

# Conversion of heterogeneous catalysis from art to science: the surface science of heterogeneous catalysis

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## Abstract

Direct combination of high pressure reaction studies with molecular level surface characterization of model catalysts has made possible the development of concepts to describe and to explain phenomena that occur during heterogeneous catalysis. These phenomena include structure sensitivity, surface reconstruction, inert chemisorbed overlayers present under reaction conditions, and interaction between the metal and the oxide support. The catalytic behavior of model systems and the roles of their different components have been investigated and explained in terms of some of these concepts. © 1998 Elsevier Science B.V.

*Keywords:* Model catalysts; Surface science; Heterogeneous catalysis

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## 1. Introduction

Professor Brian Bent of Columbia University was one of the brightest young scientists whose early departure from our midst is an irreplaceable loss. He was also my graduate student receiving his PhD at Berkeley in 1986. His research was focused on surface organic chemistry. He was a conceptual thinker. During his graduate research studies, he uncovered strong correlations between the structure and bonding of organic adsorbates on metal surfaces and that of multi-nuclear organometallic clusters. This paper is written to honor his memory and in spirit of his research focus on surface chemistry concepts of heterogeneous catalysis.

Since the 60s and early 70s, modern surface science techniques have been used to study the surface chemistry of metals in relation to their properties as catalysts. These first model catalysts were low surface area ( $\sim 1 \text{ cm}^2$ ) metal wires, foils and single crystals [1,2]. Improvements in surface specific analytical techniques have been made in parallel with advances in the ability to synthesize more complex but well characterized model catalysts. Advances towards the investigation of the behavior of such model catalysts under relevant catalytic conditions of elevated temperatures and atmospheric or greater pressures began with the development of a conjoining high pressure reactor/ultra-high vacuum (UHV) analysis system [3] (Fig. 1). This allows the correlation of precise knowledge of surface structure and composition with macroscopic catalytic properties.

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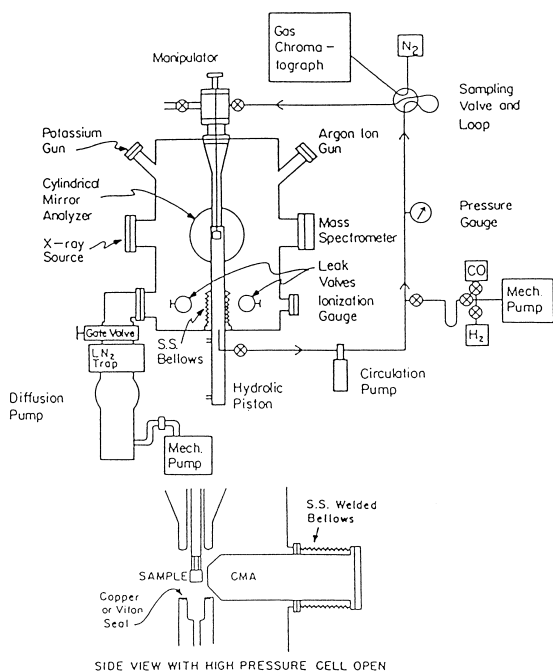


Fig. 1. Schematic of UHV/high pressure apparatus for model catalyst studies. The sample is isolatable from UHV by enclosing it in a high pressure reaction cell, where high pressure kinetics can be measured. Surface analysis takes place with the reaction cell opened.

The major drawback of these low pressure–high pressure systems was that the surface analysis had to be carried out in UHV before and after high pressure kinetic investigations. During the past few years, new techniques have been developed that permit surface characterization during the high pressure catalytic reaction. Among these are sum frequency generation spectroscopy (SFG) and scanning tunneling microscopy (STM). Both of these techniques can be used over a thirteen order of magnitude pressure range ( $10^{-10}$ – $10^3$  Torr) [4].

