

The flexible surface: new techniques for molecular level studies of time dependent changes in metal surface structure and adsorbate structure during catalytic reactions

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Abstract

The new model that emerges from the results of recent surface science studies is one of a dynamic, flexible surface that undergoes rapid adsorbate-induced restructuring on the time scale of chemisorption, or at times, slower restructuring on the time scale of catalytic surface reactions, atom diffusion-controlled faceting, or solid state reactions. Many of the unique chemical properties of the surface can be associated with its ability to restructure rapidly as adsorbate bonds form or break. Surface specific vibrational spectroscopy by sum frequency generation (SFG) and high pressure/high temperature scanning tunneling microscopy (STM) are two independent but complimentary techniques which permit molecular level studies of surfaces under dynamic conditions at high pressures. The application of these techniques allows in situ analysis of reactive surfaces during catalytic conditions. These techniques have been used to study ethylene and propylene hydrogenation on platinum surfaces. The investigations provide definitive evidence for physisorbed intermediates, stagnant chemisorbed species, and an unreconstructed surface during catalysis. The role of carbon-containing overlayers covering the surface during reactions has been identified. A detailed molecular mechanism for these two reactions can be proposed.

Keywords: Chemisorption; Flexible surface; Surface structure; Metal surface; Adsorbate structure

1. Introduction

Recent investigations of the relation between homogeneous and heterogeneous catalysis point to classes of reactions that show great similarity. Reactions that are carried out heterogeneously are divided into structure sensitive and structure insensitive categories. Structure insensitive processes are those with reaction rates that are independent of the catalyst surface structure. There appears to be good correlation between reaction mechanisms of this type, whether they are carried out homogeneously or heterogeneously. This paper focuses on the rea-

sons for this as revealed by surface science studies, and describes the results of ethylene and propylene hydrogenation studies where there are excellent correlations. From the surface science perspective, there are two reasons for advances made in correlating heterogeneous and homogeneous reaction mechanisms. First, adsorbate-induced restructuring of metal surfaces was uncovered, along with its implications for heterogeneous catalysis. Second, new techniques have become available which permit in situ studies of surfaces and reacting adsorbates at high reaction pressures and temperatures; thus, conditions that were utilized for mechanistic

studies of homogeneous reactions can now be matched by molecular surface science studies of heterogeneous processes.

2. Adsorbate-induced restructuring of metal surfaces

2.1. Evidence from qualitative studies: field ion microscopy, low-energy electron diffraction, and scanning tunneling microscopy

Recent field ion microscopy (FIM) studies have revealed that rhodium surfaces restructure when carbon monoxide is adsorbed on the heated surface [1]. The advantage of this technique is its ability to image all the surfaces simultaneously; therefore, the effect of adsorption can be observed simultaneously on the crystal faces. All the surfaces reconstruct in the presence of CO. Upon heating the rhodium tip in ultrahigh vacuum (UHV), the original surface structure can be recovered.

Low-energy electron diffraction (LEED) studies of a large number of stepped surfaces reveal restructuring in the presence of oxygen or carbon deposited by the decomposition of chemisorbed ethylene or acetylene, as compared to the clean stepped surface [2]. It has been shown that surface structures that are stable in the presence of oxygen are different from those that are stable in the presence of carbon.

Recent scanning tunneling microscopy (STM) studies have shown massive restructuring of the Pt(110) crystal face when the surface is heated in oxygen. The surface, again, restructures to give rise to a different type of surface than if heated in hydrogen or carbon monoxide. STM pictures clearly show how the platinum surface restructures when heated in high pressures of hydrogen, oxygen, and carbon monoxide [3].

The past two decades have seen a considerable accumulation of qualitative experimental evidence for adsorbate-induced restructuring of surfaces. However, because of a lack of precise knowledge about atomic locations, changes in

bond angles, and changes in bond distances, it has not been possible to place these observations on a firm structural basis. The development of surface crystallography by LEED, especially with the introduction of tensor LEED, provided a means of calculating the precise locations of atoms; both in the substrate and adsorbate layers. Below we give a few examples from quantitative studies of adsorbate-induced surface restructuring.

2.2. Evidence from quantitative studies: LEED surface crystallography

It was not until the late 1970s that the effect of adsorbates on substrate structure was noticed, primarily in the form of relaxations of substrate interlayer spacings. Contraction of the topmost interlayer spacing was found to decrease considerably upon adsorption (outward relaxation), often to near the bulk value or even slightly larger. With respect to the clean surface, this spacing expansion upon adsorption was found to increase with adsorbate coverage, as is well illustrated in the case of hydrogen adsorption on Cu(111) [4]. These chemisorption-induced atomic displacements typically amount to 0.5–0.10 Å. The effect can be understood intuitively as the adsorbate relieving, to some extent, the strong asymmetry that the bare surface creates for the outermost substrate atoms.

The existence of adsorbate-induced surface restructuring became clear in 1979 with the case of carbon on Ni(100), which formed a (2 × 2) structure [5]. In this case, glide-plane symmetry was observed through systematic extinction of certain diffraction beams, implying lateral displacement of nickel atoms. At that time, the amount of displacement could not be reliably determined; but it was expected, and later confirmed, to be considerable (on the order of 0.5 Å). In the presence of 0.25 monolayer carbon, the Ni(100) face is restructured in such a way that the four nickel atoms surrounding the carbon atom move outward; they rotate by a small angle with respect to the underlying layer (Fig.

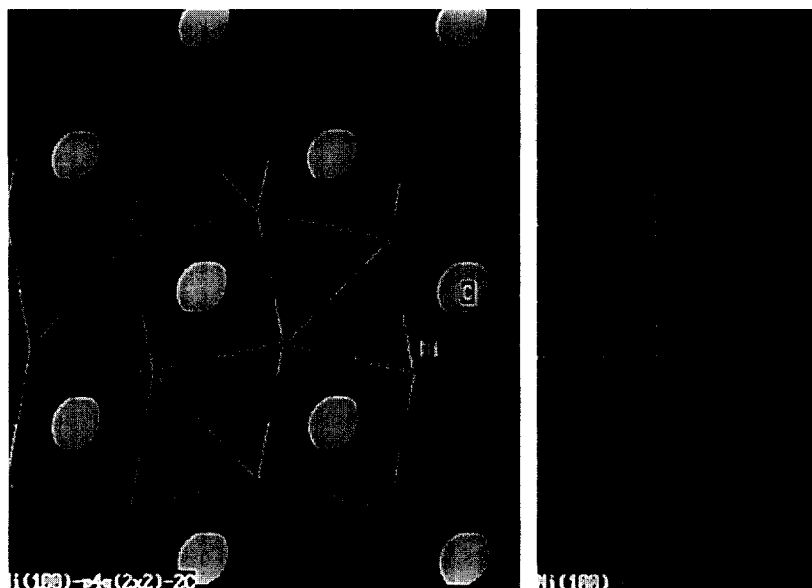


Fig. 1. Carbon chemisorption-induced restructuring of the nickel(100) surface.

