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Monitoring surfaces on the molecular level during catalytic reactions at high pressure by sum frequency generation vibrational spectroscopy and scanning tunneling microscopy

P.S. Cremer [a,b], B.J. McIntyre [a,b,1], M. Salmeron [a], Y.-R. Shen [a,c]
and G.A. Somorjai [a,b]

[a] *Materials Science Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, USA*
[b] *Department of Chemistry, University of California, Berkeley, California 94720-1460, USA*
[c] *Department of Physics, University of California, Berkeley, California 94720-7300, USA*

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Sum frequency generation (SFG), using non-linear laser optics, detects vibrational spectra of submonolayer amounts of adsorbates with excellent energy and time resolution. Scanning tunneling spectroscopy (STM) is sensitive to the atomic surface structure; readily imaging defects, steps and kinks as well as stationary adsorbed species. Both of these techniques can be used during reactions at high pressures and temperatures to obtain molecular information in situ. We report studies of propylene hydrogenation over Pt(111) crystal surfaces at atmospheric pressures and 300 K using SFG and STM. Four surface species (2-propyl, π-bonded propylene, di σ-bonded propylene, and propylidyne) were identified; the first two being implicated as reaction intermediates. The platinum surface structure remains unchanged during the reaction, consistent with the structure insensitive nature of olefin hydrogenation. Propylene decomposition induced substantial surface reconstruction.

Keywords: in situ catalysis; propylene hydrogenation; STM; SFG

1. Introduction

The possibility of studying molecular level changes that take place on surfaces *during* chemical reactions has eluded surface scientists until recently. 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:

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[1] Present address: Intel Corporation, 5200 N.E. Elam Young Parkway, Hillsboro, Oregon 97124-6497, USA.

(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 [1], while the second is more sensitive for monitoring changes of substrate surface structure during chemical reactions [2]. We report high pressure studies of propylene hydrogenation on the (111) crystal face of platinum employing these two techniques.

At 300 K and in the presence of hydrogen, C_3H_6 hydrogenates over platinum. Previous studies have shown that this reaction is relatively insensitive to the structure of the underlying metal substrate [3]. The question arises as to the bonding and chemical nature of the molecular surface intermediates formed upon the adsorption of 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 mixtures near ambient pressure.

2. SFG experiments

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) and 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 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 for abstracting samples for analysis by gas chromatography.

The sum frequency experiment has been described in detail elsewhere [1,4,5]. 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 comes 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. 1. Under these condi-

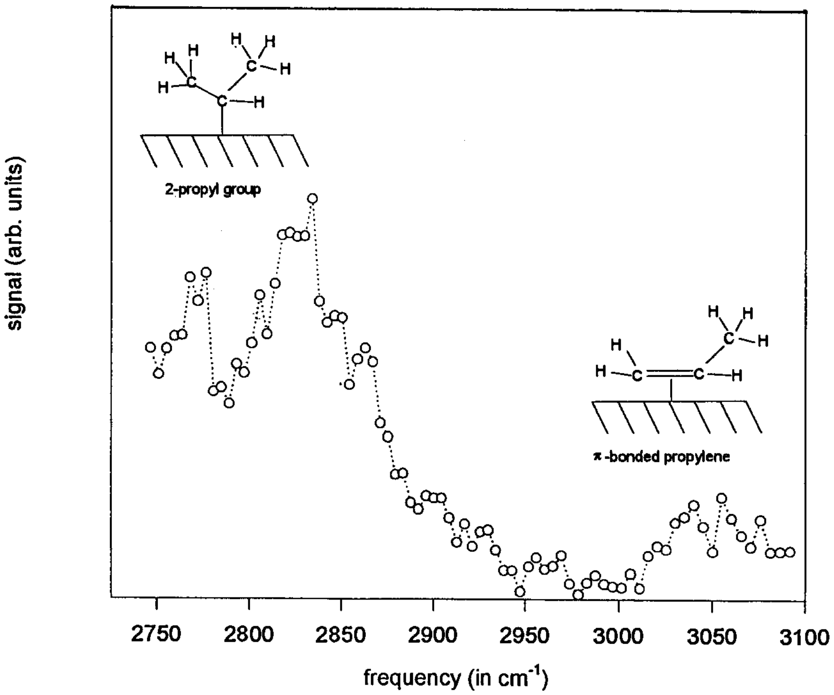

Fig. 1. SFG spectrum of propylene hydrogenation on Pt(111) at 295 K with 715 Torr H_2 and 55 Torr C_3H_6.

