(1 1 1) was carried out at 295 K, below the temperature where the dehydrogenation of cyclohexane starts to occur [3]. The gas phase spectra of a mixture of benzene and hydrogen taken as a function of reaction time at 295 K are shown in Fig. 5. The initial spectrum shows exclusively benzene by comparison with the gas phase spectra [29,30]. After 1 h, there is the appearance of two bands in the CH stretching region at 2933 and 2862 $\text{cm}^{-1}$, which increase in intensity with time. By comparison with the gas phase spectrum of cyclohexane, cyclohexene and 1,3- and 1,4-cyclohexadiene [29,31–33], the possible products of the hydrogenation of benzene, these bands are assigned to the asymmetric and symmetric $CH_2$ vibrations of cyclohexane, respectively. In the infrared spectrum of cyclohexane gas phase, the only other band of significant intensity is at 1457 $\text{cm}^{-1}$; it is approximately 3–4 times weaker than the $CH_2$ stretches. The relatively weak intensity of this band and the fact that it is in the same region as the benzene $\nu$CC vibration at 1479 $\text{cm}^{-1}$, explains why it could not be resolved. The reaction was then monitored by the evolution of the bands at 2933 $\text{cm}^{-1}$ ($\nu$CH vibration of cyclohexane) and at 673 $\text{cm}^{-1}$ ($\gamma$CH vibration of benzene) as a function of reaction time (Fig. 6). The intensity of the benzene peaks decreases and only a small proportion of benzene is consumed over a reaction time of 60 h. The intensity of the 2933 $\text{cm}^{-1}$ band initially increases rapidly, but the rate of production of cyclohexane slows down with increasing time. There are two possible explanations for this behaviour. Either there is poisoning of the reaction by the formation of a carbonaceous layer on the surface, for example, or the gas phase composition reaches an equilibrium state. In order to discriminate between these two possibilities the reaction was carried out at different temperatures. Fig. 7 shows a plot of peak intensities for benzene (673 $\text{cm}^{-1}$ band) and cyclohexane (2933 $\text{cm}^{-1}$ band) as a function of reaction time and at different reaction temperatures. The composition of the gas phase cyclohexane/benzene varies reversibly with temperature.

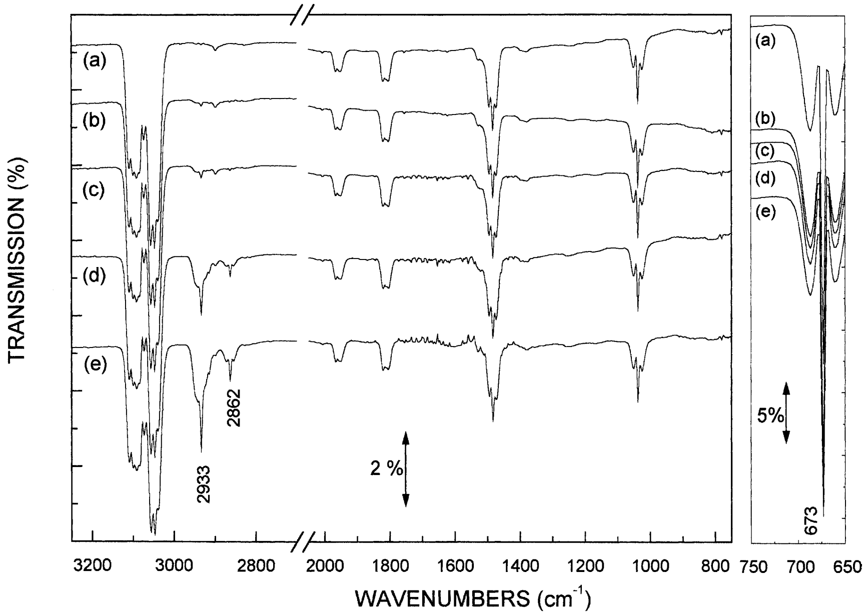


Fig. 5. Gas phase spectra obtained during the benzene hydrogenation reaction on Pt(1 1 1) at 295 K as a function of reaction time: (a) $t = 0$ min; (b) 1 h; (c) 2 h 10 min; (d) 16 h 30 min; (e) 64 h.