Observations made in these studies have brought to the fore several concepts that bear significantly on the study of heterogeneous catalysis. Structure/activity relationships have been observed in various forms. In fact, one of the central issues in catalysis is what determines a catalyst's surface structure and how this affects the reaction. As model catalyst research

has moved towards the high pressure regime, the influence of the adsorbate layer on the catalytic chemistry has become apparent. Finally, as more complex model systems have been fabricated, the importance of interactions between the metal particles and the oxide support have been observed. This paper will detail these phenomena and their catalytic importance and then discuss future directions of model catalyst research that may require our current concepts to be modified and expanded.

Surface catalytic concepts are as follows:

- Catalytic structure sensitivity
- Surface reconstruction
- Adsorbate overlayers and structure insensitivity
- Metal–support interactions.

## 2. Catalytic structure sensitivity

The term structure sensitivity, as it applies to heterogeneous catalysis, was first meant to indicate the dependence of the catalytic rate on the size of the catalyst particle. As the metal loading of a dispersed, supported catalyst is decreased, the mean metal particle size decreases as well. The structure of the metal particle's surface is dependent on particle size; the smaller is the particle, the more edge and corner atoms and higher energy faces it has. Thus, any reaction whose rate is affected by the change in particle size is said to be structure sensitive.

The powerful combination of surface crystallography by Low Energy Electron Diffraction (LEED) and reaction studies performed both under vacuum with molecular beams and in high pressure (1–20 atm) demonstrated the concept of structure sensitivity on the molecular level. It was seen that for many reactions performed over well-ordered single crystals steps and kinks at the surface are necessary to achieve high rates (Fig. 2). Hydrogen–deuterium exchange experiments performed with molecular beams on closed-packed platinum surfaces

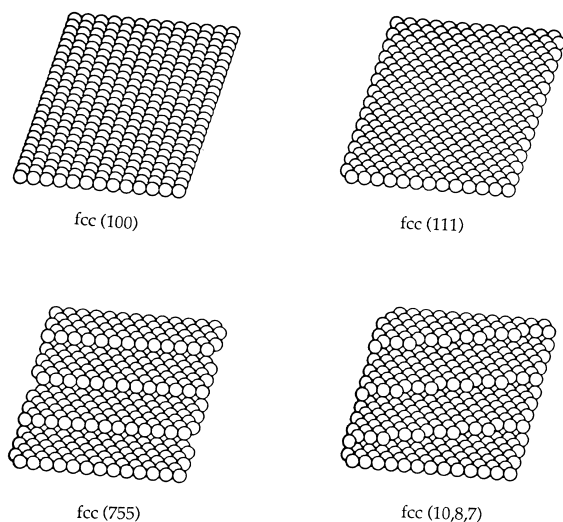


Fig. 2. Schematic of various surface faces of a face-centered-cubic metal. Rough surfaces with steps and kinks often display greater catalytic activity.

showed no detectable activity. This is despite of the fact that platinum will carry this reaction to equilibrium very quickly at atmospheric pressures. However, it was later discovered that platinum crystals cut to expose high Miller-Index planes (a high density of surface steps and kinks) catalyzed  $\text{H}_2\text{-D}_2$  exchange quite easily [5,6]. The direct correlation between low-coordination sites (present at the steps and kinks) and catalytic activity further developed the concept of structure sensitivity and led to the proposition that highly uncoordinated sites are chemically distinct in that they are capable of breaking the bond(s) in the rate determining steps of the mechanism. Thus, for any structure sensitive reaction, there should be an identifiable site or class of sites responsible for the rate determining part of the chemistry.

The special reactivity of rough surfaces is also apparent in non-catalytic surface chemistry. Thermal desorption experiments reveal that stepped surfaces are often capable of adsorbing and decomposing surface species such as adsorbed hydrocarbons and diatomic gasses at significantly lower temperatures than flat surfaces [7–9]. As an example, hydrogen is known to

desorb from the smooth Pt (111) at lower temperatures than from step and kink sites [10]. This indicates that the surface-adsorbate bonding is stronger at these sites and perhaps is the cause of the enhanced reactivity.

