

Chapter 5

Reactivity of Hydrocarbons

In this chapter an overview on different systems will be given. The interaction of Pd model catalyst with hydrocarbons with increasing complexity (more than one carbon atom) was investigated under UHV conditions and under “technical” conditions (mbar pressure), to demonstrate the applicability of PM-IRAS-spectroscopy to study different systems.

In particular results will be presented about the adsorption and reaction of ethene with hydrogen on the Pd(111) single crystal surface, and of butadiene and H₂.

5.1 Ethylene, C₂H₄

It is known from electron diffraction data [160] that ethylene (C₂H₄) is a flat molecule in the gas phase with all six atoms in a plane and with bond angles of 120°. There are three sp² hybrid orbitals and one p_z orbital per carbon atom. The sp² hybrid orbitals form one carbon-carbon σ bond and two carbon-hydrogen σ bonds. The two remaining p_z orbitals (one at each carbon, each orbital containing one electron) form a π bond between the carbon atoms. This π bond, by the nature of its sideways overlap of the constituent p_z orbitals, is weaker than the σ bond. Moreover, the electrons of the π bond are exposed above and below the plane of the molecule, determining the reactivity of alkenes toward electrophiles. The equilibrium distance between the two carbon atoms is 1.33 Å.

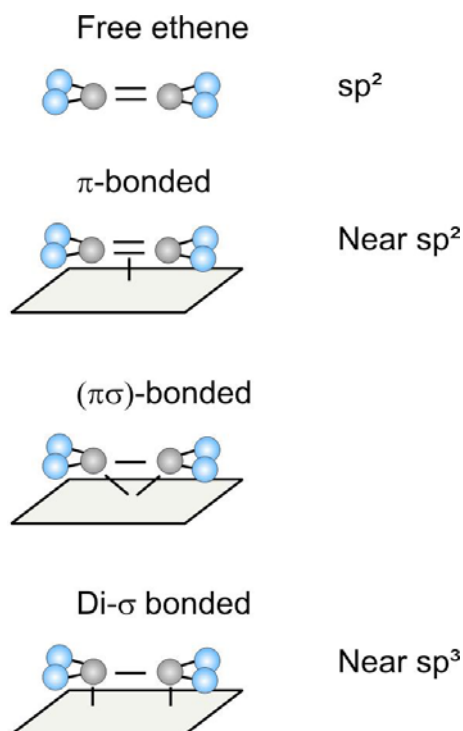


Figure 5.1: Schematic drawing of the different adsorption geometries of C_2H_4 on a metal surface. The different hybridisation characters are also reported.

The adsorption of ethylene on group VIII noble metal surfaces is a thoroughly studied prototypical reaction in surface chemistry and catalysis of alkenes on metal surfaces. Upon the adsorption on a metal surface, modifications of the geometry, of the electronic structure and of the vibrational frequencies of C_2H_4 are observed. Depending on the degree of interaction of ethylene with the metal, different adsorption geometries can occur [161]. Figure 5.1 reports schematically the different adsorption geometries of ethylene on metal surfaces. For a weak interaction with the metal, C_2H_4 bonds to only one metal atom (on-top geometry) through the π electrons and the sp^2 hybridization of the carbon atoms is almost preserved. The C-C axis is parallel to the surface. This species is referred as π -bonded ethylene in the literature. Its adsorption energy on a Pd surface was calculated to be about 60-65 kJ/mol [162,162]. If there is a stronger interaction with the metal, there is a rehybridisation of the carbon atoms towards a sp^3 character. The molecule bonds to the surface through two σ -bonds with two metal atoms in a bridge-configuration. This species is called di- σ -bonded ethylene and its adsorption energy on Pd is about 80-85 kJ/mol

[162,163]. A third structure has been reported as well [161], an intermediate metallocyclopropane structure, which has been denoted as ($\pi\sigma$)-bonded ethylene.

5.1.1 Ethylene adsorption on Pd(111)

According to the literature [164], dehydrogenation of C_2H_4 can be avoided at low temperature. Depending on the particular metal surface, π -bonded and di- σ -bonded ethylene are the major species observed for temperatures typically <200 K, while ethylidyne species ($\equiv C-CH_3$) are formed after adsorption on (111)-type surfaces at 300 K. *Gates and Kesmodel* [165] proposed π -bonded ethylene species for adsorption on Pd(111) at 150 K on the basis of HREELS. The same authors suggested that π -bonded ethylene partially converted to ethylidyne after heating the surface to 300 K. More recent DFT calculations [166] suggested instead that both π -bonded and di- σ -bonded ethylene species have approximately the same stability on the surface. On alumina supported Pd particles, *Frank et al.* [164] observed both ethylene species by means of IRAS for adsorption at 90 K.

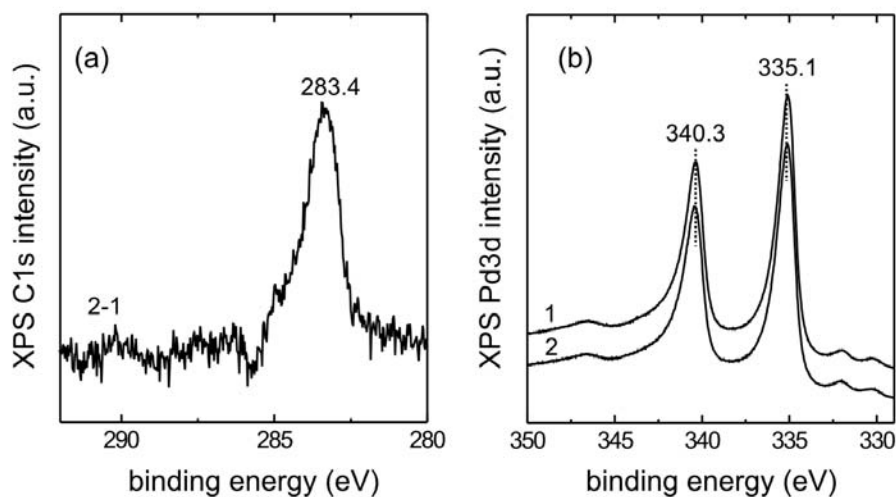


Figure 5.2: XPS in the C1s (a) and Pd3d (b) regions of 4 L C_2H_4 adsorbed on Pd(111) at 100 K: as prepared (trace 1); after C_2H_4 exposure at 100 K (trace 2). In the C1s region, only the difference spectrum (2-1) is reported.

In Figure 5.2 the adsorption of C_2H_4 at 100 K on a clean Pd(111) surface is recorded by means of XPS. A single peak in the C1s region (Fig. 5.2a) is observed at ~ 283.4 eV, characterized by a tail towards higher BE. No shift and a small intensity decrease are observed in the Pd3d region (Fig. 5.2b) after adsorption of C_2H_4 . Recent HR-XPS measurements on the same system [163], observed two major spectral features in the C1s region at 283.08 and 283.5 eV after adsorption of ethylene at 100 K. Using different photon energies the same relative emission intensities for the two peaks were always observed, indicating emission from two equivalent carbon atoms. The authors concluded that the observed low-temperature phase of C_2H_4 on Pd(111) laid flat on the surface and, in comparison with HREELS and DFT calculation, they suggested the presence of a di- σ bonded configuration.

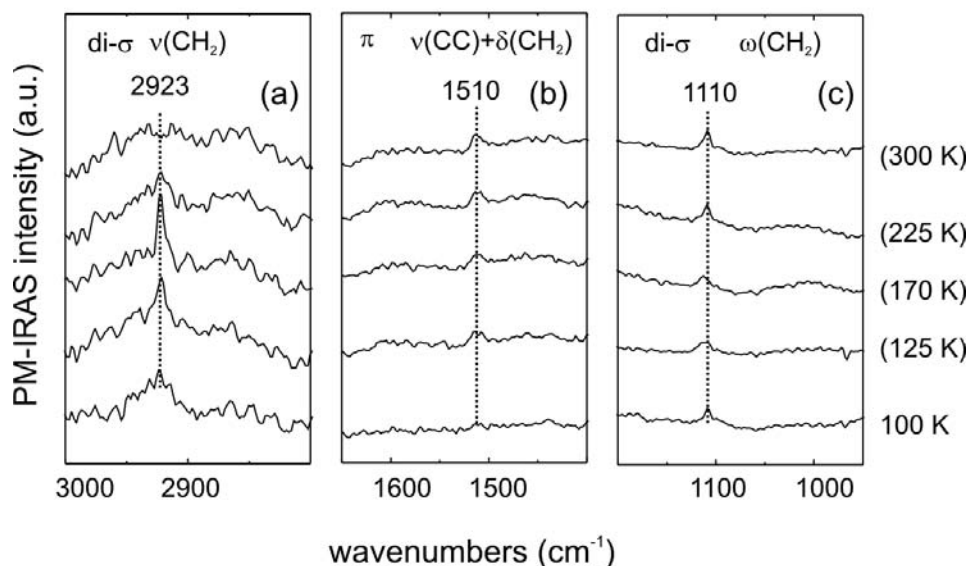


Figure 5.3: PM-IRAS spectra of 4 L C_2H_4 dosed at 100 K on Pd(111). The surface was then flashed to increasing temperature. All the spectra were acquired at 120 K.