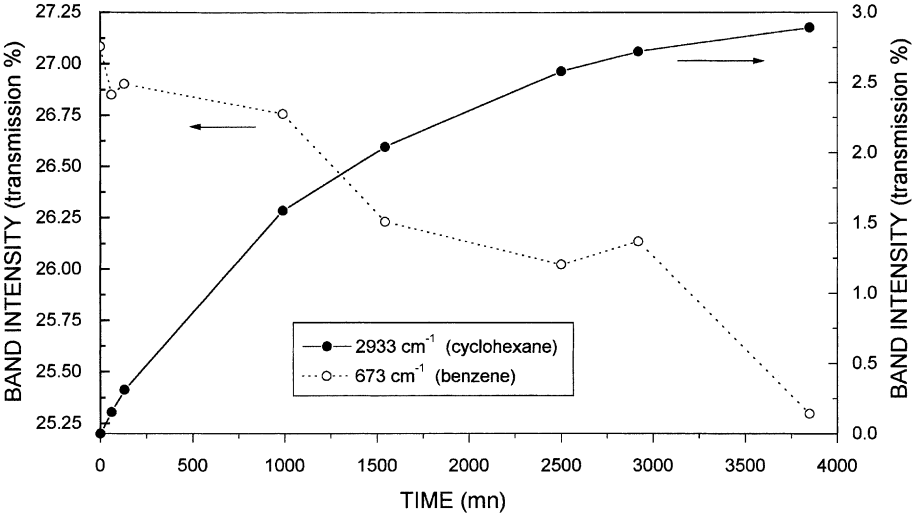


Fig. 6. Plot of the intensities of the 2933 and 673 cm$^{-1}$ bands representative of cyclohexane and benzene, respectively, as a function of reaction time on Pt(1 1 1).

With the temperature initially at 315–325 K, the benzene concentration decreases with time, while that of cyclohexane increases. After approximately 1000 min, the reaction appears to have stopped. After increasing the temperature to 395–410 K, the concentration of benzene initially decreases rapidly, as does that of cyclohexane, then a steady concentration of each is obtained. Reducing the temperature back to 295 K results in a new increase of both the benzene and cyclohexane concentrations. The reversibility of the results excludes the poisoning of the surface. We rather suggest an equilibrium between hydrogenation/dehydrogenation of cyclohexane/benzene/and partially hydrogenated by-products. Similar results

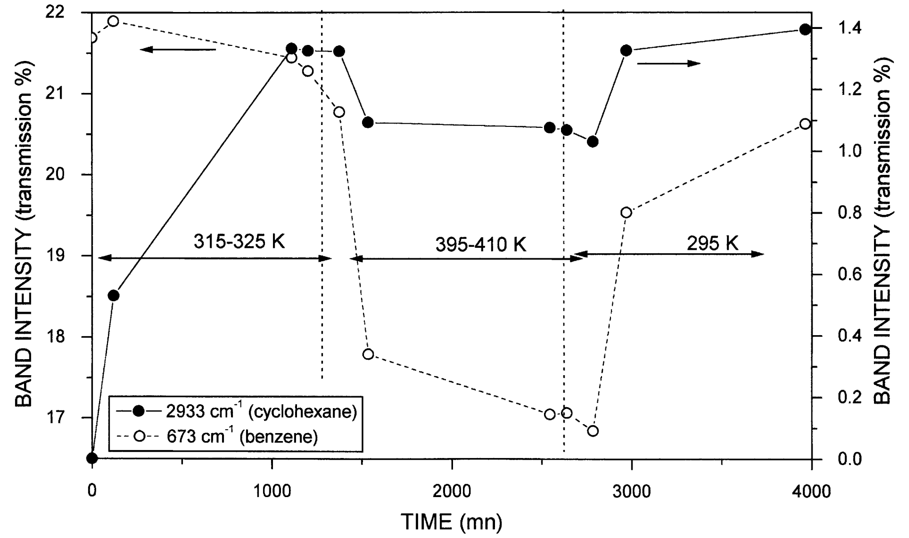


Fig. 7. Plot of the intensities of the 2933 and 673 cm$^{-1}$ bands representative of cyclohexane and benzene, respectively, as a function of reaction time at different reaction temperatures on Pt(1 1 1).