Further evidence for this idea was seen under high pressure conditions for many reactions (e.g., hydrodesulfurization, hydrocarbon hydrogenolysis, ammonia synthesis). In particular, ammonia synthesis was studied over different iron single crystal surfaces (Fig. 3). Reaction rate differences of over an order of magnitude were observed, with the highest activity seen for the more rough (111) and (210) faces [11,12] (Fig. 4). Because these particular faces uniquely expose iron atoms coordinate to 7 others ( $C_7$ ), these experiments raise the idea that these sites are responsible for the dissociative chemisorp-

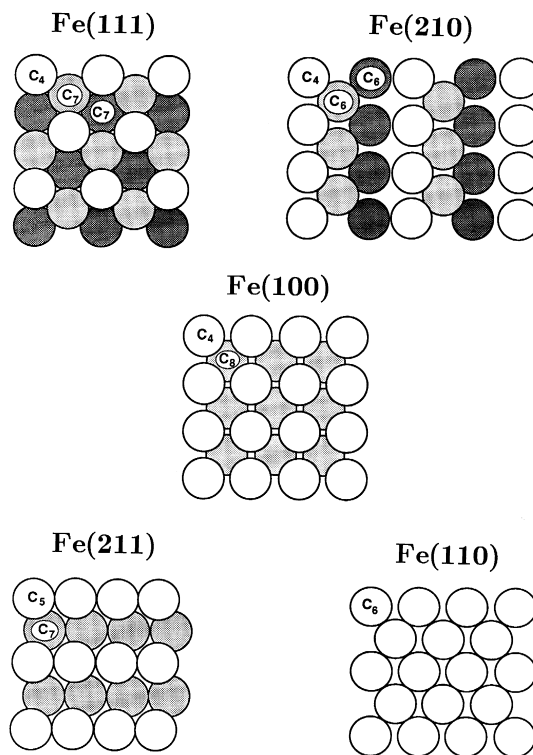


Fig. 3. Schematic of various faces of body-centered-cubic iron. The coordination of different iron atoms are given. More open structures with seven-fold coordinate iron atoms are seen to be more active for ammonia synthesis.

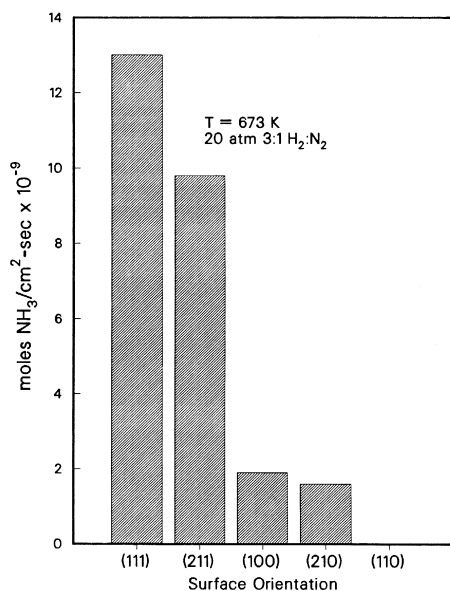


Fig. 4. Relative activity of different faces of iron single crystals for ammonia synthesis. The much greater activity of the (111) and (211) demonstrates the structures sensitivity of this reaction and suggests that the seven-fold coordinate iron sites which are common to both these faces are involved in the rate determining step that is the dissociation of nitrogen molecules to nitrogen atoms.

tion of N<sub>2</sub>, the elementary step that is believed to be rate determining.

### 3. Surface reconstruction

Many metal surfaces, particularly those of high surface free energy, will reconstruct upon the chemisorption of molecules from the gas phase. Surface science studies have demonstrated the importance of adsorbate-induced reconstructions of metal surfaces. The idea that the presence or absence of an adsorbate can cause a gentle or radical change in the equilibrium structure of the metal is sometimes used to explain the enhanced reaction rates. For instance, dissolved carbon has been implicated in the activity of palladium for methane oxidation for its potential role in modifying the metal structure under reaction conditions [13]. Furthermore, the presence or absence of a reconstruction can change the adsorption, bonding

and reaction energetics of species involved in the catalytic mechanism.