1). This occurs to maximize bonding to the carbon in the fourfold sites, which is a better way to bond to the nickel atom in the second layer underneath, in addition to bonding to the four nearest-neighbor surface nickel atoms. In

1981, another adsorbate-induced restructuring case emerged involving sulfur adsorbed on Fe(110). An unusually detailed LEED analysis found that the sulfur atoms were rearranging the iron atoms [6] in such a way as to create a

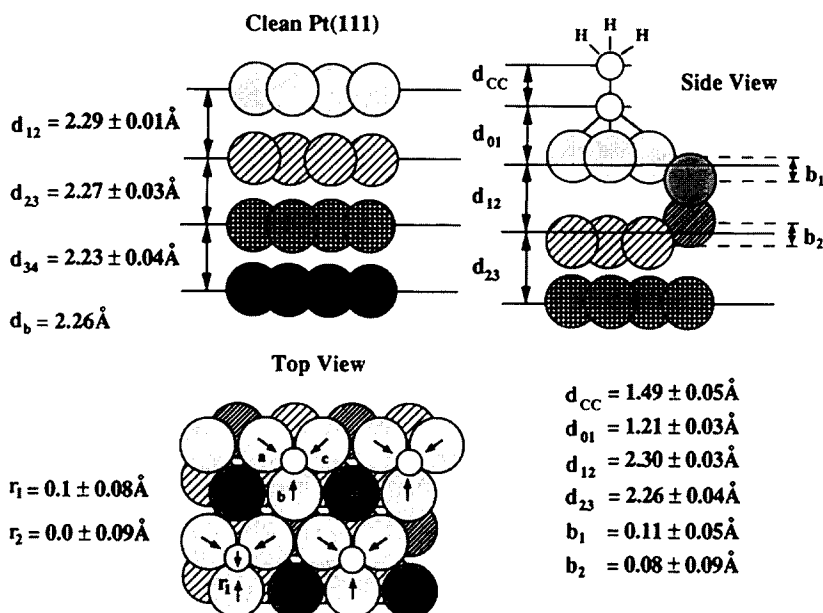


Fig. 2. Structure of chemisorbed ethylidyne on the platinum(111) crystal face that forms upon the chemisorption of ethylene at 300 K. Note the restructuring of ethylene to ethylidyne with the loss of hydrogen, as well as the buckling and rearrangement of metal atoms in the top two layers at the surface.

nearly fourfold symmetrical hollow site for its adsorption, rather than the more elongated rectangular site or the threefold coordinated site available on the unrelaxed surface.

Adsorbates can induce restructuring in the substrate layer, even when disordered in the chemisorbed state; this is the case with hydrogen on W(100). The clean W(100) [7] crystal face is already reconstructed, but adsorbed hydrogen changes it further to another structure that varies smoothly with the hydrogen coverage [8]. Sometimes a small coverage (below 0.1 monolayer) of disordered adsorbate can be sufficient to cause reconstruction of the substrate. This happens with alkali atoms in nickel, copper, palladium, and silver (110) crystal faces, which transform to the missing row structure [9–12].

Adsorbates often restructure stepped surfaces; for example, oxygen deposited on stepped platinum surfaces has been observed to produce double-height steps. Faceting has also been observed under these circumstances. Sulfur

chemisorption on Mo(100) and stepped molybdenum surfaces shows changes of surface structure (step ordering, step doubling, and faceting) as a function of sulfur coverage [13].

2.3. Adsorbate-induced restructuring by chemisorbed molecules

The first structure analyses of molecules adsorbed on metal surfaces (by LEED surface crystallography) were conducted at Berkeley around 1976 for the adsorption of acetylene and ethylene on Pt(111) [14]. A definitive structure for this system was published in 1979, proposing ethylidyne (C_2H_3) as the stable adsorbed species [15]. The surface induces the molecular rearrangement as compared to the gas-phase species. Because ethylidyne is particularly stable in organometallic clusters, it is not surprising that it is formed on a number of metal surfaces.

The surface structures of ethylidyne (C_2H_3) on the Pt(111) and Rh(111) surfaces are shown in Figs. 2 and 3. The unit cell is Pt(111)–($2 \times$

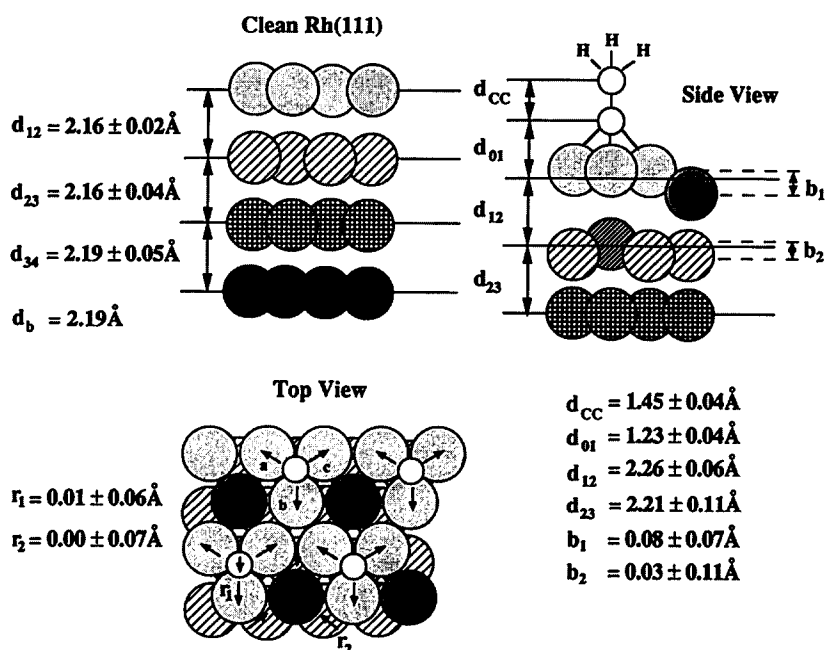


Fig. 3. Surface structure of chemisorbed ethylidyne that forms upon chemisorption of ethylene on the rhodium(111) crystal face at 300 K as determined by LEED surface crystallography. Note the rearrangement of metal atoms down to the second layer at the surface as a result of the formation of the chemisorption bond.