The low-temperature phase of ethylene on Pd(111) was also studied by PM-IRAS, following as well the evolution of the adsorbed layer upon increasing the temperature, as reported in Figure 5.3. 4 L ethylene were dosed at 100 K on Pd(111), subsequently the surface was flashed to increasing temperature and the corresponding spectra were all acquired at 100 K. Bands appear at 2923 cm^{-1} (Fig. 5.3a), at 1510 cm^{-1} (Fig. 5.3b) as well as at $\sim 1100\text{ cm}^{-1}$ (Fig. 5.3c), presumably due to two different coordinated ethylene species on the Pd(111) surface. According to previous IRAS [164] and HEELS studies [163], di- σ

bonded ethylene is present with signals at 2923 cm^{-1} ($\nu(\text{CH}_2)$) and, presumably, at $\sim 1100\text{ cm}^{-1}$ ($\omega(\text{CH}_2)$), while the band at 1510 cm^{-1} should correspond to $\nu(\text{CC})$ of π -bonded ethylene. A recent DFT work [166] suggested that modes around 1000 and 1200 cm^{-1} , as well as the mode at 1500 cm^{-1} , are due to coupled C=C stretching and CH_2 bending motions. Furthermore, they found that the calculated vibrational frequencies for the di- σ adsorption mode on a Pd surface are very similar to those found for the π -bonded mode. The same authors attributed the feature at 1500 cm^{-1} to C=C and CH_2 modes of π -bonded ethylene, while the band at $\sim 1130\text{ cm}^{-1}$ was attributed to CH_2 scissor mode (with considerable fraction of C=C stretching character) of di- σ bonded ethylene. Therefore, from the analysis of the PM-IRAS features of Fig. 5.3, it is possible to conclude that both di- σ bonded and π -bonded ethylene species are adsorbed on the Pd(111) surface at low temperature. After flashing the sample to increasing temperature, no drastic shift in frequency is observed and no other bands develop. Probably, under the applied conditions (UHV/low coverage), the amount of the dehydrogenated product ethylidyne is too low to be detected by PM-IRAS. Partial desorption of the adsorbed layer after heating to 300 K may also be considered [167]. Former TPD study on Pd(111) [37] showed that the weakly adsorbed π -bonded ethylene species desorbed at low temperatures ($\sim 200\text{ K}$), while di- σ bonded ethylene desorbed at $\sim 300\text{ K}$. The peak at 1510 cm^{-1} observed in Fig. 5.3 was assigned to π -bonded ethylene. However, in lights of previous TPD results [37], the spectroscopical features observed in Fig. 5.3 after flash to 225 K and 300 K can be probably assigned to C_nH_n fragment species from ethylene decomposition.

The thermal evolution of C_2H_4 from 100 K to higher temperature was followed as well by XPS, as illustrated in Figure 5.4. The Pd(111) surface was exposed to 4 L C_2H_4 at 100 K, subsequently heated to the indicated temperatures and then cooled down to 100 K, where the spectra have been measured. Fig. 5.4b shows a comparison between the Pd3d trace of the sample “as prepared” and of the sample after C_2H_4 adsorption at 100 K. No shift is observed in the Pd3d BE after C_2H_4 adsorption. The XPS spectra in the C1s region (Fig. 5.4a) from 100 to 250 K show a broad peak at $\sim 283.5\text{ eV}$, which could be attributed to di- σ ethylene. The second peak developing with increasing (flashing) temperature at $\sim 286\text{ eV}$ is presumably due to CO adsorbed from the background. After flashing the sample to 300-400 K, the peak at lower BE decreases in intensity and shifts to 284 eV. Unfortunately, due to the low resolution of the XPS setup, it is not possible to clarify the nature of the observed

shift. It may be due to partial desorption of the adsorbed layer and to partial dehydrogenation to form ethylidyne species (ethylidyne was observed on Pd particles up to 250-300 K [164,168]) and carbon deposits, see [164,168]. A recent combined high-resolution XPS and TDS study [163] did not observe conversion of ethylene adsorbed at 100 K on Pd(111) to ethylidyne by heating from 100 to 350 K.

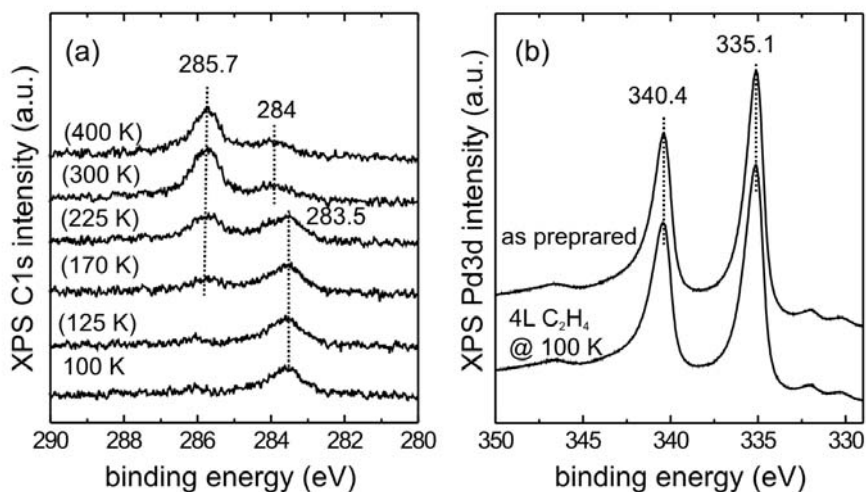


Figure 5.4: XPS spectra in the C1s (a) and Pd3d (b) regions of 4 L C₂H₄ adsorbed at 100 K on Pd(111). As for the PM-IRAS experiment, the surface was subsequently flashed to increasing temperatures and the corresponding spectra were recorded at 100 K.

Ethylidyne is observed after dosing ethylene on Pd(111) directly at 300 K, as shown in Figure 5.5. PM-IRAS spectra are taken at 300 K as a function of ethylene pressure on Pd(111) up to a pressure of 10 mbar. Spectra 1 and 2 are taken at 10^{-5} and 10^{-4} mbar C₂H₄, respectively. The intense feature at 1332 cm^{-1} present in both spectra is due to a methyl bending vibration ($\delta(\text{CH}_3)$) of adsorbed ethylidyne species. *Stacchiola et al.* [169] suggested that ethylidyne species occupy fcc-hollow sites on Pd(111). At 1805 cm^{-1} a small broad feature is due to adventitious CO adsorbed from the background. The CO peak appears quite pronounced in the PM-IRAS spectra because of the larger dynamic dipole moment of the $\nu(\text{CO})$ mode compared to the weaker ethylene vibrations. Increasing the ethylene pressure to the mbar range, the peak assigned to methyl vibration shifts to 1339 cm^{-1} and increases in intensity, (as well as the peak due to CO adsorbed from the background).