Such surface reconstruction has been implicated in the oscillatory behavior of CO oxidation [14] and the reduction of NO by CO, both on Pt (100) [15]. Without adsorbates the Pt(100) surface shows a reconstruction in which the top layer of platinum atoms assumes a buckled, pseudo-hexagonal form. Above sufficient local coverages, carbon monoxide adsorption lifts this reconstruction to form a (1 × 1) overlayer on the (100) surface. Oxygen has a low sticking probability with the reconstructed surface and so only adsorbs on the unreconstructed (1 × 1) surface. During reaction, CO adsorbs on the hexagonal surface until it reaches sufficient coverage to form islands of (1 × 1). Oxygen begins to adsorb on defects and free surface vacancies in the CO filled (1 × 1) regions where it can quickly react to form CO<sub>2</sub>. When there is no longer enough CO adsorbed to hold the (1 × 1) phase, oxygen can no longer adsorb and the surface again is recovered with CO. The rate of CO<sub>2</sub> formation is controlled by the relative amount of hexagonal and (1 × 1) surfaces.

The invention of scanning probe microscopies with nanometer scale resolution has made direct observation of surface reconstructions readily possible on various surfaces. The main advantage of scanning probe microscopies (particularly Scanning Tunneling Microscopy, STM) is that they provide local molecular level information as opposed to an average quantity over millions of molecules such as is obtained by laser spectroscopy techniques. This provides opportunities to study the role of local reconstructions and surface defects in catalytic reaction. This defect chemistry can be compared with that already known for the average of a well-ordered, single crystal surface. Furthermore, STM and other scanning probe microscopies can be operated at under catalytic conditions.

The importance of studying catalyst surfaces under reaction conditions is easily seen from high temperature, high pressure STM experi-

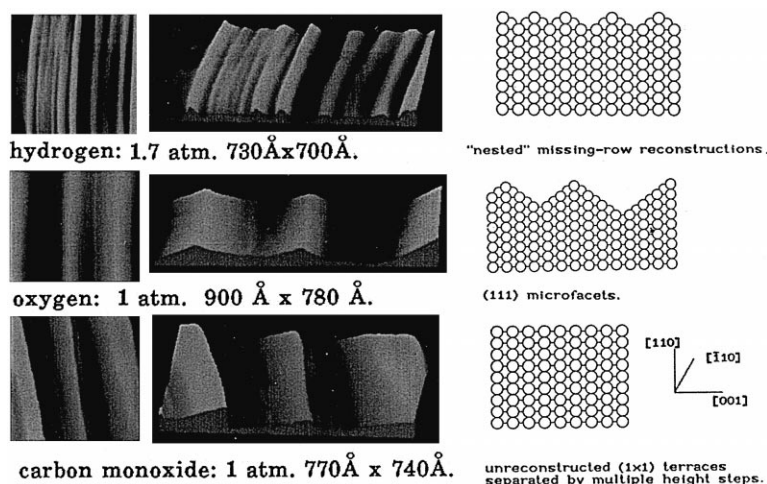


Fig. 5. Reconstruction of platinum (110) as seen by high pressure STM. Hydrogen ambients produce nested missing row constructions. Oxygen ambients lead to microfaceting of the crystal into (111) regions. Exposure to carbon monoxide restores the unreconstructed (100) surface.

ments. Chemisorption at high pressures and temperatures is capable of reconstructing the surface on a scale rarely caused by chemisorption under vacuum. A high temperature, high pressure STM was designed and constructed so that a single crystal or other model catalyst could be prepared and characterized in an UHV environment and then be exposed to atmospheric gas pressures and temperatures up to a 150°C [16]. Afterwards, the gasses could be pumped out and the sample restored to vacuum to repeat the experiment. In the following experiments, the gas was introduced to the sample, which was then heated at 450 K for 4–5 h. The sample was cooled and then imaged before the gas was pumped out with a turbomolecular pump so that the next gas could be introduced.