$2)-C_2H_3$ and $Rh(111)-(2 \times 2)-C_2H_3$, respectively. Ethylidyne occupies an fcc hollow site on the $Pr(111)$ surface, but it occupies an hcp hollow site in the $Rh(111)$ surface [16,17]. These different site adsorptions cause very different substrate restructurings as induced by the adsorbed organic molecule. There is a small 1.3% expansion of the top interlayer spacing in clean $Pt(111)$ and an equally small contraction in $Rh(111)$. In both structures the three metal atoms to which the ethylidyne is bonded (a , b and c in Figs. 2 and 3) are buckled out of the surface relative to the unbonded top layer atoms (labeled d) by an amount that seems larger on platinum than on rhodium. This suggests stronger plat-

inum–carbon bonding. In the second metal layer, an opposite buckling occurs that can be understood as a result of the displacements in the first layer. In both metals, 25% of the second layer atoms sit below triplets of outward buckled top layer atoms. They are thus pulled outward more than the other 75% of the second layer metal atoms, which are held deeper by atoms in the bulk (in Pt this effect is further aided by the 0.1 Å lateral motion in the top layer). The rising second layer atoms are distant from the adsorption site in Pr, but right under that site in Rh.

The physical reason for the difference in site preference for ethylidyne on $Pt(111)_{fcc}$ and $Rh(111)_{hcp}$ is still not understood. Calculated

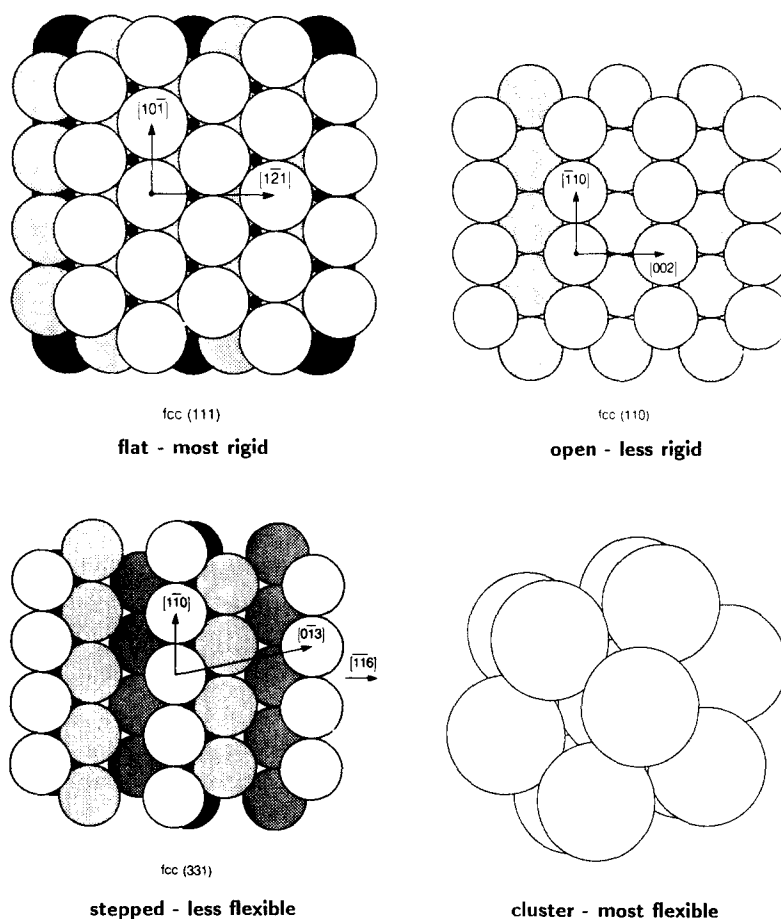


Fig. 4. Models of surface divided according to their atomic coordination. Atoms in the close-packed (111) surfaces of fcc metals have the highest coordination. Their relaxation is small, and chemisorption-induced restructuring is most difficult. These we call rigid surfaces. Clusters have the lowest coordination accompanied by large relaxation and thermodynamically favorable chemisorption-induced restructuring. These are the most flexible. The more open fcc (110) surface and stepped surface show intermediate flexibility.

total energies for the two sites are practically indistinguishable. The lateral top metal layer relaxations, if believable despite their large error bars, may hold a clue. A lateral triangular contraction, as on platinum, may be favored at the fcc site because this corresponds to platinum atoms rolling in the least corrugated direction on the second metal layer. The corresponding argument with a slight lateral triangular expansion would explain the hcp site on rhodium.

The phenomenon of adsorbate-induced relaxations and buckling strongly suggests a picture of cluster-like bonding of adsorbates. The bonding between adsorbate and substrate appears to be very local, primarily involving the nearest-neighbor atoms in the substrate. Next-nearest neighbors already respond much less to the presence of an adsorbate. The cluster-like picture is also consistent with structural and vibrational comparisons of bonding at metal surfaces, and in complexes containing just a few metal atoms. The local structures and properties of adsorbates on surfaces and metal clusters are remarkably similar.