were observed by Su et al. [37] for hydrogenation/dehydrogenation of cyclohexene on Pt(1 1 1). In the infrared spectra, at 400 K, there are bands which cannot be attributed to benzene or cyclohexane. At this temperature, the concentration of cyclohexane decreases indicating the formation of less hydrogenated products. Since the benzene pressure also diminishes when the temperature is increased, a partially hydrogenated intermediate of the hydrogenation reaction (cyclohexene and/or cyclohexadiene) must be present. A better knowledge of the equilibrium between reactants and products with temperature would require further investigations.

Species adsorbed on the surface during the hydrogenation reaction at 295 K were observed by the use of p- and s-polarised infrared light (Fig. 8). Initially there is a narrow band at 2916 $cm^{-1}$ with a smaller and broader one at 2959 $cm^{-1}$. As the reaction progresses, the latter band increases in intensity. In the low frequency region of the spectrum, the baseline is too sloped for any bands to be resolved. However, by comparison with the RAIR spectra of Haq et al. [21] of benzene adsorbed on Pt(1 1 1) at 300 K, it is clear that the adsorbed species during the hydrogenation reaction cannot be attributed to molecularly adsorbed benzene. Nor can these bands be attributed to adsorbed cyclohexane, in agreement with surface studies which have shown that cyclohexane dehydrogenates to benzene at 300 K on Pt(1 1 1) [34,35]. Due to the lack of bands in the spectrum, it is difficult at this time to identify more precisely the adsorbed species.

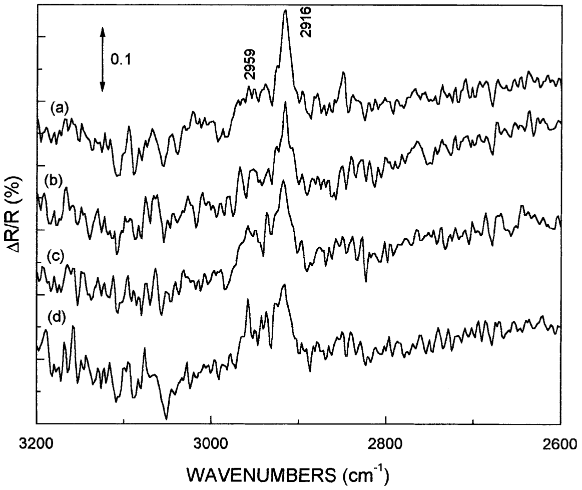


Fig. 8. Ratioed IR spectra of the surface species during the benzene hydrogenation reaction on Pt(1 1 1) as a function of reaction time: (a) 0 mn; (b) 16 h 30; (c) 48 h; (d) 64 h.

Fig. 9 shows the RAIR spectra obtained at UHV after the reactant gases have been pumped out of the reactor after 64.5 h of reaction. There are three bands in the CH stretching region at 2961, 2927 and 2854 $cm^{-1}$. In the low frequency region of the spectrum there is a broad band at 1382 $cm^{-1}$ with smaller bands at 1258 and 857 $cm^{-1}$. As with the species observed in situ, this spectrum is not that of molecularly adsorbed benzene or cyclohexane. The most likely assignment of this species is an adsorbed $C_6H_9$ species as observed by Henn et al. following the adsorption of cyclohexene [36] and cyclohexane [34] on