It was found that ambient pressures of hydrogen, oxygen and carbon monoxide cause the surface of a Pt (110) crystal to reconstruct (Fig. 5). Under 1.6 atm hydrogen, the surface exhibits various missing-row type reconstructions along the [110] direction. In contrast, under 1 atm oxygen, the platinum surface massively reconstructs into (111) facets of 100–300 Å corrugation. The Pt(110) surface is restored by atmospheric pressure of carbon monoxide and the

process is reversible so that each structure is indicative of the adsorbate on the surface.

#### 4. Weakly bound intermediates and structure insensitivity

One of the puzzles of heterogeneous catalysis has been that of the adsorbate overlayer. It has been observed that for many reactions, there is a significant coverage (almost monolayer) of inert adsorbates that do not directly take part in the catalytic reaction [17,18]. In the case of hydrodesulfurization on molybdenum and rhenium, reaction proceeds for more than  $10^4$  turnovers during the residence time of the spectator sulfur overlayer [19]. How this overlayer effects the catalytic chemistry and indeed how the reaction can occur at all over such a surface crowded with spectator species is an important question. Recent research and new characterization techniques suggest that the answer lies in reconsidering the dynamics of this adsorbed layer and role of weakly bound adsorbates in catalysis.

Microcalorimetry techniques have been developed that are capable of directly measuring

the heats of adsorption of various molecules as a function of coverage [20,21]. These results indicate that at high pressures over a metal catalyst surface, a significant fraction of the adsorbed species are weakly bound. These species are perhaps key players in structure insensitive reactions as it is likely that the chemistry of the strongly bound adsorbates should be effected significantly by the structure of the substrate. Such high coverage systems often exhibit chemistry different from that seen under vacuum, again underscoring the need for high pressure surface science techniques.

Recently, techniques have become available that allow the direct observation of surface adsorbates under high pressures. Infrared–Visible Sum Frequency Generation (SFG) spectroscopy is one such technique. SFG is a second-order nonlinear process in which a photon from a visible laser (green) and a tunable IR laser are combined at the surface to produce a photon with the sum of frequency (blue). The infrared beam is tuned across the spectrum of interest and the sum-frequency beam is detected. The probability for the sum frequency process increases when the IR beam is in resonance with a molecular vibration. Furthermore, selection rules require that the media have orientational order and be lacking inversion symmetry. This is only accomplished at an interface and thus provides this technique with its surface specificity. Hydrogenation and oxidation reactions over single crystal model catalysts have been studied with this technique and unique knowledge as to the composition of the surface species, both spectators and reaction intermediates has been gained.

#### 4.1. Ethylene hydrogenation over Pt(111)

Having long been studied by ultra high vacuum techniques and higher pressure IR spectroscopies, much was known about ethylene chemistry on Pt(111) before the advent of Infrared–Visible SFG. Many of the surface species, such as ethylidyne, di- $\sigma$  ethylene and  $\pi$ -ethylene,

had already been identified by vacuum experiments on model catalysts [22–24]. The surface chemistry of ethylene was studied by infrared–visible SFG during a catalytic reaction by using a UHV compatible bell jar as a batch reactor and the gas phase composition was measured by gas chromatograph [4,25].