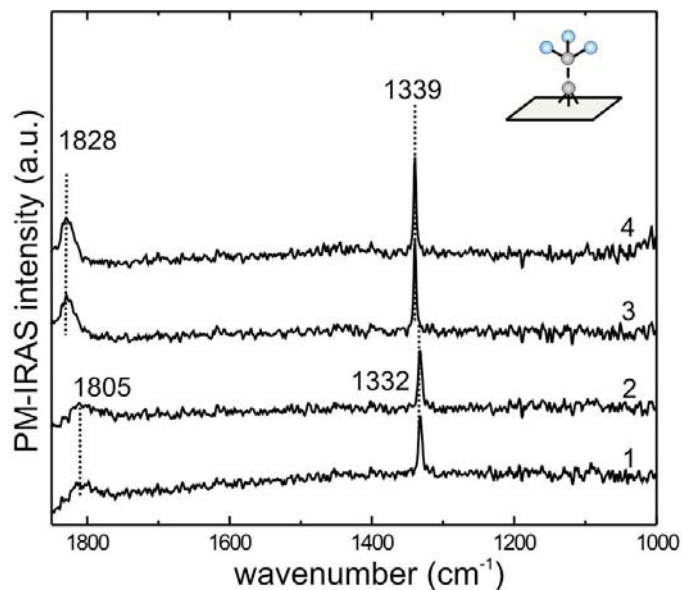


Figure 5.5: PM-IRAS spectra of C_2H_4 adsorbed on Pd(111) at 300 K for different pressures: in 10^{-5} mbar (trace 1); in 10^{-4} mbar (trace 2); in 1 mbar (trace 3); in 10 mbar (trace 4).

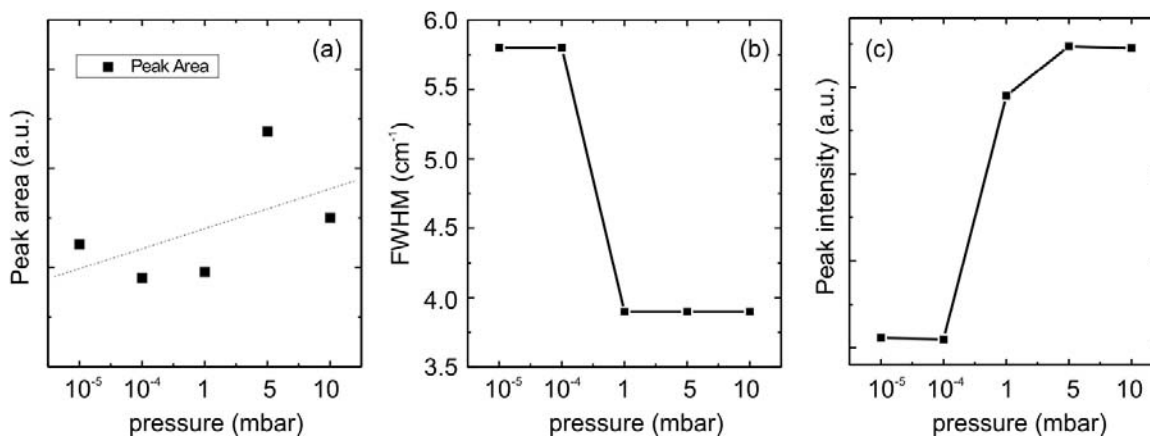


Figure 5.6: (a) Plot of the integrated area of the $1332\text{-}1339\text{ cm}^{-1}$ feature in the PM-IRAS spectra of Fig. 5.5 as a function of ethylene pressure. (b) Plot of the full width at half maximum (FWHM) of the $1332\text{-}1339\text{ cm}^{-1}$ feature in the PM-IRAS spectra of Fig. 5.5 as a function of ethylene pressure. (c) Plot of the intensity of the $1332\text{-}1339\text{ cm}^{-1}$ feature in the PM-IRAS spectra of Fig. 5.5 as a function of ethylene pressure.

Changes in the spectral feature of the ethylidyne related peak as a function of the C_2H_4 pressure are reported in Figure 5.6. As the pressure increases, there is an increase in the peak area (Fig. 5.6a), as well as an increase in the peak intensity (Fig. 5.6c), which could indicate that more ethylidyne can be accommodated on the surface. At mbar pressure the peak shifts $+7\text{ cm}^{-1}$ and the FWHM decreases (Fig. 5.6b). The sharpening of the peak may be related to ordering of adsorbed ethylidyne species.

Ethylene adsorption on Pd(111) at 300 K was also followed by XPS (Figure 5.7). The C1s XPS spectrum (Fig. 5.7a) of ethylidyne on Pd(111) shows one broad peak at $\sim 283.9\text{ eV}$ (calculated coverage = 0.21 ML) and CO adsorbed from the background with a feature at $\sim 286\text{ eV}$ (calculated $\theta(\text{CO}) = 0.15\text{ ML}$, using the (2x2)-CO structure at saturation coverage as a reference). The XPS spectra of Fig. 5.7 were acquired after several minutes of exposure, and thus the CO-related peak shows up predominantly. *Sock et al.* [163] observed two peak components at 283.70 and 284.05 eV, corresponding to the inner and outer carbon atoms of ethylidyne, respectively, after 100 L C_2H_4 on Pd(111) at 300 K.

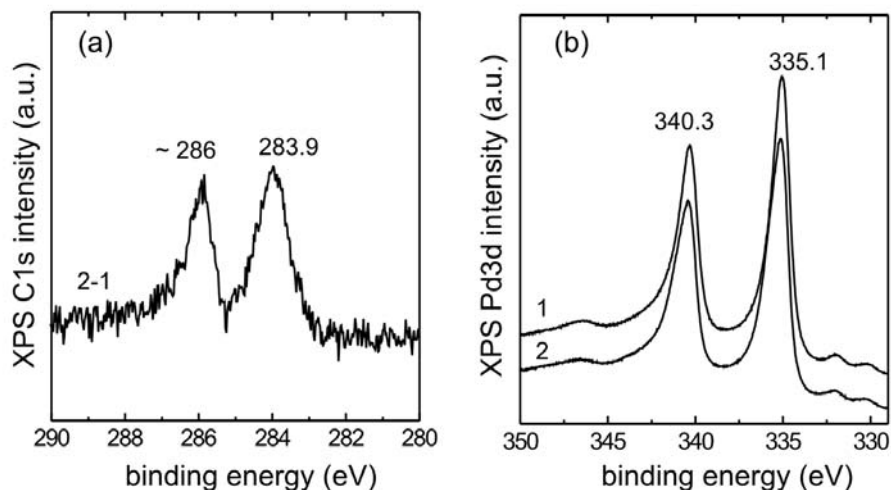


Figure 5.7: XPS spectra in the C1s (a) and Pd3d (b) regions of C_2H_4 adsorbed at 300 K on Pd(111): as prepared (trace 1); in 10^{-6} mbar C_2H_4 at 300 K (trace 2). In the C1s region, only the difference spectrum (2-1) is reported.

5.1.2 Ethylene and H₂ adsorption on Pd(111)

Ethylene hydrogenation on a metal surface is a thoroughly studied reaction which has been used as a model to understand hydrogenation reactions of more complicated alkenes. Despite the apparent simplicity of C₂H₄ hydrogenation, its chemistry is rich and complicated and still some questions remain unsolved. It is generally believed that this reaction follows the general features proposed by Horiuti and Polanyi in 1934 [170]. The Horiuti-Polanyi mechanism suggests that ethylene is adsorbed on the surface of transition metals by using one of the carbon-carbon double bonds and that hydrogen is adsorbed dissociatively. Subsequent hydrogenation to adsorbed ethyl takes place. Finally the ethyl intermediate hydrogenates to ethane, C₂H₆, which desorbs in the gas phase. *Cremer and Somorjai* [171] demonstrated that the more likely mechanism for ethylene hydrogenation goes through the π -bonded species and showed that ethylidyne species are only spectator species during the reaction. *Doyle et al.* [172] reported that under UHV conditions Pd particles have a higher activity for ethylene hydrogenation to ethane than Pd(111) (which was reported to be inactive).

In the following, co-adsorption experiments under UHV conditions on Pd(111) will be presented. Subsequently, ethylene hydrogenation reaction under mbar pressure will be discussed.

Figure 5.8 shows a series of PM-IRAS spectra for ethylene (10 L) adsorbed on hydrogen precovered (5 L H₂ exposure) Pd(111) at 100 K, and annealed to increasing temperatures. At 100 K (trace 1) a sharp peak is observed at 933 cm⁻¹, which is assigned to a HCH bending mode ($\omega(\text{CH}_2)$) of π -adsorbed ethylene species. (No peaks were observed at ~2920 cm⁻¹ for the $\nu(\text{CH}_2)$ stretching mode, thus excluding the presence of di- σ bonded ethylene). This corroborates the finding that π -bonded ethylene is formed on a H-covered surface (see [173] and references therein). Increasing the surface temperature causes a broadening of the peak, probably due to the formation of different ethylene species on H/Pd(111). At 200 K (spectrum 5) π -bonded ethylene is still present on the surface, but its feature around 950-930 cm⁻¹ is not anymore well defined. According to the literature [174], π -bonded species (formed under the same condition applied in Fig. 5.7) should desorb at 250 K.