3. The flexible surface: a new dynamic model of surfaces

The phenomena of relaxation and surface reconstruction of clean surfaces indicates that surface atoms occupy sites that are not the same as their bulk equilibrium position: surface atoms are not rigid and are not located at the sites predicted from knowledge of the bulk structure. The surface is flexible and its inward relaxation becomes larger with a decrease in surface atom neighbors. Chemisorption again relocates the surface atoms into new positions that are, again, different from the bulk-like state. The close-packed low Miller index surfaces with large coordination numbers are the most rigid and relocate the least (Fig. 4). The more open rough or stepped surfaces are less rigid (or more flexible), and small clusters are likely to be the most flexible. In the past, several structural configura-

tions of small clusters were known to have the same thermodynamic stabilities. The phenomena of chemisorption-induced restructuring of surfaces indicates how flexible the surface is to accommodate surface chemistry, chemisorption, or catalysis. The surface atoms move into positions that permit the establishment of maximum bond strength and optimum bond orientation up chemisorption. When the chemisorbed system substrate–adsorbate cluster breaks up, the surface atoms relocate to accommodate the new chemical environment. The dynamic restructuring of surfaces is perhaps the key reason for their unique chemical behavior in accommodating chemical changes of different kinds. This new dynamic model of surfaces suggests that chemical change is associated with rearrangement of substrate atoms. This model may explain many of the puzzles of surface chemistry; for example, rough surfaces are more active in breaking adsorbate chemical bonds [18]. Steps and kinks dissociate hydrogen and other diatomic molecules at lower temperatures and hold them with high binding energy. Thermal activation is another phenomenon that can be rationalized by the dynamic surface model. The adsorption of reactive molecules on reactive surfaces at low temperatures does not result in bond breaking or in molecular rearrangement. However, as the temperature is increased, the breaking of selected bonds will take place at well-defined temperatures for a given adsorbate–substrate system. This was first observed in the 1930s when molecular adsorbates (oxygen or nitrogen) were found to undergo dissociative chemisorption at certain temperatures. This was called the physisorption to chemisorption transition. For hydrocarbons, sequential loss of hydrogen and simultaneous molecular rearrangement occurs at well-characterized temperatures on a transition metal surface with a given surface structure. These bond scission processes occur at much lower temperatures at surface irregularities (steps and/or kinks) — on more flexible surfaces where atom rearrangements are of larger magnitude. Recently, a molecular

mechanism has been proposed that considers surface restructuring as a driving force for dissociative chemisorption. This model also predicts a coverage dependence for the phenomenon, as the chemisorption of more molecules should lower the activation energy for surface restructuring [19].

4. Correlations between substrate restructuring and catalysis

Scanning tunneling microscopy (STM) provides direct evidence for the restructuring of metal substrates during catalytic reactions [20]. An STM which can be operated at high pressures (2 atm) and temperatures ($< 240^{\circ}\text{C}$) has been built in my laboratory, and has been used to detect surface reaction-induced restructuring of metal surfaces [3]. The platinum surface exhibits atomic details of its surface structure and ordered domains when exposed to hydrogen. In the presence of oxygen, the platinum surface becomes faceted and exhibits large areas composed of different crystal faces. In the presence of carbon monoxide, the surface becomes rather smooth. These changes of surface structure are completely reversible, as shown when platinum is heated alternately in hydrogen or oxygen. Adsorption-induced restructuring can occur on the chemisorption time scale (10^{-15} s for charge transfer, or 10^{-12} s for vibrational times). There is also evidence that adsorbate-induced restructuring can occur on the time scale of catalytic reactions (seconds). Carbon monoxide oxidation to CO_2 or ammonia [21,22] reacting with NO to produce N_2 and H_2O shows oscillatory behavior under certain circumstances of temperature and reactant partial pressures [23]. The reaction rate alternates periodically between two values. One reason for the oscillation is the periodic restructuring of the surface. In this situation, the sticking probability of one of the reactants is greater on one type of surface structure, while the sticking probability of the other reactant is greater on the surface structure of the other

type. Thus, the reaction rate alternates between the two branches of the reaction: one takes place on the CO or NO covered metal surface, and the other takes place on the oxygen or ammonia covered surface. When the catalytic cycle involves oxidation and reduction of metal surface sites with the speed of the turnover rate, this may also be viewed as a periodic surface reconstruction, as oxidation and reduction will change atomic distances and restructure the surface with the period of the turnover frequency [24].

Another important feature of catalytic reactions that can be reinterpreted based on the dynamical restructuring model is the structure sensitivity and insensitivity of catalytic reactions [24]. This is one of the most successful classifications in heterogeneous catalysis — the division of reactions into structure-sensitive and structure-insensitive types. Structure-sensitive reactions change their reaction rate as the originally clean surface structure changes. Ammonia synthesis is one example that exhibits extreme structure sensitivity [25,26]. Structure-insensitive reactions maintain their rates regardless of the initial surface structure. Hydrogenation reactions, especially the well-studied ethylene hydrogenation to ethane, have proven to be structure insensitive [27]. Although it is not too difficult to rationalize a correlation between the structure of the clean surface and its reactivity, it is very difficult to understand how structure-insensitive reactions can occur because the nature of bonding of some reaction intermediates depends on the surface structure. Thus, in order to explain structure-sensitive reactions in light of the dynamical restructuring model of surfaces, all one has to invoke is that there is a correlation between the clean surface structure and the restructured surface that is active during the catalytic reaction. We explain structure insensitivity by arguing that the surface is restructured before the reaction commences. Thus the clean metal surface is inactive for the reaction. The chemisorption of the first monolayer of reactants restructures the surface on a time scale

much faster than the catalytic turnover times. This chemisorption-induced restructuring process creates the active sites. In this circumstance, the concentration of catalytically active sites depends on adsorbate coverage of reactant pressure and not on the structure of the freshly prepared catalyst. Both hydrogenation of olefins and hydroformylation on some metal surfaces are reactions that belong to this class of catalytic processes.

5. Monitoring surfaces on the molecular level (by sum frequency generation vibrational spectroscopy and scanning tunneling microscopy), during catalytic reactions of ethylene and propylene hydrogenation over Pt(111), at high pressure

Until recently, the possibility of studying molecular level changes that take place on surfaces during chemical reaction has eluded surface scientists. Here we report two independent but complementary techniques developed in our laboratory for molecular level studies of surfaces, under dynamic reaction conditions, at high pressures:

1. Surface specific vibrational spectroscopy by sum frequency generation (SFG)
2. High pressure/high temperature scanning tunneling microscopy (STM).

The first technique more readily yields the molecular structure of adsorbates and reaction intermediates [28], while the second is more sensitive for monitoring changes of substrate surface structure during chemical reactions [29]. We report high pressure studies of ethylene and propylene hydrogenation on the (111) crystal face of platinum employing these two techniques.