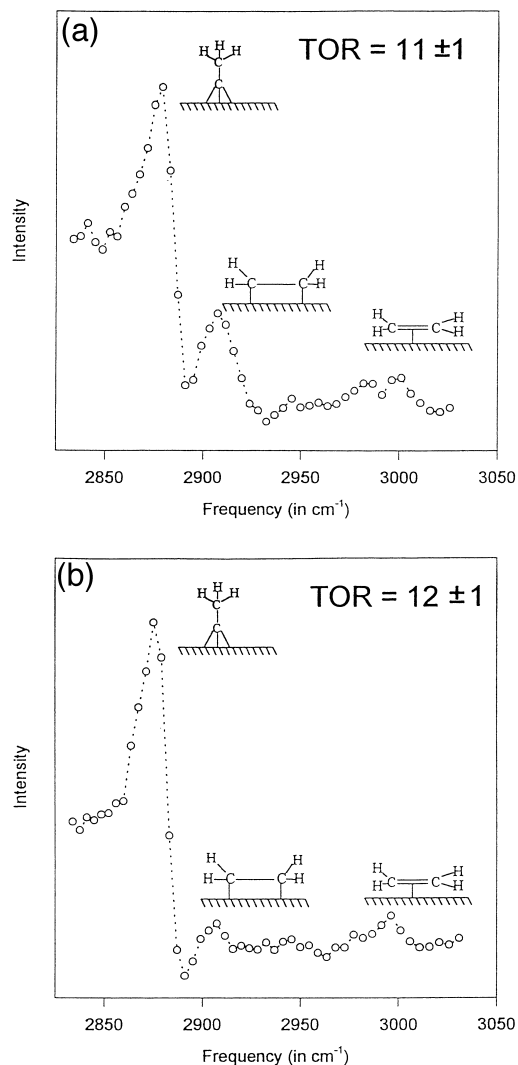


Fig. 6. Sum frequency spectrum during ethylene hydrogenation over Pt (111) single crystal. Surface contains ethylidyne, and  $\pi$ -bonded and di- $\sigma$  bonded ethylene. (a) Spectrum of crystal surface initially exposed to reaction gasses. (b) Spectrum of surface initially pre-dosed with ethylidyne and then exposed to reaction gasses. The turnover rate is independent of di- $\sigma$  ethylene coverage.

Under catalytic conditions (room temperature, 110 Torr  $H_2$ , 35 Torr  $C_2H_4$ ), most of the platinum surface is covered with ethylidyne, a stable dehydrogenated form of ethylene, which has been shown to be a spectator in the ethylene hydrogenation reaction [26] (Fig. 6a and b). The other peaks have been assigned to the C–H symmetric stretches of di- $\sigma$  ethylene, a nearly  $sp^3$  hybridized species with the C–C bond parallel to the surface and finally a physisorbed  $\pi$ -bonded species. The weak signal of the resonance in the  $\pi$ -bonded ethylene is explained by the metal-dipole selection rule. The image dipole induced in the metal cancels the component of the molecular dipole parallel to the surface and thus signal off from C–H stretches whose dynamic dipole is almost parallel to the surface is weak. This spectrum is reproducible, stable and constant during reaction.

The rate of ethylene hydrogenation was shown to be independent of both the di- $\sigma$  ethylene signal and the ethylidyne signal by comparing experiments where the crystal is pre-dosed with a saturation coverage of ethylidyne to one where it is not pre-dosed. Ethylidyne competes for sites with the di- $\sigma$  species and hinders its formation. Thus, the pre-reaction addition of ethylidyne reduces the surface coverage of di- $\sigma$  ethylene. However, the signal from the  $\pi$ -bonded species is the same as irrespective of the coverage of the other species as does the rate of ethylene hydrogenation. This indicates that neither ethylidyne (as was previously known from  $^{14}C$  tracer studies) [26] nor the di- $\sigma$  ethylene is the active intermediate. Because the signal form of the  $\pi$ -bonded ethylene remained constant as did the reaction rate, it is most likely that this weakly bound species is the reactive intermediate.

By using known coverages of  $\pi$ -bonded ethylene prepared in UHV as a calibration, it was determined that its coverage under catalytic conditions was 2–8% of a monolayer. This corresponds to an absolute turnover rate of  $\sim 275$  ethane molecules/surface intermediate per s,  $\sim 25$  times higher than the turnover rate as

estimated by the number of platinum atoms at the surface (turnover rates are usually given in molecules/surface atom per s). Thus, because of its capabilities both under vacuum and high pressures, SFG spectroscopy allowed for the first time the determination of an absolute turnover rate.

#### 4.2. CO oxidation over Pt(111)

Similarly, carbon monoxide oxidation was studied under reaction conditions using SFG [27]. The reaction was carried out in two temperature regimes: above and below the ‘light off’ temperature. Below this temperature, the major spectral species is CO bound to the atop site on the platinum lattice. The signal from this species decreases with increasing surface temperature while the oxidation rate increases (Fig. 7). This produces a strong negative order dependence of the rate on surface concentration of atop CO indicating that it is a poison for the reaction.