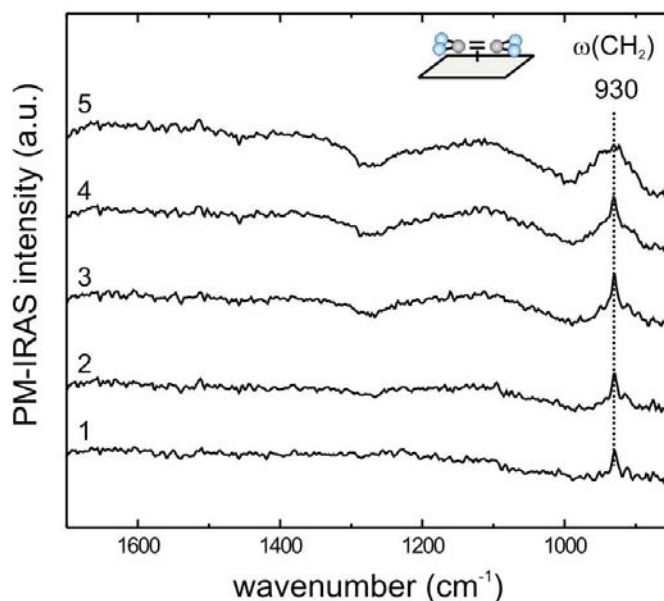


Figure 5.8: PM-IRAS spectra of C_2H_4 dosed at 100 K on hydrogen precovered Pd(111) surface: (1) 10 L C_2H_4 were dosed on Pd(111) at 100 K after 5 L H_2 adsorbed at the same temperature. The surface was then heated to increasing temperatures: (2) 135 K; (3) 155 K; (4) 170 K; (5) 200 K.

As observed by PM-IRAS (Fig. 5.8) and former IRAS experiments [174], the presence of pre-adsorbed hydrogen affects the adsorption of ethylene. Only π -bonded species are detected (by PM-IRAS) on the surface when hydrogen is pre-dosed on Pd(111). Hydrogen occupies three-fold hollow sites and thus (partially) blocks di- σ bonded ethylene, while π -bonded species can still adsorb on on-top sites. Therefore, ethylene is mainly bonded in a π -configuration on H/Pd(111) at low temperature [173]. These C_2H_4 species were also measured on H/Pd(111) by XPS (Figure 5.9). The Pd3d intensity (Fig. 5.9b) decreases lightly after the adsorption of ethylene on H/Pd(111) at 100 K, and no shift in BE is observed. In the C1s region (Fig. 5.9a) a peak at ~ 283.6 eV is observed, which could be attributed to π -bonded ethylene species [163]. A smaller amount of CO adsorbed from background pressure is also observed at ~ 286 eV.

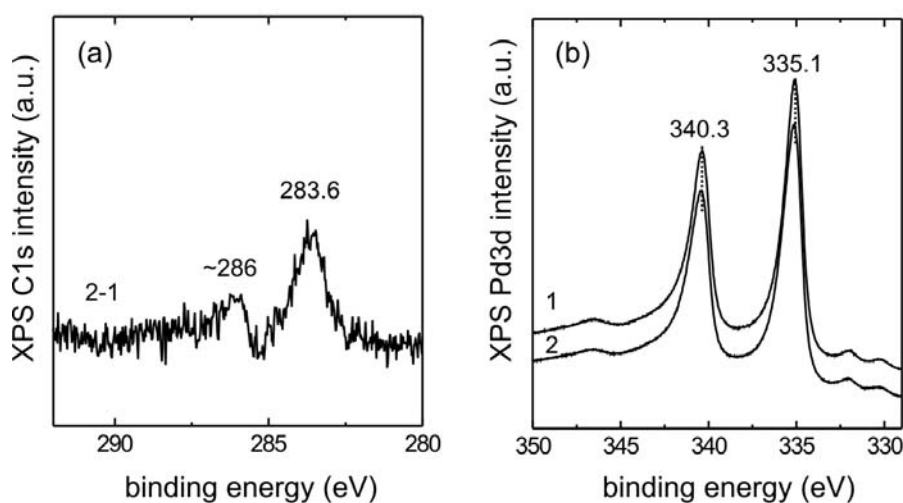


Figure 5.9: XPS spectra in the C1s (a) and Pd3d (b) regions of 10 L C₂H₄ added on hydrogen precovered (5 L H₂ exposure) Pd(111) surface: as prepared (trace 1); after H₂ and C₂H₄ exposure (trace 2). In the C1s region, only the difference spectrum (2-1) is reported.

The observed binding energies in the C1s region for di- σ - and π -bonded ethylene and ethylidyne are very close together, i.e. 283.4 eV (Fig. 5.2), 283.6 eV (Fig. 5.9) and 283.9 eV (Fig. 5.7), respectively. Based on previous XPS data [163] and on the present PM-IRAS measurements, the observed BE for the C1s signals were assigned to the corresponding species.

Doyle et al. [172, 175] reported that under low pressure conditions ethylene hydrogenation to ethane does not occur on Pd(111) in contrast to the Pd particles, while *Stacchiola et al.* [174] observed small amounts of ethane (only a few percent) by TPD.

Ethylene hydrogenation at millibar pressure was followed by PM-IRAS for different conditions (Figure 5.10): 100 mbar 4:1 (H₂:C₂H₄) gas mixture was dosed on Pd(111) at 350 K (traces 1-3) and at 375 K (traces 4,5). No intermediate species could be detected under the two different reaction conditions (Fig. 5.10a). Only a small signal was observed at ~ 1930 cm⁻¹ related to adsorbed CO from the background. Due to the weak intensity of this peak, the CO coverage is estimated to be below 0.1 ML. The small amount of adsorbed CO did not influence the activity of Pd(111) for ethylene hydrogenation. CO poisoning of

ethylene hydrogenation over Pt catalysts was observed when high pressure (>1 Torr) CO was introduced in the gas mixture (10 Torr C_2H_4 , 100 Torr H_2) [176,177].

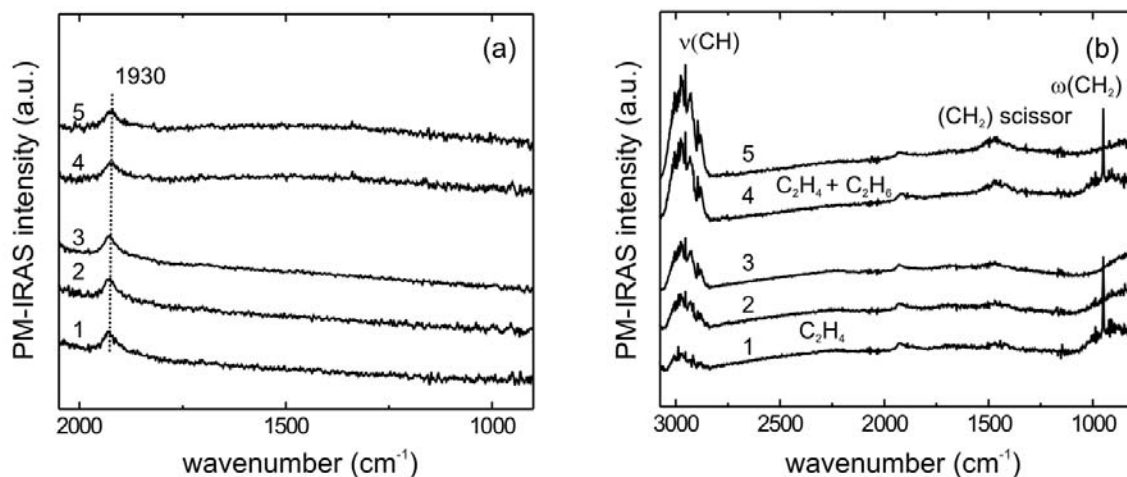


Figure 5.10: (a) Surface (p-s) and (b) gas-phase (p+s) PM-IRAS spectra measured during ethylene hydrogenation at mbar pressure on Pd(111) of 100 mbar 4:1 ($H_2:C_2H_4$) gas mixture: at 350 K after 5 min (trace 1), 10 min (trace 2), and 22 min (trace 3); at 375 K after 5 min (trace 4) and 10 min (trace 5).