At 300 K and in the presence of hydrogen, C_2H_4 and C_3H_6 hydrogenate over platinum. Previous studies have shown that this reaction is insensitive to the structure of the underlying metal substrate [30]. The question arises as to the bonding and chemical nature of the molecu-

lar surface intermediates formed upon the adsorption of C_2H_4 and C_3H_6 from the gas phase that hydrogenate to propane. In pursuit of this question, we carried out SFG and STM studies near 300 K and H_2 and C_3H_6 near ambient pressure.

5.1. SFG experiments of propylene hydrogenation over Pt(111)

All high pressure SFG studies were conducted in a batch reactor that was coupled to an ultrahigh vacuum chamber via a gate valve. In addition to the CaF_2 windows needed to pass the infrared laser beam for the SFG experiment, the UHV portion of the chamber was equipped with several of the diagnostic tools for investigation of surfaces. These included a mass spectrometer, a retarding field analyzer for Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), as well as a high resolution electron energy loss spectrometer (HREELS).

After the sample was cleaned in UHV, the batch reactor was isolated by closing the gate valve to the pumps. Hydrogen and propylene

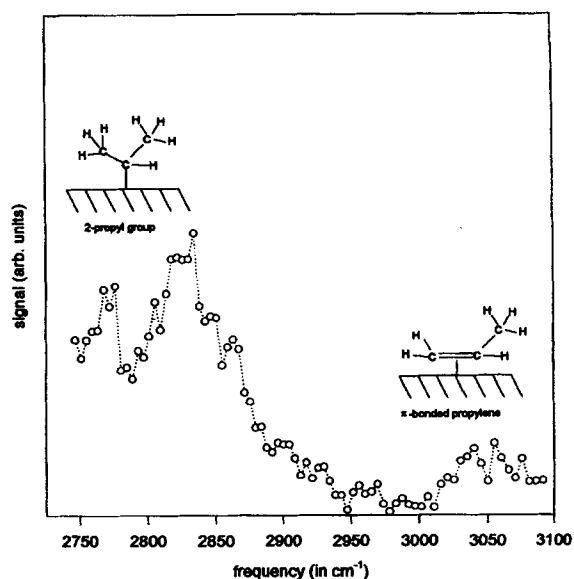


Fig. 5. SFG spectrum of propylene hydrogenation on Pt(111) at 295 K with 715 Torr H_2 and 55 Torr C_3H_6 .

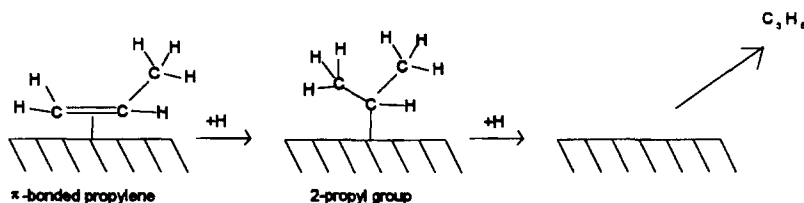


Fig. 6. Schematic representation of propylene hydrogenation on Pt(111) through a π -bonded intermediate onto 2-propyl and then propane.

were then introduced through a manifold equipped with a Baratron gauge for measuring the pressure. The high pressure batch reactor was equipped with a recirculation pump and a sampling port in the reaction loop to extract samples for gas chromatography analysis.

A sum frequency experiment has been described in detail elsewhere [28,31,32]. Briefly, signal is obtained (in the dipole approximation) only where inversion symmetry is broken. In the present system, both the isotropic gas phase and the fcc lattice of the platinum single crystal possess inversion symmetry. Only at the interface between the bulk metal crystal and the gas phase is inversion symmetry broken. Hence, a vibrational spectrum come mainly from the interface in this experiment.

The vibrational spectrum from propylene hydrogenation under conditions of 715 Torr hydrogen and 55 Torr propylene is shown in Fig. 5. Under these conditions the vibrational spectrum shows the presence of two distinct features. Below 2850 cm^{-1} are two peaks which can be assigned to the half hydrogenated secondary propyl group bonded to the surface through the middle carbon [Pt-CH(CH₃)₂] and a broad feature above 3000 cm^{-1} which corresponds to π -bonded propylene [33]¹. These two species provide convincing evidence for a step-wise hydrogenation mechanism (Fig. 6). Propylene is physisorbed to the surface through its π molecular orbital. It hydrogenates first at the outer carbon of the carbon-carbon double bond to form a secondary propyl group. This species

is hydrogenated to propane which desorbs from the surface. The fact that no other intermediate species such as 1-propyl (CH₃CH₂CH₂-Pt) or propylene (Pt=CHCH₂CH₃) are observed helps rule out other possible mechanisms.

Upon evacuation of the reactor cell, a complicated spectrum emerges from a mixture of decomposition products, as well as half hydrogenated allyl bonded propyl groups (Fig. 7). The decomposition products, such as propylidyne (M \equiv CCH₂CH₃) were stable on the surface for hours. The dramatic change in the surface vibrational spectrum demonstrates the great difference between observing reaction intermediates in situ and thermodynamically stable species that are found during post reaction analysis.

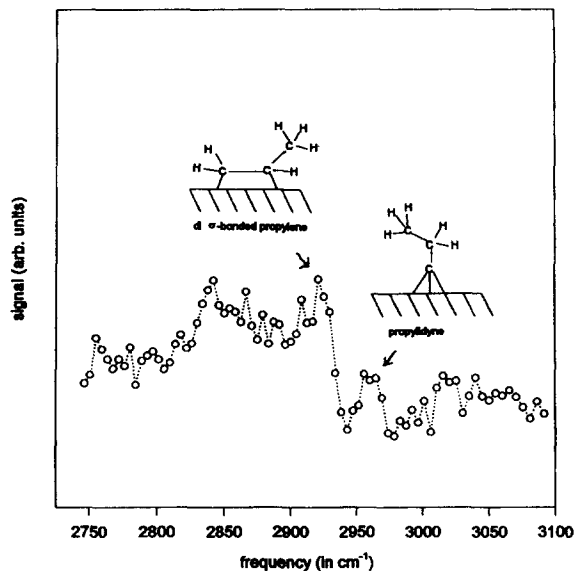


Fig. 7. SFG spectrum of surface species on Pt(111) after reactants have been removed.

¹ Proof of the assignments were made by UHV calibrations with propylene and propyl moieties.