tions 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 [$Pt-CH(CH_3)_2$] and a broad feature above 3000 cm^{-1} which corresponds to π-bonded propylene (proof of the assignments was made by UHV calibrations with propylene and propyl moieties [6]). These two species provide convincing evidence for a stepwise hydrogenation mechanism (fig. 2). 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 ($CH_3CH_2CH_2-Pt$) or propylidene ($Pt=CHCH_2CH_3$) 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. 3). The decomposition products, such as propylidyne ($M\equiv CCH_2CH_3$) 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.

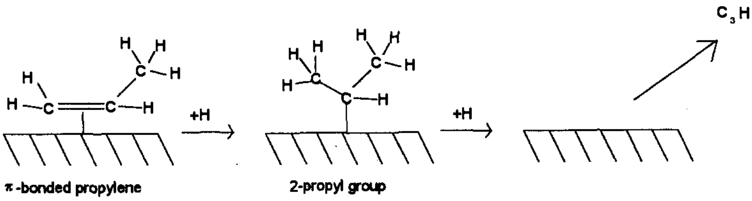

Fig. 2. Schematic representation of propylene hydrogenating on Pt(111) though a π-bonded intermediate onto 2-propyl and then propane.

3. STM experiments

High pressure STM studies of propylene hydrogenation over Pt(111) were carried out in a reactor equipped 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 could be 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 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 $(\sqrt{3} \times \sqrt{3})$ R30 structure that provided

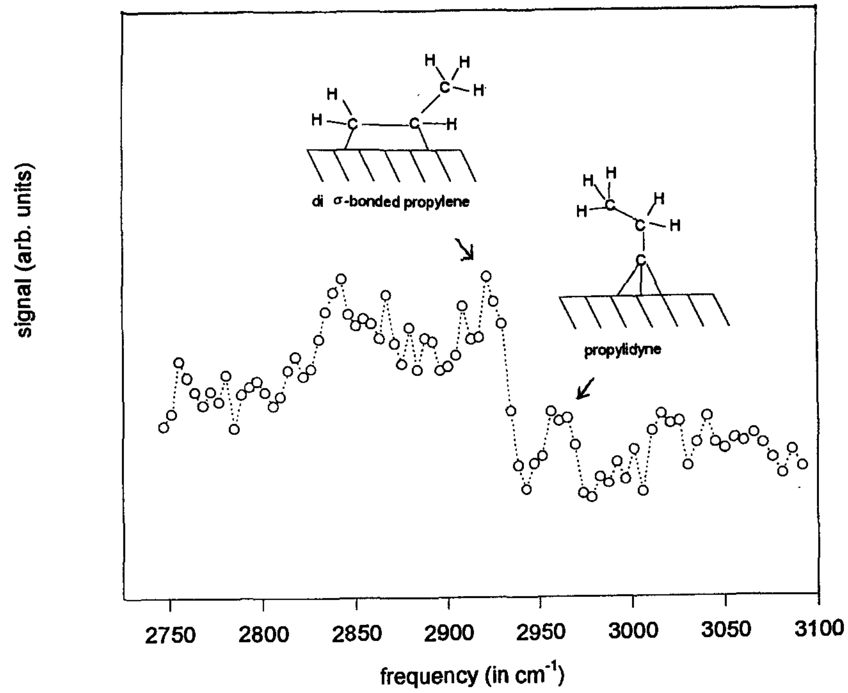

Fig. 3. SFG spectrum of surface species on Pt(111) after reactants have been removed.

strong passivation against adsorption of foreign species [7]. Transfer was performed by use of a vacuum "suitcase" equipped with a small ion pump and a 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 $H_2 : C_3H_6$ (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. 4 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 required specific sites on the metal surface in order to proceed.