When the 100 mbar 4:1 ($H_2:C_2H_4$) gas mixture was dosed at 350 K, the initial (p+s) spectrum (Fig. 5.10b, trace 1) showed only features due to the reactant C_2H_4 . After a few minutes of reaction, the product ethane was already visible in the gas phase (Fig. 5.10b, trace 2), and after only 22 minutes of reaction ethylene completely converted into ethane (Fig. 5.10b, trace 3). When the same gas mixture was dosed at 375 K, C_2H_6 was observed as gas phase product already after a few minutes (Fig. 5.10b, trace 4). At this temperature, 100% conversion of ethylene to ethane was reached after only 10 minutes. In fact, ethylene hydrogenation is known as one of the fastest heterogeneous catalytic reactions [171].

5.2 Summary

Di- σ bonded and π -bonded ethylene configurations and ethylidyne species have been detected on Pd(111) under different conditions using a combination of XPS and PM-IRAS. PM-IRAS spectra of ethylene adsorption at low temperature on a hydrogen-precovered

Pd(111) surface showed (mainly) π -bonded C_2H_4 species due to (partial) site blocking of hydrogen (adsorbed on hollow-sites).

Pd(111) has been reported to be rather inactive for ethylene hydrogenation to ethane under UHV conditions, while PM-IRAS (p+s) gas phase spectra showed that at elevated pressure and temperature (100 mbar, 350-375 K) complete hydrogenation to ethane occurs on Pd(111) single crystal after only few minutes of reaction. The observed different activity of Pd(111) for ethylene hydrogenation under UHV and at elevated pressure emphasizes the importance of being able to investigate heterogeneous catalytic systems within a wide pressure range. PM-IRAS is a powerful *in-situ* technique for studying heterogeneous catalytic systems from UHV to atmospheric pressures.

During high pressure ethylene hydrogenation *in-situ* PM-IRAS (p-s) surface spectra did not detect any intermediate species, probably due to low concentration of the involved species and/or to their adsorption geometry (i.e. molecules laying flat on the surface). Therefore, a direct proof of the reaction mechanism can not be given.

5.3 Butadiene

The hydrogenation of 1,3-butadiene on Pd single crystals and alumina supported Pd particles has been recently studied in our group following the reaction under elevated pressure by gas chromatography (GC measurements performed by J. Silvestre Albero). Detailed information has been obtained on the catalytic behavior of the different Pd model catalysts [178,179,180].

Here the butadiene/Pd(111) system is investigated using XPS, LEED and IRAS in order to gain information on adsorption geometries and stability, on the nature of intermediates during the hydrogenation reaction and on the state of the surface (i.e. change in oxidation state, formation of carbon deposits) “*post-mortem*”. In contrast to the order followed in the previous chapters, high pressure butadiene measurements are firstly considered. After describing the catalytic behaviour of the butadiene/Pd(111) system, spectroscopic measurements under UHV are discussed, which information may help to better understand the reported kinetic behaviour.

The catalytic hydrogenation of 1,3-butadiene is an interesting process, both from an industrial and academic point of view. There are four reaction products (1-butene, trans/cis-2-butene and n-butane) and, consequently, regioselectivity is required to obtain the desired compound [181,182]. Previous studies have shown that Pd catalysts are highly active and highly selective towards butene formation while Pt catalysts mostly yield n-butane via complete hydrogenation [183].

Silvestre et al. have shown that the catalytic activity and selectivity in the 1,3-butadiene hydrogenation reaction on Pd catalysts depend both on the crystallographic orientation [178] and the Pd particle size [179]. Additionally, the same authors have shown that the presence of CO traces can modify to a great extent the selectivity towards the intermediate hydrogenated products by reducing the surface hydrogen concentration.

Besides catalytic activity and selectivity, another important aspect in these hydrogenation reactions is the catalyst deactivation both through strongly adsorbed surface species and/or carbon deposit formation. In this sense, the formation of carbonaceous deposits under reaction conditions was proposed as responsible of the increased selectivity of Pd catalysts after achieving steady state conditions in the 1,3-butadiene hydrogenation reaction [184]. However, in spite of the crucial role of carbonaceous deposits, to our knowledge there are no studies about the stability of butadiene on Pd surfaces together with analysis about the nature of the surface species present after the reaction, i.e. such as CH_x and/or C species. Therefore, in order to understand the role for carbonaceous species during selective 1,3-butadiene hydrogenation, this reaction was followed at atmospheric pressure by IRAS and by on-line gas chromatography (GC measurements were performed together with Silvestre Albero). XPS and LEED were employed for pre- and post-reaction surface analysis. Adsorption and desorption of butadiene was studied in UHV by XPS, following the C1s and Pd3d signals.

5.3.1 Ambient pressure 1,3-butadiene measurements

Figure 5.11 shows GC kinetic measurements of 1,3-butadiene hydrogenation on Pd(111) at 300 K. In the first minutes of the reaction 1,3-butadiene is hydrogenated to the three butenes (1-butene, trans-2-butene and cis-2-butene) as primary products. It is noteworthy that 1-butene, the least stable thermodynamically product, is the main product

after the first hydrogenation step. Interestingly, there is also some n-butane formation after a few minutes, resulting from subsequent hydrogenation of adsorbed and/or re-adsorbed butenes. After complete 1,3-butadiene consumption (ca. 75 min), 1-butene is re-adsorbed on the surface providing two reaction processes, i.e. n-butane formation through hydrogenation and trans/cis-2-butene formation through isomerization. Figure 5.11 shows as inset the pre- and post-reaction LEED images. As can be observed, the clean Pd(111) crystal exhibits the typical hexagonal arrangement while after 6h reaction time the LEED pattern is diffuse. This is a clear indication of the presence of adsorbed surface species, most probably adsorbed butadiene together with some disordered carbonaceous species. It is interesting to notice that the original LEED pattern can be recovered after a high temperature flash (900 K) which can be explained by desorption of butadiene and/or dissolution of the carbon species in the Pd bulk.

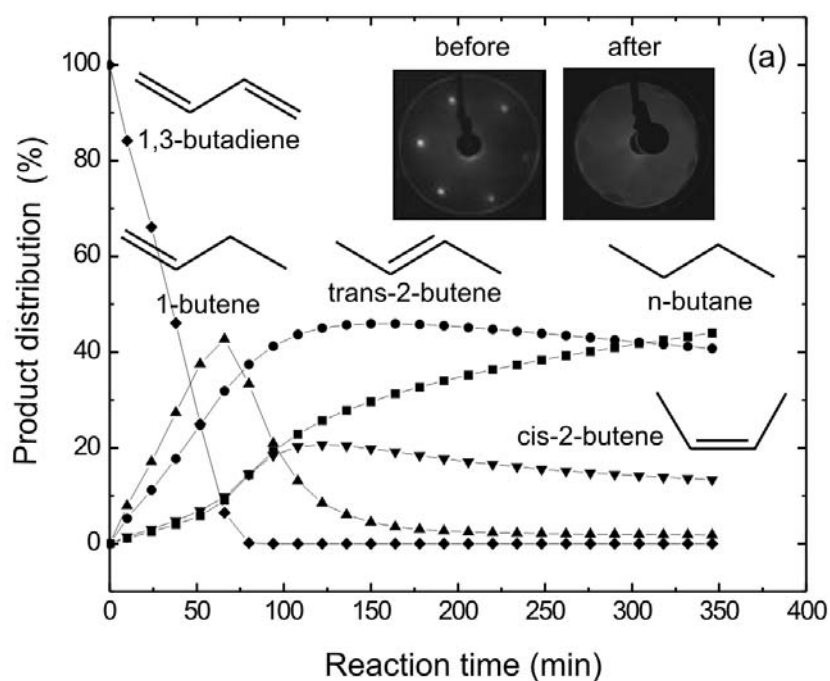


Figure 5.11: (a) Product distribution versus reaction time for 1,3-butadiene hydrogenation reaction on Pd(111) at 300K. The reaction gas mixture consisted of 5 mbar C_4H_6 , 10 mbar H_2 and Ar as carrier gas to bring the total pressure to 1 bar. LEED images of Pd(111) before and after the high pressure reaction are also reported as inset.