5.2. Molecular surface studies of ethylene hydrogenation at high pressures

The kinetics and structure insensitivity of ethylene hydrogenation have been thoroughly investigated [34–36]. High pressure catalytic hydrogenation studies have also been carried out on supported catalysts by several groups using transmission infrared spectroscopy to monitor surface species on Pd, Rh, Ir, Ru, and Pt supported by either silica or alumina [37–44]. Work on Pd/SiO₂ by Beebe and Yates, using transmission infrared spectroscopy, demonstrated that ethylene hydrogenated in the presence or absence of ethylidyne [37], and ethylidyne was present on the surface at high ratios of ethylene/H₂. However, as the reaction mixture became leaner in hydrocarbon, the ethylidyne was slowly removed from the surface. This suggested that ethylidyne was not involved in ethylene hydrogenation, but rather a spectator species during the reaction. This work was later repeated on a Pt/SiO₂ catalyst where similar results were obtained [42].

5.2.1. Evidence for reaction intermediates

Transmission infrared spectroscopy has also been used to monitor supported surfaces under some non-catalytic conditions. These studies were performed to identify adsorbed species that may be present during hydrogenation. Moshin et al. showed that both π -bonded and di- σ bonded ethylene are hydrogenated when H₂ was flowed over a Pt/Al₂O₃ catalyst that is precovered with these species at low temperature [40]. Further, they found evidence that the di- σ bonded species, but not the π -bonded one, was capable of forming ethylidyne upon annealing. Del la Cruz et al. found that when low pressures of hydrogen (10⁻⁵ Torr range) were introduced to a Pt/SiO₂ sample precovered with ethylene, some ethyl species might be observed [39].

Surface specific non-linear optical techniques such as SFG allow catalytic surfaces to be monitored during reactions at high pressures.

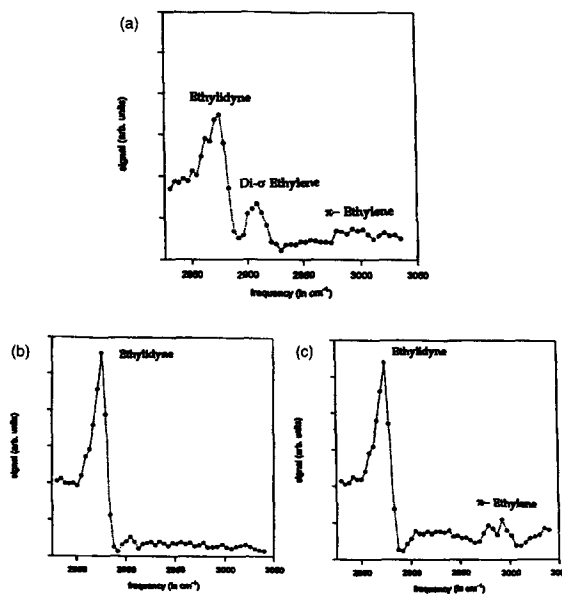


Fig. 8. (a) The SFG spectrum obtained during ethylene hydrogenation on Pt(111) at 110 Torr H₂ and 35 Torr C₂H₄ at 295 K monitored with SFG. (b) The same surface after removing the reactants. (c) The same surface after recharging the reactor with 110 Torr H₂ and 35 Torr C₂H₄.

We have used SFG to monitor the platinum single-crystal catalyst surface during the ethylene hydrogenation reaction, over a variety of conditions of ethylene and hydrogen pressures [43]. The hydrogenation experiments were carried out while the Pt(111) surface was monitored in situ with SFG, and the ethane formation rate in the gas phase was monitored by gas chromatography. Under conditions of 110 Torr H₂ and 35 Torr C₂H₄ at 295 K, a turnover rate of 4.8 was measured while three distinct features were observable on the surface (Fig. 8a). The peak at 2880 cm⁻¹ was ethylidyne and the smaller peak near 2910 cm⁻¹ was from di- σ bonded ethylene. Weak intensity was observable at around 3000 cm⁻¹, which can be assigned to π -bonded ethylene. The reason that the π -bonded species was hardly visible is that dynamic dipoles of adsorbates in the surface plane are cancelled by image dipoles created inside the metal (this is the so-called surface dipole selection rule for metal surfaces). This spectrum remained unaltered on the surface for

hours while the turnover rate remained unchanged. After the reaction mixture was removed, the ethylidyne peak grew to saturation coverage and the other peaks disappeared (Fig. 8b). Upon recharging the reaction cell with ethylene and hydrogen in the same proportions, the ethylidyne peak remained unaltered, while the intensity from the di- σ bonded species did not return. The high frequency low intensity peak, however, was again present (Fig. 8c). This demonstrated the direct competition for sites between the ethylidyne and di- σ bonded ethylene. Because a high rate of turnover was again observed during the second run, it was concluded that the hydrogenation of di- σ bonded ethylene was a minor reaction channel to ethylene hydrogenation. Therefore, it was concluded that hydrogenation through the π -

bonded species was the more likely mechanism to account for the majority of ethane formation under most conditions.

5.2.2. STM experiments of propylene and ethylene hydrogenation over Pt(111)

High pressure STM studies of propylene and ethylene hydrogenation over Pt(111) were carried out in a reactor with a load-lock sample introduction port, a view port for in situ infrared heating of the sample in gas atmospheres, and several gas introduction valves. Turbo molecular and ion pumps were used to lower the pressure in the load-locked and reaction chambers for sample preparation before reaction.

The Pt(111) samples were prepared and characterized by standard surface science tools (AR⁺ sputtering, annealing, LEED, and AES) in a