Control experiments performed by annealing the sample to temperatures in excess of 770 K in propylene to form carbon clusters gave rise to substantial surface reconstruction (fig. 5). The steps were no longer straight with many kinks or protrusions in the steps that are pinned on top of some of the clusters. This demon-

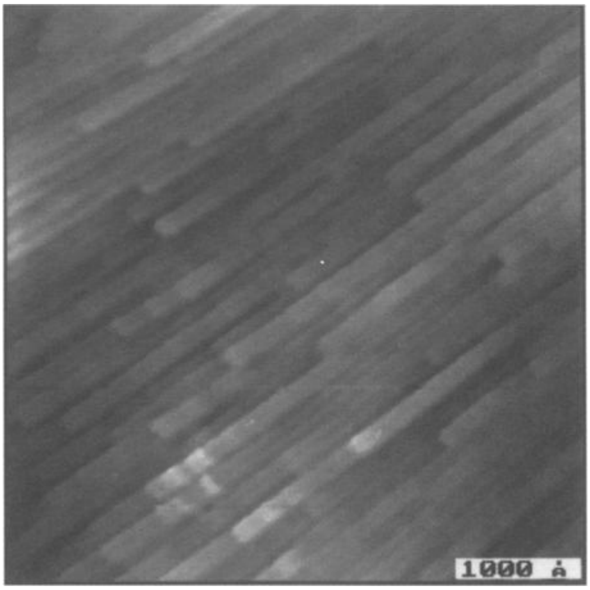

Fig. 4. STM image of 10 : 1 mixture of hydrogen to propylene above a Pt(111) crystal at room temperature.

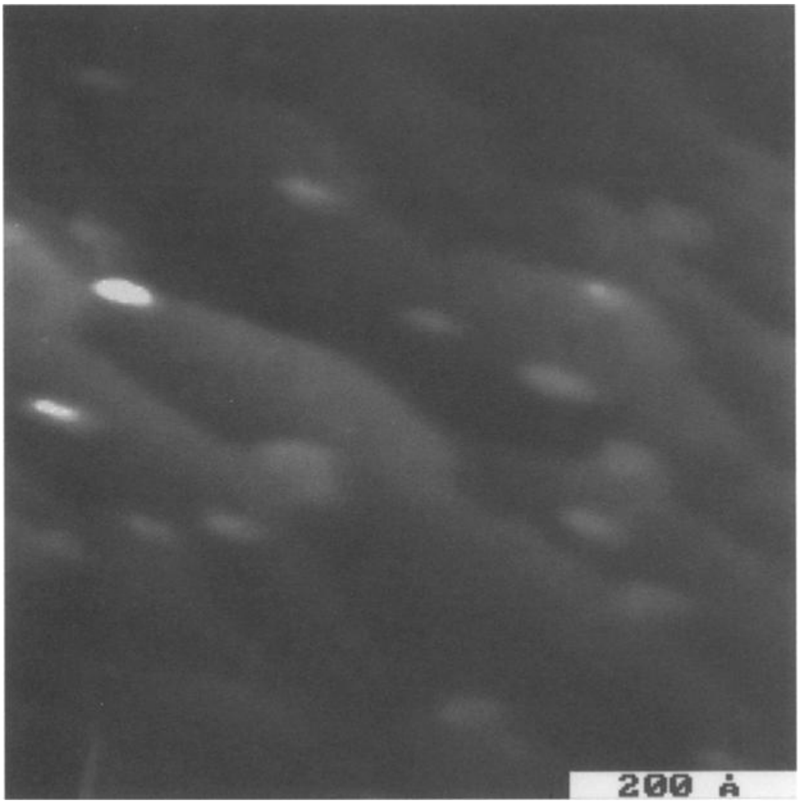

Fig. 5. STM image of carbon clusters decomposed on the Pt(111) surface by annealing to temperatures over 770 K.

strated clearly that had surface reconstruction occurred during reaction the STM was indeed sensitive enough to observe it.