The selectivity of 1,3-butadiene hydrogenation is defined by the ratio of 1,2-H addition (yielding 1-butene) to 1,4-H addition (yielding 2-butene) to adsorbed butadiene. Consequently, this process is in part governed by the geometry of the adsorbed molecule on the surface. Previous studies by near-edge X-ray absorption fine structure (NEXAFS) and high-resolution electron energy loss spectroscopy (HREELS) on Pd single crystals have shown that butadiene preferentially adsorbs via the two double bonds in a di- π configuration [184]. However, DFT calculations of butadiene adsorption on Pd(111) suggest the 1,2,3,4-tetra- σ adsorption state with a total adsorption energy of $-166 \text{ kJ}\cdot\text{mol}^{-1}$ [186]. In order to identify the nature of the surface species during the reaction we have performed IRAS measurements on the Pd(111) crystal under *in-situ* reaction conditions. Unfortunately, only gas-phase and no surface species could be observed in the spectra probably due to the flat adsorption of the different molecules on the surface. In fact, only those molecules having a dipole moment component normal to the surface will contribute to the IRAS signal. An absence of surface signals was also reported in previous PM-IRAS studies of butadiene hydrogenation on Pt(111) and Pt₃Sn(111) [187]. Adsorption studies of 1,3-butadiene on Pd(110) by HREELS and NEXAFS have also shown that the molecule adsorbs parallel on the surface [188].

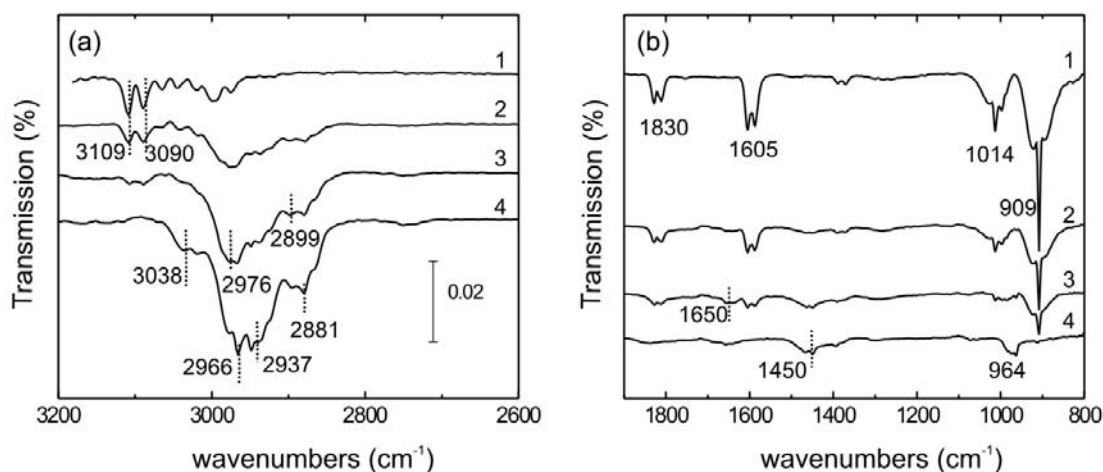


Figure 5.12: IRAS spectra following the gas phase evolution during 1,3-butadiene hydrogenation reaction on Pd(111) at 300 K in the CH stretching (a) and bending (b) regions: after 3 min (trace 1), 20 min (trace 2), 40 min (trace 3) and 60 min (trace 4) reaction time. Reaction conditions: 10 mbar 2:1 ($\text{H}_2:\text{C}_2\text{H}_4$) gas mixture dosed at 300 K.

Figure 5.12 shows IRAS spectra of 1,3-butadiene hydrogenation under mbar pressure on Pd(111) at 300 K. At the beginning of the reaction the IR spectra exhibit the characteristic bands of (pure) 1,3-butadiene in the gas-phase (Fig. 5.12a and 5.12b, spectra 1). The main bands are in the range $\sim 2980\text{--}3110\text{ cm}^{-1}$, corresponding to a combination of symmetric and asymmetric νCH and νCH_2 in-plane stretching vibrations (Fig. 5.12a) and at 1830 cm^{-1} , 1605 cm^{-1} , 1014 cm^{-1} and 909 cm^{-1} , corresponding to $\text{C}=\text{CH}_2$ stretching, $\text{C}=\text{C}$ stretching, CH bending and CH_2 twisting and wagging vibrations, respectively (Fig. 5.12b). With reaction time, the characteristic bands of butadiene progressively decreased, while new bands appeared at 2976 cm^{-1} and 2899 cm^{-1} , which can be attributed to the formation of 1-butene after 40 min (Fig. 5.11a and b; spectra 3). At long reaction times (60 min), the bands of 1-butene vanished and new IR bands appeared at 3038 cm^{-1} , 2937 cm^{-1} and 964 cm^{-1} , characteristic of 2-butenes (Fig. 5.12a and b, traces 4). In addition, peaks appearing at 2966 cm^{-1} and 2881 cm^{-1} are a clear fingerprint of n-butane formation. These results agree well with the corresponding GC measurements. At the beginning of the reaction, butadiene is hydrogenated mainly to 1-butene through 1,2-hydrogen addition (Fig. 5.12a and b, spectra 3, after 40 min), while once 1,3-butadiene has been completely consumed, 1-butene is re-adsorbed yielding n-butane through hydrogenation and trans/cis-2-butene through isomerization (Fig. 5.12a and b, spectra 4, after 60 min). The consumption of 1,3-butadiene is slightly faster in the IRAS experiment due to the smaller volume of the IR cell, as compared to the reaction chamber used for GC measurements.

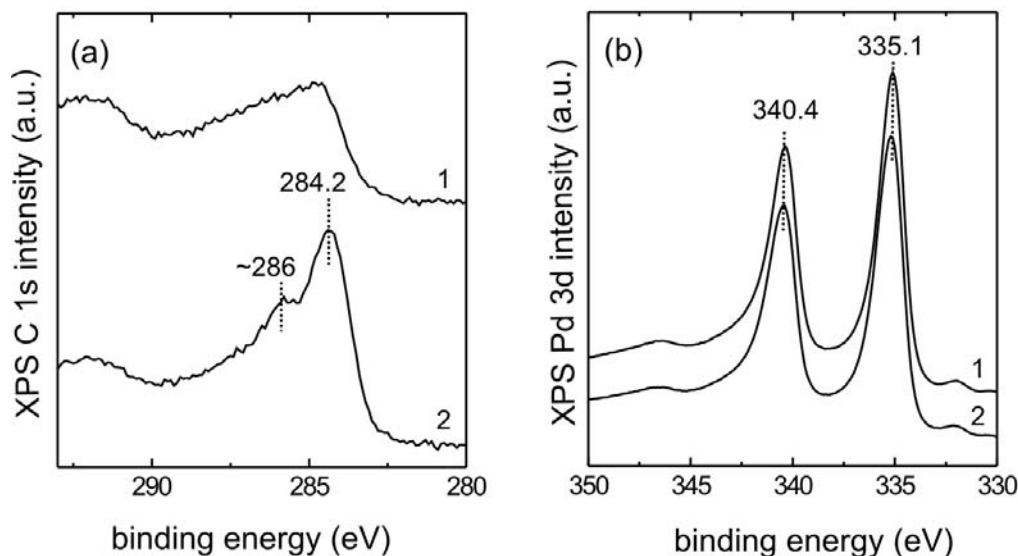


Figure 5.13: Post-reaction XPS in the C1s (a) and Pd3d (b) regions after 60 min high pressure 1,3-butadiene hydrogenation reaction at 300 K on Pd(111). As already observed, the two “bumps” observed in trace 1 (clean surface) in (a) are Pd-satellite peaks due to the non-monochromatic X-ray source used (see section 2.2).