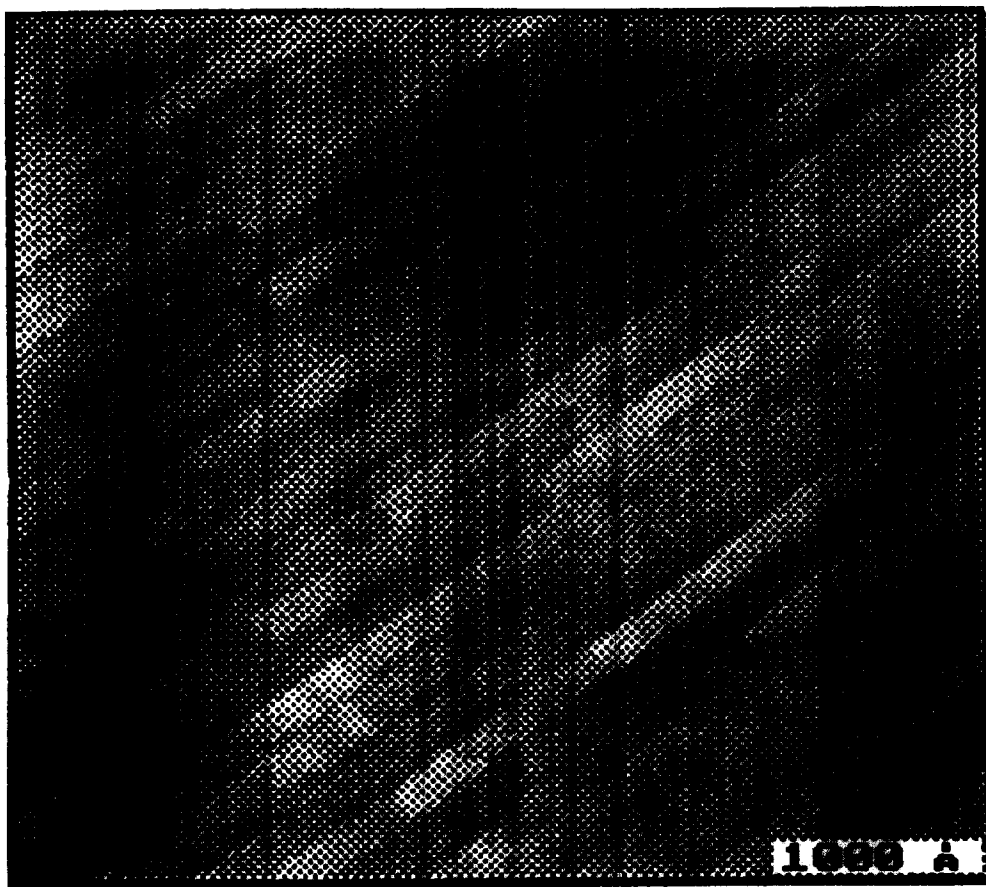


Fig. 9. STM image of 10:1 mixture of hydrogen to propylene above a Pt(111) crystal at room temperature.

separate UHV chamber. Prior to transfer to the STM reaction cell, a sacrificial layer of S was prepared by exposure to H_2S . This formed a $(\sqrt{3} \times \sqrt{3})\text{R}30$ structure that provided strong passivation against adsorption of foreign species [44]. Transfer was performed by use of a vacuum 'suitcase' equipped with a small ion pump and linear motion positioner. Once in the reactor cell, the S layer was removed by heating the sample in O_2 . This O_2 treatment removed small amounts of C contamination as well.

When a $\text{H}_2:\text{C}_3\text{H}_6$ (10:1) mixture is left in equilibrium with the surface at 1 atm and room temperature, STM images reveal featureless terraces separated by straight monatomic height steps. It should be noted that under these conditions the surface is catalytically active and propylene is being hydrogenated to propane during STM imaging; as shown by independent

exposure to identical conditions. The high mobility of the surface species prevented their resolution with the STM. Fig. 9 shows the step structure of this catalytically active surface.

The most significant result of the in situ STM images is that the underlying platinum atoms were not significantly reconstructed by the adsorbed species. Lack of reconstruction is consistent with the structure insensitive nature of the olefin hydrogenation reaction. Indeed, any surface intermediate that would cause surface atoms to restructure would probably be an indication that the reaction requires specific sites on the metal surface in order to proceed.

Control experiments performed by annealing the sample to temperature in excess of 770 K in propylene to form carbon clusters gave rise to substantial surface reconstruction (Fig. 10). The steps were no longer straight, with many kinks

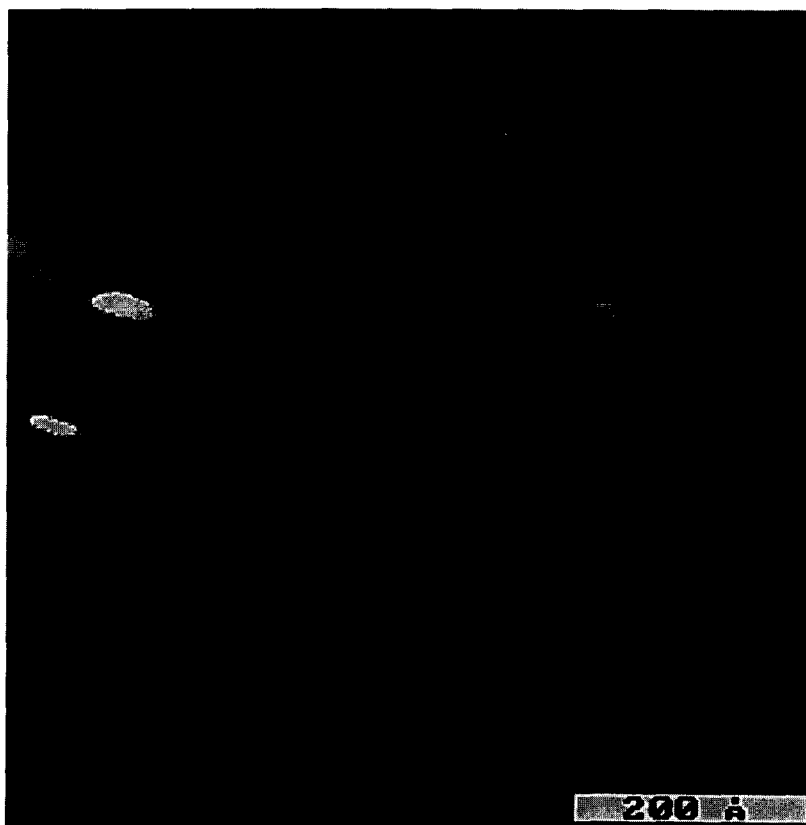


Fig. 10. STM image of carbon clusters decomposed on the Pt(111) surface by annealing to temperatures over 770 K.

or protrusions in the steps that were pinned to the top of some clusters. This demonstrated clearly that, had surface reconstruction occurred during the reaction, the STM was indeed sensitive enough to observe it.

