# The first measurement of an absolute surface concentration of reaction intermediates in ethylene hydrogenation

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The first measurement of a turnover rate with respect to surface intermediate concentration in a high pressure heterogeneous catalytic reaction is reported. By using infrared–visible sum frequency generation to study the hydrogenation of ethylene on Pt(111), it was found that the surface concentration of $\pi$-bonded ethylene, the key reaction intermediate, represented approximately 4% of a monolayer. Thus the absolute turnover rate per surface adsorbed ethylene molecule is 25 times faster than the rate measured per platinum atom. To explain these results, we propose a model of weakly adsorbed ethylene intermediates reacting on atop sites.

**Keywords:** absolute surface intermediate concentration; ethylene hydrogenation; reaction intermediates in catalysis

## 1. Introduction

The activity of heterogeneous transition metal catalysts has been traditionally measured in terms of a turnover rate per exposed metal atom [1]. Since the concentration of catalytically active sites could not be determined, the assumption that each metal atom represented one active site was made. However, this convention merely provides a lower bound for the rate of product formation per active site. More desirable would be a measurement of catalytic activity per active surface intermediate; however, carrying out such a measurement under realistic reaction conditions has been elusive until now. The difficulty stems from the lack of techniques available for monitoring surfaces on the molecular level under high pressures of reactant gases in such a way that one could distinguish between molecules that turn over and those that are only spectators during the reaction. Instead, in studies using model single crystal catalysts, the surface has been monitored under ultra-high vacuum (UHV) conditions before and after reaction to determine its composition and structure. This corresponds to a thirteen order of magnitude difference in pressure between analytical and reaction conditions. Such ex situ analysis of the surface of heterogeneous catalysts has led to the notion of a "pressure gap" in the characterization of the catalyst surface. To bridge this gap we have used infrared–visible sum frequency generation (SFG), a surface specific vibrational spectroscopy capable of providing chemically specific information at both high and low pressures (i.e. UHV and atmospheres of gases), and developed a UHV/batch reactor system equipped with rate monitoring capability via gas chromatography for the in situ study of heterogeneous catalytic surfaces [2]. The importance of this technique is that it can provide information on the molecular structure of adsorbed reaction intermediates as well as provide a measurement of their surface coverage under realistic reaction conditions. Using this spectroscopy, we have monitored the surface of a Pt(111) catalyst during ethylene hydrogenation. These results identify the key reaction intermediate as well as provide the first determination of its surface concentration under high pressure catalytic reaction conditions.

## 2. Results and discussion

Fig. 1 shows the vibrational spectrum of ethylene hydrogenation on Pt(111) at 295 K with 100 Torr $H_2$ and 35 Torr $C_2H_4$. The conventional turnover rate (TOR) *per platinum atom* as determined by gas chromatography is $11 \pm 1$ ethylene molecules converted to ethane per second. The largest peak in the vibrational spectrum at 2878 $cm^{-1}$ is the $\nu_s(CH_3)$ of ethylidyne ($M{\equiv}CCH_3$), a decomposition species which resides in the fcc three-fold hollow site and is present on the surface during reaction. It has been previously shown on both single crystal surfaces and supported catalysts that this species plays little role in the reaction [3,4]. The feature at 2910 $cm^{-1}$ is from the $\nu_s(CH_2)$ of chemisorbed ethylene. This species is usually referred to as di-$\sigma$-bonded ethylene because the carbon–carbon double bond of the gas phase molecule is broken and two sigma bonds are formed with the underlying platinum surface atoms. The small peak just below 3000 $cm^{-1}$ is the $\nu_s(CH_2)$ of weakly bonded (or physisorbed) ethylene [5]. The molecule's $\pi$ orbital bonds directly with the underlying platinum surface and it is