Beside catalytic activity and selectivity, deactivation is another important aspect of heterogeneous catalysis. For many hydrocarbon reforming reactions one of the main reasons of deactivation is the dehydrogenation to carbonaceous (CH_x) and C species. In order to quantify the possible effect of carbon deposits on the deactivation for 1,3-butadiene hydrogenation post-reaction XPS analysis was performed. Figure 5.13 shows the C1s and Pd3d signals for the Pd(111) single crystal after 60 min reaction time (after the IRAS measurements of Fig. 5.12). As can be observed, the C1s spectra exhibit a single band centered at 284.2 eV which corresponds to carbon species (CH_x and/or C) adsorbed on the surface together with some remaining butadiene. These carbon species are typically responsible for the deactivation of the catalyst with reaction time. However, a quantitative analysis of the carbon deposits yields a carbon coverage of 0.3 ML. Although the amount of carbon formed after 60 min reaction time at 300K is not negligible, most of the surface is still clean and no significant deactivation was observed in repeated GC measurements. This is also evident from the kinetic measurements shown in Fig. 5.11 where the consecutive 1-butene hydrogenation reaction (after 75 min reaction time) exhibits a similar catalytic activity to that of 1,3-butadiene hydrogenation, i.e. the hydrogenation activity of both molecules alone on a clean surface is quite similar. The deactivation of the hydrogenation reaction due to carbon deposits must therefore be of minor importance, at least on our

timescales. This is in disagreement with previous studies on Pd model catalysts where a clear deactivation of the subsequent butene hydrogenation process was observed together with the formation of important carbon deposits (~ 1 ML) [183]. However, the longer reaction time (6h) together with the higher reaction temperature (340 K) used in [183] can account for the observed differences. Similar higher carbon deposits (1-1.5 ML) were also observed during methanol decomposition on Pd(111) at 300K [115]. After flashing the surface to high temperatures (above 600 K, spectra not shown), the peak at 284.2 eV disappears, due probably to carbon dissolution (migration) into Pd bulk at high temperatures. Additionally, the absence of any shift in the Pd3d binding energy after reaction (Fig. 5.13b) and the absence of any signal around 282 eV in the C1s region (Fig. 5.13a) rule out the formation of a Pd-carbide phase [189]. This may be again due to the shorter reaction time and the low reaction temperature used. In fact, *Stachurski et al.* reported bulk carbide formation on Pd catalysts after acetylene hydrogenation at 373 K [190]. Summarizing, post-reaction XPS analysis shows that the effect of deactivation by carbon deposits formation is negligible under the reaction conditions applied. The same reaction conditions were used by *Silvestre et al.* in recent investigations on Pd single crystals [178] and Pd nanoparticles [179].

The selectivity towards the first hydrogenated products (butenes) is strongly affected by the adsorption strength (stability) of both the reactant and the intermediate reaction products. Previous DFT calculations on butadiene and butene adsorption on Pd(111) suggest that 1,3-butadiene adsorption is ~ 79 kJ \cdot mol $^{-1}$ stronger than that of the most strongly adsorbed butene, i.e. 1-butene [186]. This was experimentally confirmed by kinetic analysis of competitive butadiene-butene hydrogenation reactions [184]. Thus, the presence of strongly adsorbed 1,3-butadiene will avoid the re-adsorption and hydrogenation of butene intermediates to n-butane, consequently increasing the selectivity. However, if the adsorption of butadiene is too strong undesired dehydrogenation processes may occur, which produce coke and lead to catalyst deactivation. The interaction of 1,3-butadiene with Pd(111) was therefore studied in more detail by UHV measurements.

5.3.2 1,3-butadiene measurements under UHV

In order to gain more insight into the stability and reactivity of butadiene adsorbed on Pd(111) we have performed adsorption-desorption XPS measurements under UHV. Figure 5.14a shows XPS data acquired in the C1s region during the (multilayer) growth of 1,3-butadiene on Pd(111) (the spectra shown are already divided by the C1s trace of the clean Pd(111) surface). At low butadiene exposure (0.5 L), the C1s XPS spectrum exhibits a broad band centered at 284.0 eV (trace 1). An increase in the exposure of 1,3-butadiene to 1 L ($\theta(\text{C}_4\text{H}_6) = 0.25$ molecules of butadiene/Pd atom) produces a shift in the binding energy to 284.7 eV, together with a low energy tail at ~ 284 eV (trace 2). A further increase in the butadiene dose to 20 L produces a symmetric peak centered at 285.1 eV (trace 5). Obviously, this increase in the amount of adsorbed butadiene is accompanied by a decrease in Pd3d intensity (Figure 5.14b). However, it is interesting to note that in spite of having a butadiene multilayer after 20 L dose, there is still a strong (but reduced) Pd3d signal.

Figure 5.14c and d show the quantitative analysis of the XPS data. The (2x2)-3 CO saturation structure of CO on Pd(111) was used to quantify the carbon coverage as a function of butadiene exposure (Fig. 5.14c). The carbon coverage increased with butadiene dose up to a plateau when the crystal is saturated. According to these results, exposure of only 1 L butadiene is enough to create one layer of carbon on the Pd surface. Taking into account that each butadiene molecule has four carbon atoms, this carbon coverage will correspond to a butadiene coverage of 0.25 molecules butadiene/Pd surface atom (this will be defined as butadiene monolayer). An increase in the butadiene dose produced a multilayer up to saturation at 20 L, which corresponds to four layers of butadiene. The formation of a monolayer already after 1 L dose also explains the shift in the C1s binding energy with butadiene exposure (Figure 5.14d.) Below monolayer coverage, the adsorbed butadiene molecules interact directly with the surface and then exhibit a lower C1s binding energy (284.0 eV). However, after monolayer formation (1 L), additional butadiene molecules start to adsorb in a multilayer and exhibit a smaller interaction with the surface, leading to a sudden shift to higher binding energies (285.0 eV; this value being constant for further butadiene exposure).

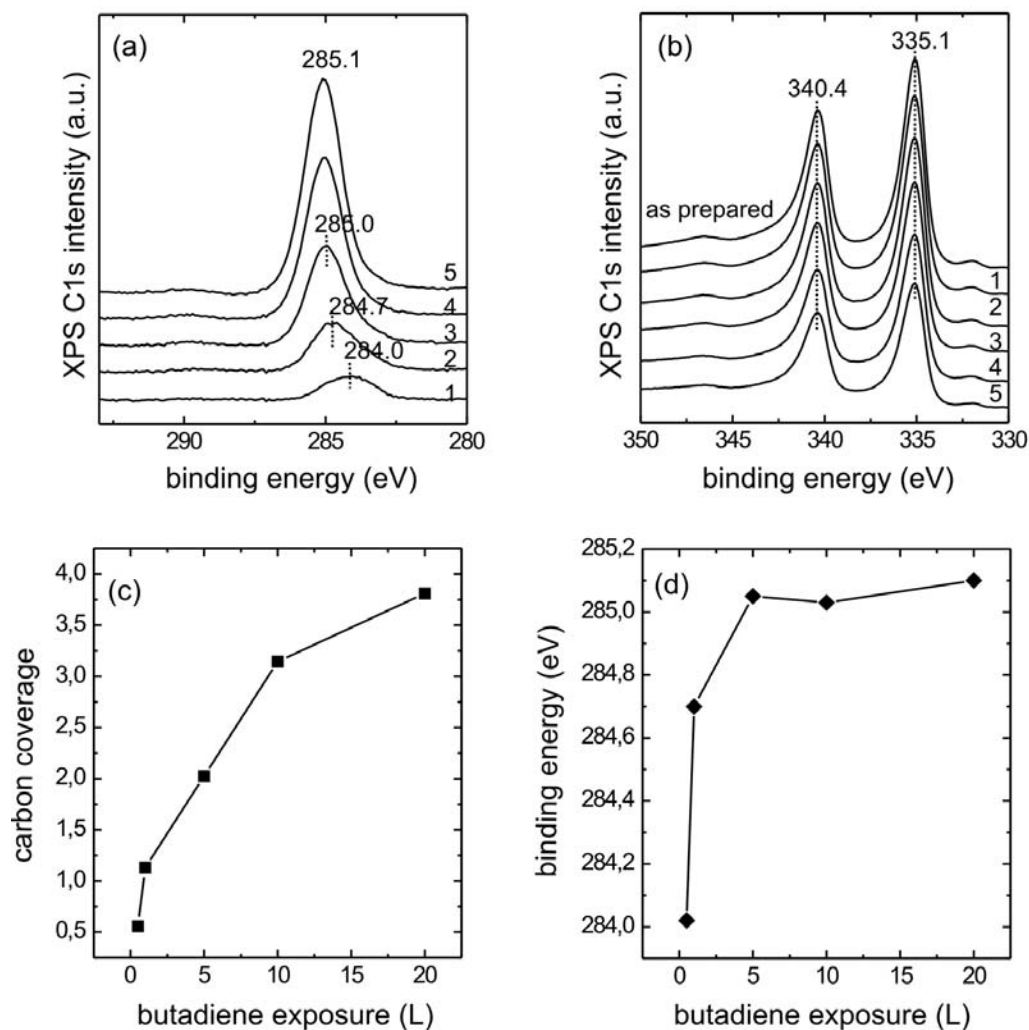


Figure 5.14: XPS spectra in the C1s (a) and Pd3d (b) region during butadiene growth on Pd(111) at 100 K. Spectra were taken after 0.5L (trace 1), 1L (trace 2), 5L (trace 3), 10L (trace 4) and 20L (trace 5) butadiene exposure. XPS analysis of carbon coverage (c) and C1s binding energy shift (d) as a function of butadiene exposure at 100K are reported as well.