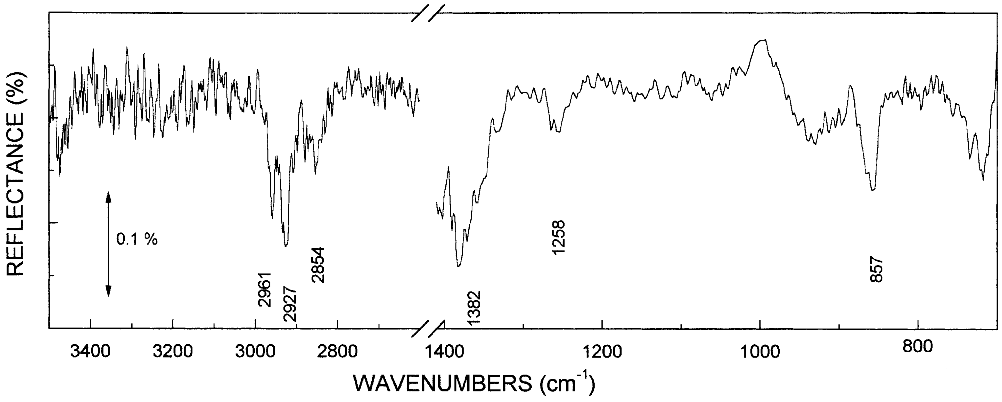


Fig. 9. RAIR spectrum obtained after evacuation of the reactor at 295 K following benzene hydrogenation on Pt(1 1 1).

Table 1
Vibrational frequencies (cm$^{-1}$) of $C_6H_9$ adsorbed on Pt(1 1 1)

| This work | Cyclohexene/Pt(1 1 1) 290 K [36] |
|---|---|
| 2961 | |
| 2927 | 2930 (br) $\nu$(C–H) |
| 2854 | 1450 $\delta CH_2$ |
| 1382 | 1355 $\omega CH_2$ |
| 1258 | 1290 $\tau CH_2$ |
| | 1160 $\rho CH_2$ |
| | 1080 $\nu CC + \rho CH_2$ |
| | 920 $\nu CC + CCH$ |
| 857 | 855 $\nu CC + CCH$ |

Pt(1 1 1) and by Su et al. [37]. Table 1 gives the band positions and assignments for such a species with reference to the HREELS results of Henn et al. [36]. Such an allylic structure which looks like a partially hydrogenated benzene ad-species [31,35–37] could be an intermediate species for partial or total hydrogenation/dehydrogenation of benzene/cyclohexane.

## 4. Conclusions

In this work, RAIRS has been used to follow catalytic reactions on well-defined monocrystalline samples of small area. It allows the simultaneous measurement of the evolution of the gas phase and the surface species which can emerge after elimination of the contribution of the gas phase by the use of s- and p-polarisations. Such species have been observed during the benzene hydrogenation on Pt(1 1 1) but not during the buta-1,3-diene hydrogenation on $Pd_8Ni_{92}$(1 1 1).

This technique is comparable to SFG for the observation of ad-species, but in addition, gas phase analysis is also possible. It could be greatly improved by the addition of a photoelastic modulator (polarisation modulation FTIR spectroscopy) [38] which would allow s- and p-polarised contributions to be measured at the same time (i.e., under exactly the same experimental conditions).

This new interesting field of surface investigations is very important for the observation of surface species under environmental conditions and identification of the precursors or intermediates of catalytic reactions in order to determine the pathways of the reaction.