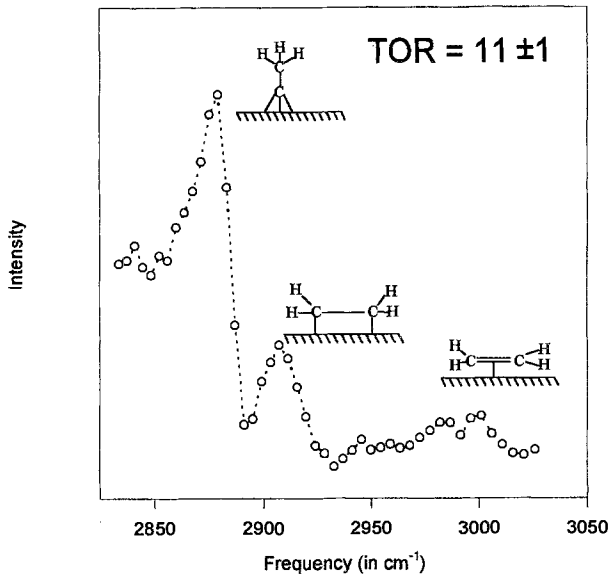


Fig. 1. The vibrational spectrum of the hydrogenation of ethylene with 100 Torr $H_2$ and 35 Torr $C_2H_4$ at 295 K on an initially clean Pt(111) surface. The turnover rate (TOR) is 11 ± 1 molecules/(Pt atom s).

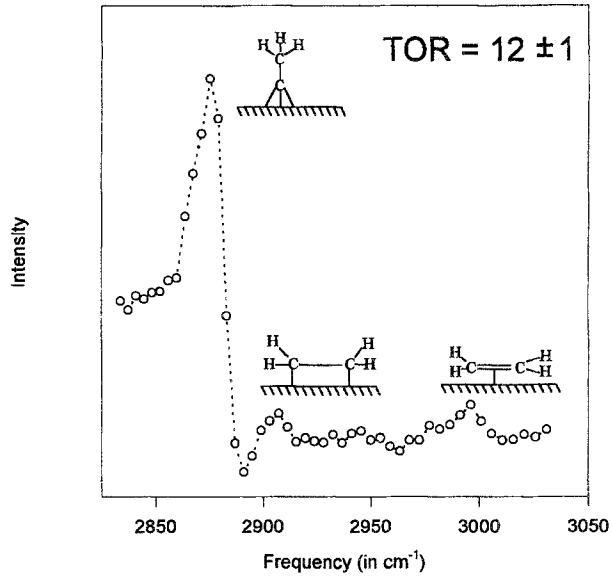


Fig. 2. The vibrational spectrum of the hydrogenation of ethylene at the same conditions as above, but on a Pt(111) crystal that was first saturated with ethylidyne. The turnover rate (TOR) is 12 ± 1 molecules/(Pt atom s).

often called $\pi$-bonded ethylene. The intensity of this feature is weak because the C–H bond axis lies nearly in plane with the metal surface and much of the oscillator strength is canceled by its image dipole in the metal lattice [6].

By predosing a saturation coverage of ethylidyne, it can be demonstrated that this species competes directly for adsorption sites with di-$\sigma$-bonded ethylene under reaction conditions. Indeed, when a saturation coverage of ethylidyne is present very little di-$\sigma$-bonded ethylene adsorbs on the surface, and yet the concentration of $\pi$-bonded ethylene remains unaffected (fig. 2). Further, the reaction continues to take place at almost exactly the same rate as in fig. 1. This is strong evidence that $\pi$-bonded rather than di-$\sigma$-bonded ethylene is the key intermediate in ethylene hydrogenation. It should be emphasized that the other surface species present, di-$\sigma$-bonded ethylene and ethylidyne, are spectators and do not contribute to the turnover rate in any significant way [7]. Interestingly, only these strongly chemisorbed species are normally detectable by studies in UHV, while the weakly bound $\pi$-bonded ethylene is more readily found at atmospheric reaction conditions.

UHV spectroscopic measurements were conducted to calibrate the concentration of $\pi$-bonded ethylene on Pt(111) under reaction conditions. The calibration was achieved by exposing the clean Pt(111) surface to a near saturation coverage of oxygen at room temperature followed by exposure to ethylene at 120 K (fig. 3) [8,9]. This results in a mixture of $\pi$-bonded and di-$\sigma$-bonded ethylene on the surface at concentrations of 6% of a monolayer and 10% of a monolayer respectively [7]. Using the spectrum of fig. 3 as a reference reveals that the intensity of the 3000 $cm^{-1}$ peak in figs. 1 and 2 corresponds to approximately 4% (error bars from 2–8%) of a monolayer of reactive $\pi$-bonded ethylene[#1]. This means that the turnover rate for ethylene hydrogenation is actually 25 times faster per reactive intermediate species than when estimated per exposed platinum atom. Therefore, the absolute turnover rate of physisorbed ethylene is approximately 275 ethane molecules formed *per surface intermediate* per second under the above conditions.

[#1] The error bars for this result are a factor of 2 at the 90% confidence level using worst case assumptions about C–H bond reorientation.