The stability of adsorbed butadiene was addressed by performing temperature programmed XPS, monitoring the remaining surface species via their C1s and Pd3d signals (Figure 5.15a and 5.15b, respectively). As observed in the C1s spectra, increasing the sample temperature to 125 K (Fig. 5.15a, trace 2) produced a small decrease in intensity, probably due to desorption of weakly bound butadiene from the multilayer (see also Figure 5.15c for quantitative data). Surprisingly, a further increase in sample temperature to 500 K

produced a BE shift towards higher values, but without change in the peak area and intensity (trace 4). Only above 500 K there is a decrease in peak intensity, together with a shift to lower binding energies (traces 5 and 6). The high stability of adsorbed butadiene towards desorption and decomposition on Pd(111) is similar to that reported previously for the same molecule on Pt(111) [191]. C_4H_6 -TPD spectra after butadiene adsorption on Pt(111) at 100 K showed only desorption from the physisorbed layer but not of chemisorbed butadiene. By following the H_2 signal, the authors observed butadiene decomposition (0.15 ML C_4H_6), i.e. dehydrogenation and hydrogen evolution at 370, 398 and 585 K together with surface carbon formation, as detected by AES. The high stability of butadiene adsorbed on close-packed surfaces, i.e. Pd(111) and Pt(111), is a clear evidence of the strong interaction between the diene molecule and the metal surface. A strong adsorption of butadiene on close-packed Pd(111) surfaces may be responsible for the blocking effect on hydrogen adsorption on well-defined Pd nanoparticles supported on Al_2O_3 [179], which present mainly (111) facets.

It is also worth noting the shift of the C1s binding energy in the 125-500 K range. NEXAFS and HREELS studies of butadiene adsorption on Pd(111) have shown an increase in the bond strength of (di- π bonded) butadiene when the temperature was increased from 95 K to 300 K [185]. The absence of butadiene desorption below 500 K together with the BE shift to higher values is an indication of a change in the adsorption mode of the adsorbed molecule with increasing temperature. It is noteworthy that butadiene decomposition, i.e. dehydrogenation to carbonaceous deposits (CH_x and C species), will shift the C1s binding energy to lower values (~ 284.0 eV). However, the occurrence of partial dehydrogenation processes, i.e. butadiene dehydrogenation to butylidyne, can not be ruled out. According to Figure 5.14a, butadiene decomposes above 500 K, most probably through dehydrogenation, producing CH_x and C species on the surface, as indicated by the shift of the C1s signal to lower binding energies (284.0 eV), values typical of carbon and hydrocarbon species on the Pd surface [113,130]. A further increase to 1000 K induces the complete disappearance of the C1s signal, due to carbon migration into the Pd bulk (Figure 5.14c and 5.14d).

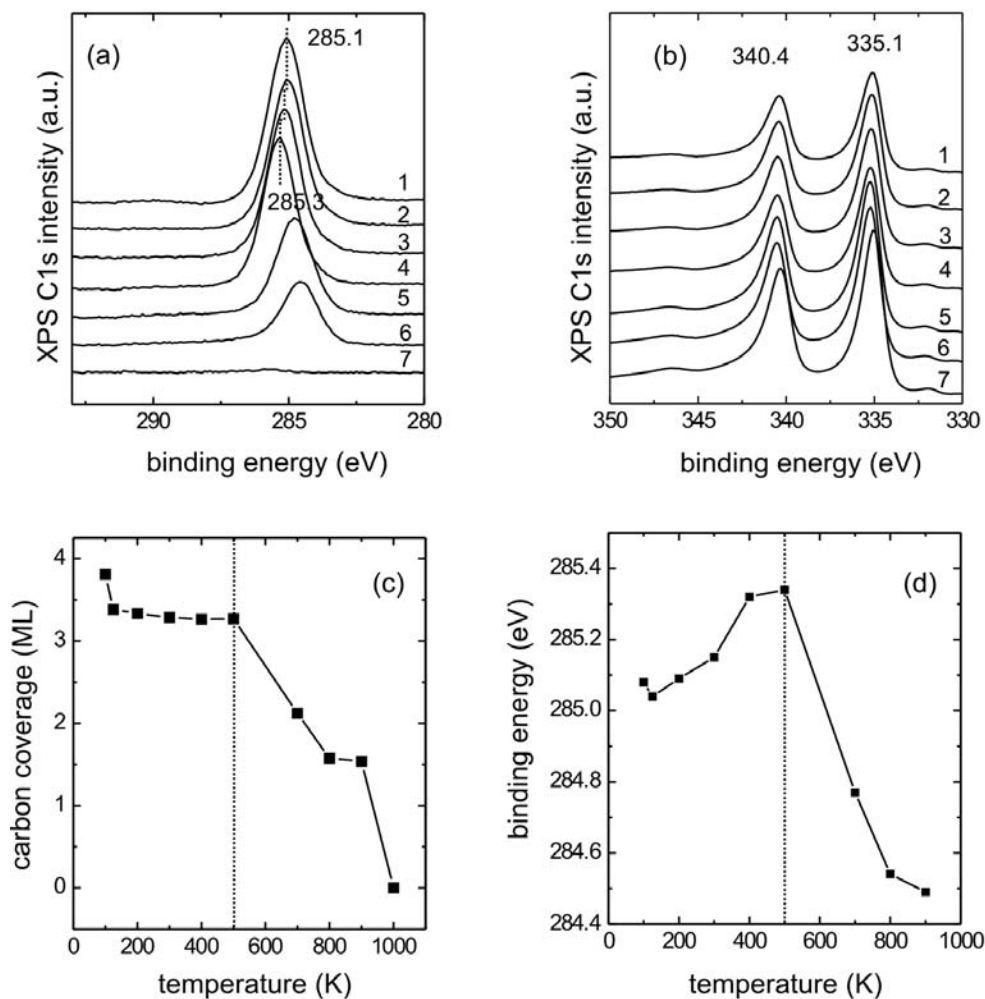


Figure 5.15: XPS spectra in the C1s (a) and Pd3d (b) region during C_4H_6 -temperature programmed desorption (TPD) after multilayer butadiene formation on Pd(111) at 100 K. Spectra were taken at 20 L butadiene (trace 1), flash at 125 K (trace 2), 300 K (trace 3), 500 K (trace 4), 700 K (trace 5), 800 K (trace 6) and 1000 K (trace 7). XPS analysis of carbon coverage (c) and binding energy changes (d) for the C1s peak as a function of temperature during the C_4H_6 TPD experiment are also shown.

5.4 Summary

High pressure kinetic studies of selective 1,3-butadiene hydrogenation at 300 K on Pd(111) showed 1-butene, trans-2-butene and cis-2-butene as primary products. After butadiene has been completely consumed, 1-butene could re-adsorb on the surface giving

n-butane through hydrogenation and trans/cis-2-butene through isomerization. The evolution of the gas phase during the high pressure hydrogenation reaction was also followed by IRAS, and these results are in good agreement with what reported by previous GC data. Post-reaction XPS studies showed a rather small amount of carbon deposit on the surface (0.3 ML) due to adsorbed butadiene species and/or carbon deposits. Accordingly, the deactivation due to carbonaceous species under the reaction conditions used may be of minor importance (no carbon poisoning effect was observed during the reaction).

XPS measurements of butadiene desorption under UHV showed that C_4H_6 is highly stable on the Pd(111) surface up to 500 K (no evidence for desorption and/or decomposition were detected). Above this temperature, butadiene decomposition (dehydrogenation) occurred (C1s XPS analysis showed a shift to lower binding energies together with a decrease in the peak intensity). Above 800 K the C1s signal completely disappeared due to carbon dissolution into the Pd bulk. Interestingly, in the 125-500 K range the C1s shifted to higher binding energies (with no change in intensity) indicating a change in the adsorption mode of the molecule with temperature.