At temperatures above ‘light off’, the surface spectrum is dominated by a broad band indica-

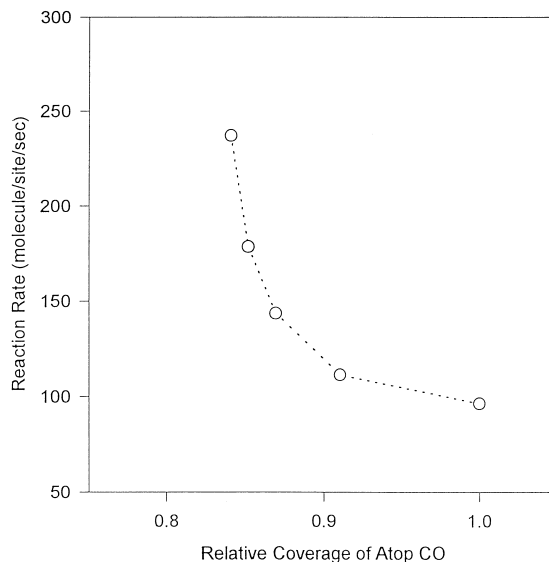


Fig. 7. Rate sensitivity of CO oxidation over Pt (111) at 590 K to coverage of atop site CO as determined by Infrared–Visible Sum Frequency Generation Spectroscopy.

tive of an incommensurate layer of CO and this feature (shown in Fig. 8) is correlated with oxidation rate.

#### 4.3. STTI of sulfur / carbon monoxide overlays

The reactivity of overlayer covered surfaces can be understood if the bonding structures of these strongly bound species are flexible enough to allow the ready adsorption, reaction and desorption of more weakly bound species. Compression of such an elastic overlayer of sulfur by adsorption of carbon monoxide was seen on platinum and rhenium surfaces by LEED and STM [28]. A 0.25 monolayer  $p(2 \times 2)$  sulfur structure was prepared on the (0001) face of rhenium by decomposition of  $H_2S$ . Carbon monoxide was then exposed at  $5 \times 10^{-9}$  Torr

#### *In situ* SFG Spectra of CO Oxidation with 250 Torr CO/50 Torr O<sub>2</sub>

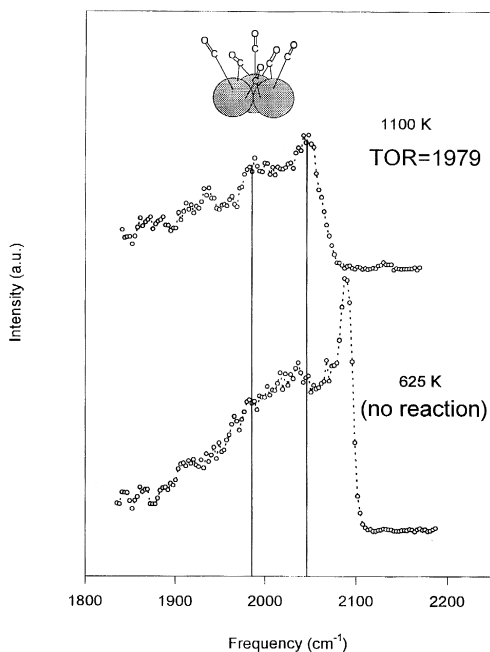


Fig. 8. *In situ* spectra of CO oxidation over Pt (111). The largest feature at 625 K is due to atop CO. This peak is absent at 1100 K where the turnover-frequency of the reaction is 1979 molecules per site per second.