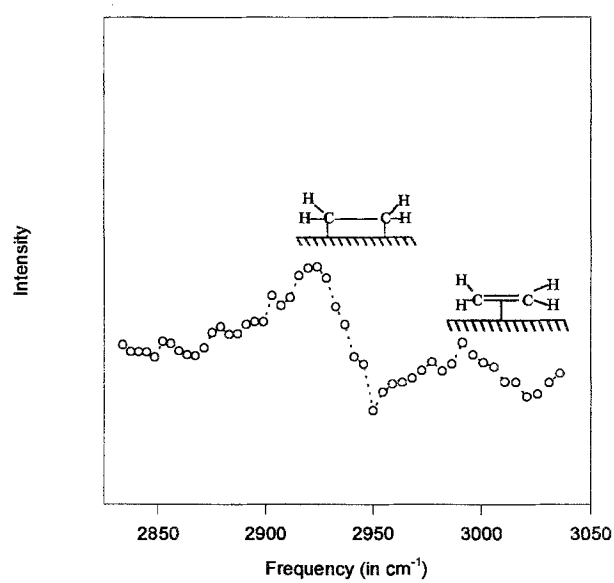


Fig. 3. The UHV calibration spectrum for $C_2H_4$/O/Pt(111) system at 120 K. The system shows two peaks for ethylene corresponding to 0.10 ML of di-$\sigma$-bonded ethylene at 2915 $cm^{-1}$ and 0.06 ML of $\pi$-bonded ethylene at 2995 $cm^{-1}$.

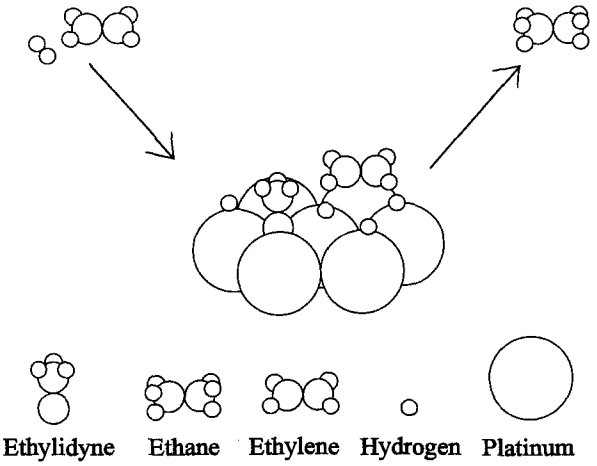


Fig. 4. Schematic representation of surface adsorbates during ethylene hydrogenation.

The concentration of surface intermediates is too high for this reaction to be dominated by defects. In fact, it has been demonstrated that the rate of ethylene hydrogenation is independent of the platinum surface structure over which the reaction takes place (a so-called structure insensitive reaction) [10]. Evidence from inorganic cluster analogs and homogeneous phase catalysis suggests that the reaction probably occurs on atop sites [11,12]. Such sites would, of course, lead to a structure insensitive reaction, because they are available on all crystal faces. The concentration of surface intermediates is much lower than one intermediate per surface platinum atom and remains constant at approximately 4% of a monolayer over a wide range of ethylene pressures. Therefore, this represents a saturation coverage of $\pi$-bonded ethylene under reaction conditions, consistent with the kinetics of ethylene hydrogenation which are nearly zero order in ethylene partial pressure above approximately 25 Torr of $C_2H_4$ [13].

It has been observed that ethylene hydrogenation is unaffected by decomposition species present on the surface during reaction [3,4]. Because the concentration of reaction intermediates is only 4% of a monolayer and the saturation coverage for the decomposition species, ethylidyne, is only 25% of monolayer, it appears that there should always be sufficient sites available on which the reaction may occur. We, therefore, propose a model in which $\pi$-bonded ethylene adsorbs on atop sites where it can be hydrogenated to ethane in the presence of mechanistically unimportant decomposition species. Fig. 4 shows a schematic representation of surface adsorbates during the hydrogenation process.

The ability to identify molecular structure and to monitor the surface concentration of active intermediates with chemical specificity during reaction should greatly contribute toward understanding of the molecular details of a wide range of heterogeneous catalytic reactions. It will be invaluable to exploit SFG vibrational spectroscopy to explore the nature of the surface chemical bonds and the concentration of intermediate species for a wide range of catalytic reactions. Significantly, it has been shown for ethylene hydrogenation, that the surface species present under UHV conditions are different than under ambient reaction conditions. Indeed, this is probably the first of many reactions that will show significantly different surface chemistry at high pressures now that the pressure gap can be bridged.

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