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## References

[1] P.S. Cremer, G.A. Somorjai, J. Chem. Soc., Faraday Trans. 91 (1995) 3671–3677.
[2] P.S. Cremer, B.J. McIntyre, M. Salmeron, Y.R. Shen, G.A. Somorjai, Catal. Lett. 34 (1997) 11–18.
[3] X. Su, K. Kung, J. Lahtinen, R.Y. Shen, G.A. Somorjai, Catal. Lett. 54 (1998) 9–15.
[4] P.W. Jacobs, G.A. Somorjai, J. Mol. Catal. A 131 (1998) 5–18.
[5] G.A. Somorjai, G. Rupprechter, J. Phys. Chem. B 103 (1999) 1623–1638.
[6] X.D. Zhu, H. Suhr, Y.R. Shen, Phys. Rev. B 35 (1987) 3047–3050.
[7] Y.R. Shen, Nature 337 (1989) 519–525.
[8] Y.R. Shen, Surf. Sci. 299/300 (1994) 551–562.
[9] R.G. Greenler, J. Chem. Phys. 44 (1966) 310.
[10] J.P. Boitiaux, J. Cosyns, S. Vasudevan, Appl. Catal. 6 (1983) 41–51.
[11] J. Massardier, J.C. Bertolini, A.J. Renouprez, Proceedings of the Ninth Congress on Catalysis, Vol. 3, 1988, p. 1222.
[12] A.C. Michel, L. Lianos, J.L. Rousset, P. Delichère, N.S. Prakash, J. Massardier, Y. Jugnet, J.C. Bertolini, Surf. Sci. 416 (1998) 288–294.
[13] L. Lianos, Y. Debauges, J. Massardier, Y. Jugnet, J.C. Bertolini, Catal. Lett. 44 (1997) 211.
[14] J.C. Bertolini, Appl. Catal. A 191 (2000) 15–21 and references therein.
[15] G. Tourillon, A. Cassuto, Y. Jugnet, J. Massardier, J.C. Bertolini, J. Chem. Soc., Faraday Trans. 92 (1996) 4835–4841.
[16] J.C. Bertolini, A. Cassuto, Y. Jugnet, J. Massardier, B. Tardy, G. Tourillon, Surf. Sci. 349 (1996) 88–96.
[17] S.A. Stanislaeus, B.H. Cooper, Catal. Rev. Sci. Eng. 36 (1994) 75.
[18] S.D. Lin, M.A. Vannice, J. Catal. 143 (1993) 539–553.
[19] S. Lehwald, H. Ibach, J.E. Demuth, Surf. Sci. 78 (1978) 577–590.
[20] M. Abon, J.C. Bertolini, J. Billy, J. Massardier, B. Tardy, Surf. Sci. 162 (1985) 395–401.
[21] S. Haq, D.A. King, J. Phys. Chem. 100 (1996) 16957–16965.
[22] J.E. Demuth, H. Ibach, S. Lehwald, Phys. Rev. Lett. 40 (1978) 1044.
[23] Y. Jugnet, N.S. Prakash, J.C. Bertolini, S.C. Laroze, R. Raval, Catal. Lett. 56 (1998) 17–21.
[24] V.E. Bondybey, J.W. Nibler, Spectrochim. Acta A 29 (1973) 645–658.

[25] Y. Furukawa, H. Takeuchi, I. Harada, M. Tasumi, Bull. Chem. Soc. Jpn. 56 (1983) 392–399.

[26] A.J. Barnes, J.D.R. Howells, J. Chem. Soc., Faraday Trans. 69 (1973) 532.

[27] I.W. Levin, R.A.R. Pearce, W.C. Harris, J. Chem. Phys. 59 (1973) 3048.

[28] E. Gallinea, B. Cadioli, Vib. Spectrsoc. 13 (1997) 163–174.

[29] C.J. Pouchert, The Aldrich Library of FT-IR Spectra, Vol. 3, Vapor phase, 1st Edition, Aldrich Chem. Co., Milwaukee, 1989.

[30] N.C. Chen, L.P. Ford, R.I. Masel, Catal. Lett. 56 (1998) 105–109 and references therein.

[31] C.L.A. Lamont, M. Borbach, R. Martin, P. Gardner, T.S. Jones, H. Conrad, A.M. Bradshaw, Surf. Sci. 374 (1997) 215–228 and references therein.

[32] N. Neto, C.D. Lauro, E. Castellucci, S. Califano, Spectrochim. Acta A 23 (1967) 1763–1774.

[33] H.D. Stidham, Spectrochim. Acta 21 (1965) 23–32.

[34] M.E. Bussell, F.C. Henn, C.T. Campbell, J. Phys. Chem. 96 (1992) 5978–5982.

[35] D.P. Land, W. Erley, H. Ibach, Surf. Sci. 289 (1993) 237–246.

[36] F.C. Henn, A.L. Diaz, M.E. Bussell, M.B. Hugenschmidt, M.E. Domagala, C.T. Campbell, J. Phys. Chem. 96 (1992) 5965–5974.

[37] X. Su, K.Y. Kung, J. Lahtinen, Y.R. Shen, G.A. Somorjai, J. Mol. Catal. A 141 (1999) 9–19.

[38] D. Blaudez, T. Buffeteau, J.C. Cornu, B. Desbat, N. Escafre, M. Pezolet, J.M. Turlet, Thin Solid Films 242 (1994) 146–150.