4. Discussion

There are many techniques for studying external surfaces on the molecular level in ultrahigh vacuum (UHV), or at low pressures in the range of 10^{-9}–10^{-5} Torr. Those that are most widely used utilize electron or ion scattering to determine surface structure (LEED, RHEED), surface composition (AES, ISS, SIMS), and the oxidation state of surface atoms (XPS). For those who desire to study the behavior of surfaces at higher pressures without loosing the opportunity of atomic level scrutiny, more complex systems had to be designed. A reaction cell was needed that could:

(1) be operated at high pressures (atmospheres) and high temperatures (1000 K);

(2) enclose the small area sample (~ 1 cm^2) before, during, and after exposure to the reactive ambient gas or liquid;

(3) allow the sample to be transferred into the low pressure of UHV environment where surface analysis commenced using a combination of surface science techniques.

Several generations of low pressure/high pressure instruments were designed and built in our laboratory and elsewhere that permitted surface analysis *before or after the reaction*, but were incapable of monitoring the surface while reaction was occurring. These techniques were mainly responsible for uncovering many of the molecular ingredients of surface reactions; whether stoichiometric (chemisorption) or catalytic (many turnovers). These included the role of substrate surface structure (including steps and kinks) in forming the adsorbate chemical bond, adsorbate-induced restructuring, the coadsorption bond, and the role of surface diffusion in controlling reactivity.

Both SFG vibrational spectroscopy and STM can provide molecular level information about chemical and structural changes that occur on surfaces *during catalytic reactions at high pressures and complementary elevated temperatures.* SFG, because of its superior signal to noise qualities, can detect adsorbed species in concentrations less than 1% of a monolayer. As the spectrum in fig. 1 demonstrates SFG can detect the presence of catalytic reaction intermediates in situ on solid surfaces.

The major limitation of SFG has been its limited frequency range (2650–4000 cm^{-1}), which only allowed the observation of stretching modes. However, the availability of new non-linear optical crystals, such as $AgGaS_2$, will permit us to extend this range to 1100–4000 cm^{-1} in the near future.

STM is sensitive to the atomic surface structure, and is especially suitable for imaging defects, steps and kinks at high pressures and elevated temperatures. It cannot at present image mobile surface species, which includes most small chemisorbed organic molecules at 300 K or above. However, STM detects stationary species like those that form upon propylene decomposition, as well as readily detects adsorbate-induced surface restructuring if it occurs during chemisorption or a catalytic reaction.

While surface restructuring could not be detected in the presence of 1 atm of hydrogen and propylene gas mixtures, it was instantly detectable under 1 atm of CO. Thus, these two techniques (SFG vibrational spectroscopy and STM) provide complementary molecular information during catalytic reactions when applied at high pressures and elevated temperatures. At present, the rapid depolarization of the $ZrBa(TiO_3)_2$ ceramics (which permit movement of the STM tip), as temperature rises near or above their Curie temperature ~ 450 K, limits the accessible temperature range in these studies. It is hoped that more suitable piezoelectric materials will be found to permit higher temperature STM operation, which will make many more catalytic reactions available for investigation.

The application of these techniques allows in situ analysis of reactive surfaces during catalytic reactions. This includes detection of short lived reactive intermediates in small surface concentrations and reaction induced restructuring of metal surfaces. The investigations reported here already provided definitive evidence for a physisorbed intermediate and an unreconstructed surface during catalysis. In light of this, it is likely that new molecular surface phenomena which have eluded detection until now will become observable.

Acknowledgement

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References

[1] Y.R. Shen, Nature 337 (1989) 519.
[2] J. Wintterlin and R. Behm, in: *Scanning Tunneling Microscopy I*, eds. H. Güntherrodt and R. Wiesendanger, Springer Series in Surface Science, Vol. 20 (Springer, Berlin, 1992) ch. 4.
[3] P. Otero-Schipper, W. Wachter, J. Butt, R. Burwell and J. Cohen, J. Catal. 50 (1977) 494.
[4] X. Zhu, H. Suhr and Y.R. Shen, Phys. Rev. B 35 (1987) 3047.
[5] Y.R. Shen, *The Principles of Nonlinear Optics* (Wiley, New York, 1984).
[6] P. Cremer, Y.R. Shen, and G.A. Somorjai, to be published.
[7] K. Hayek, H. Glassl, A. Gutmann, H. Leonhard, M. Prutton, S. Tear and M. Welton-Cook, Surf. Sci. 152 (1985) 419.