STM images of the Pt(111) surface have also been collected in situ with 1 atmosphere of hydrogen and ca. 79 Torr of ethylene [45]. Under these conditions no hydrocarbon overlayer was formed; hence any change in the surface could be directly attributable to the reaction. The STM images showed no observable change of the surface structure from that observed for clean platinum. This is direct evidence that there was little reconstruction of metal atoms during hydrogenation in the absence of ethylidyne. Such an observation was not surprising because major surface restructuring during reaction would have indicated structure sensitivity to reactants. Its absence was consistent with the structure insensitive nature of this reaction.

The large body of data that has been collected by surface science and catalytic studies has gone a long way in providing an overall picture of the chemistry involved in ethylene hydrogenation over the late transition metals. It is the aim of this discussion to tie together results of this work and to provide a molecular mechanism for the hydrogenation of ethylene.

Hydrogenation studies of ethylene combined with the in situ high pressure ethylidyne monitoring by transmission infrared spectroscopy have clearly demonstrated that ethylene hydrogenation is not noticeably affected by the presence or absence of ethylidyne. The lack of any important effect of ethylidyne on ethylene hydrogenation has presented something of a

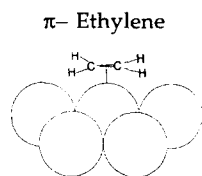


Fig. 11. π -bonded ethylene adsorbed on a top site of Pt(111).

Ethylene Hydrogenation

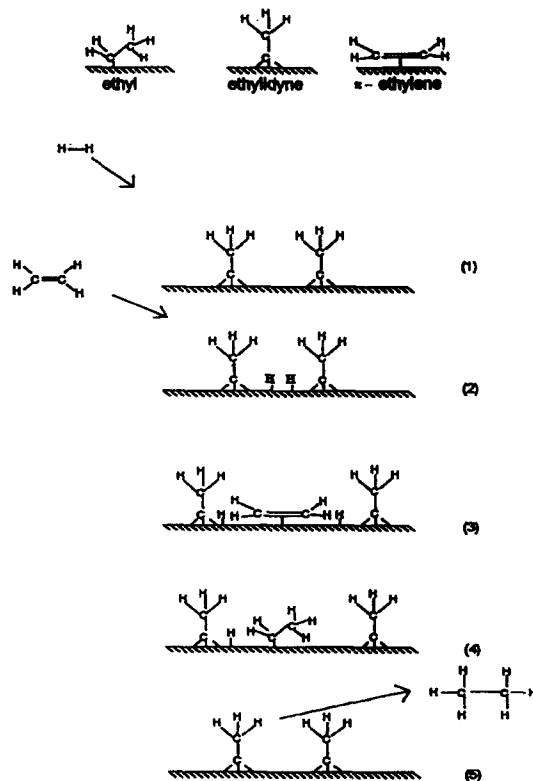


Fig. 12. Proposed mechanism for ethylene hydrogenation.

dilemma, because models of ethylidyne covered surfaces reveal that there is little room left for the adsorption of ethylene for reaction. Ethylene must therefore hydrogenate either in a second layer above the ethylidyne, in a manner similar to that proposed by Thomson and Webb [46], or compress the ethylidyne overlayer in order to be able to adsorb. Both STM studies and extended Hückel calculation have indicated that ethylidyne is very mobile on the surface during reaction conditions. These results would tend to favor the compression explanation. However, the exact source of the insensitivity of ethylene hydrogenation to ethylidyne overlayer has yet to be demonstrated.

The structure sensitivity of ethylene decomposition on the low index faces of the platinum metals under UHV conditions stands in marked contrast to the structure insensitivity of the hydrogenation process at high pressures. Indeed, once the various partially dehydrogenated hydrocarbon overlayers form, only low coordination sites may be left on which catalytic hydrogenation can occur. This may provide an explanation for the surface structure insensitivity of hydrocarbon covered surfaces during ethylene hydrogenation. However, hydrogenation also has been demonstrated to occur without the presence of these overlayers at high H_2/C_2H_4 ratios and the reaction still remains structure insensitive. Therefore, the key intermediate in this reaction must react on a low coordination site regardless of whether a permanent hydrocarbon overlayer is present or not. This is because the need for high coordination sites, which are crystal face specific, would make the reaction structure sensitive.

From thermal desorption studies on Rh(111), Bowker et al. speculated that the weakly bound form of ethylene could be the key intermediate in ethylene hydrogenation. Because ethane formation was only observed concurrently with ethylene desorption, they postulated that the key intermediate in ethane formation must lie in the desorption trajectory of ethylene. They also speculated that steric hindrance would block the incorporation of hydrogen into more strongly bound ethylene. A direct correlation to the homogeneous hydrogenation on Wilkinson's catalyst was made.

Studies in our own laboratory using in situ high pressure SFG show direct evidence for the π -bonded intermediate. During high pressure hydrogenation on Pt(111) both di- σ bonded ethylene and π -bonded ethylene were found to be present on the surface in the absence of a saturation coverage of ethylidyne (Fig. 8a). However, when the surface was saturated with ethylidyne only the π -bonded species and ethylidyne were present under reaction conditions (Fig. 8c). This demonstrate that di- σ bonded

ethylene and ethylidyne compete directly for sites. Because the di- σ bonded species is directly affected by the presence of ethylidyne while the rate of the hydrogenation reaction is not, we conclude that the di- σ bonded species plays only a minor role in the hydrogenation mechanism to produce ethane. The key reaction intermediate should, therefore, be π -bonded ethylene.

Hydrogenation via the π -bonded species would indeed help explain both the lack of structure sensitivity as well as the high turnover rate of this reaction. The more weakly adsorbed π -bonded species is assumed to bond on a top site (Fig. 11). This bonding site would, of course, be available on all metal crystal planes. Fig. 12 is a schematic representation of the mechanism we propose for this reaction. The π -bonded ethylene adsorbs directly to the metal surface on an atop site where it is stepwise hydrogenated through the ethyl intermediate in either the presence or absence of ethylidyne.

6. Conclusion

Structure insensitive reactions appear to be those where reactants first produce a stagnant, strongly adsorbed overlayer of atoms or molecules that occupy all high coordination surface sites. In this circumstance, reaction intermediates weakly bound to a single metal atom are converted to products. The strongly bound adsorbates have sufficient mobility on the metal surface not to interfere with the catalytic process. Ethylidyne and propylidyne are the strongly bound adsorbates and π -bonded ethylene or propylene are the weakly bound reaction intermediates on Pt(111) during ethylene and propylene hydrogenation at 300 K and at atmospheric pressures.

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