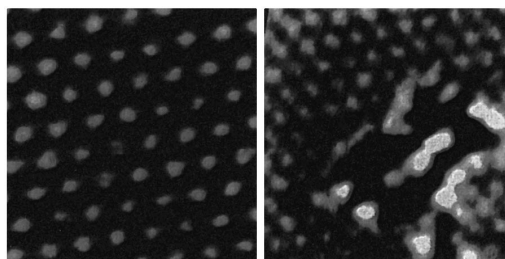


Fig. 9. STM image of sulfur on Re (0001) before and after exposure to CO. The ordered bright maxima are due to individual atoms in a  $p(2 \times 2)$  sulfur overlayer. (Image size  $40 \text{ \AA} \times 40 \text{ \AA}$ ) After CO expose a hole has formed in this overlayer with compressed sulfur structures seen at its perimeter. The CO molecules, which are not usually visible in STM images have displaced the sulfur in this region. (Image size  $55 \text{ \AA} \times 55 \text{ \AA}$ ).

and over a period of minutes the  $p(2 \times 2)$  was replaced by a more dense ( $\sqrt{3} \times \sqrt{3}$  R30). This LEED pattern corresponds to a 0.33 monolayer coverage. However, the average sulfur coverage as measured by Auger spectroscopy was unchanged, indicating that the sulfur had been compressed in certain regions. When investigated by STM, it was observed that upon exposure to CO the sulfur atoms at the periphery of defects were compressed into the trimer structures associated with the ( $\sqrt{3} \times \sqrt{3}$  R30) structure (Fig. 9). Carbon monoxide itself is rarely imageable by STM and here appears as 'clean' areas of the surface surrounded by compressed sulfur.

## 5. Oxide films and metal–support interactions

In its most basic form, the industrial heterogeneous catalyst consists of a metal component dispersed on a metal oxide support. Thus, much work has been done incorporating the metal and metal oxide components into model catalysts.

The main experimental difficulty involved with the study of metal oxides is that they are insulators and so tend to charge when exposed to incident electrons required with so many of the surface specific techniques available (e.g., X-ray photoelectron and Auger spectroscopies,



electron energy loss spectroscopy). Because of this, the most common practice is to prepare thin metal oxide films on a conducting substrate to allow charge dissipation. Much work has been done growing and characterizing these ultra-thin (1–50 nm) metal oxide films with the goal of retaining synthetic control over the structure and stoichiometry of the oxide. This has been accomplished with some success in various research groups by judicious choice of both the metallic substrate and the growth conditions. A partial list of epitaxially grown metal oxide thin films includes:  $\text{Al}_2\text{O}_3/\text{NiAl}(110)$  [29],  $\text{Al}_2\text{O}_3/\text{Ta}(110)$  [30],  $\text{Al}_2\text{O}_3/\text{Mo}(110)$  [31],  $\text{Fe}_2\text{O}_3/\text{Pt}(111)$  [32],  $\text{TiO}_2/\text{Pt}(111)$  [33],  $\text{Cr}_2\text{O}_3/\text{Cr}(110)$  [34],  $\text{NiO}/\text{Ni}(111)$  [35],  $\alpha\text{-MgCl}_2/\text{Pd}(111)$  [36].

One area in which the metal and metal oxide component have been shown through model catalysts to have a chemical synergy is the case of carbon monoxide and carbon dioxide hydrogenation over rhodium [37–39]. Thin (sub-

monolayer) films of various metal oxides were grown on rhodium foils and the dependence of the hydrogenation rate on the coverage of the oxide was measured. A drastic increase in the hydrogenation rate was observed for a certain class of oxides ( $\text{TiO}_x$ ,  $\text{TaO}_x$ ,  $\text{NbO}_x$ ) at coverages between 0.2 and 0.7 monolayers (Fig. 10). This is as opposed to a system like  $\text{FeO}_x/\text{Rh}$  where the  $\text{CO}_2$  hydrogenation decreases monotonically with coverage as would be expected from a simple site blocking mechanism as the surface area of the active rhodium decreases.

This maximum in the rate as coverages around 1/2 monolayer was postulated to be due to an enhanced catalytic activity at the linear metal/metal oxide/gas interface. From XPS measurements of the oxidation state of the metal oxide cation before and after the reaction, a correlation was drawn between the reducibility and Lewis-acidity of the metal oxide under reaction conditions and the hydrogenation rate enhancement. This rate enhancement is attributed to the formation of a Lewis acid-base complex of adsorbed CO or  $\text{H}_2\text{CO}$  and an exposed metal cation at rhodium/metal oxide boundary which facilitates the cleavage of the C=O bond.

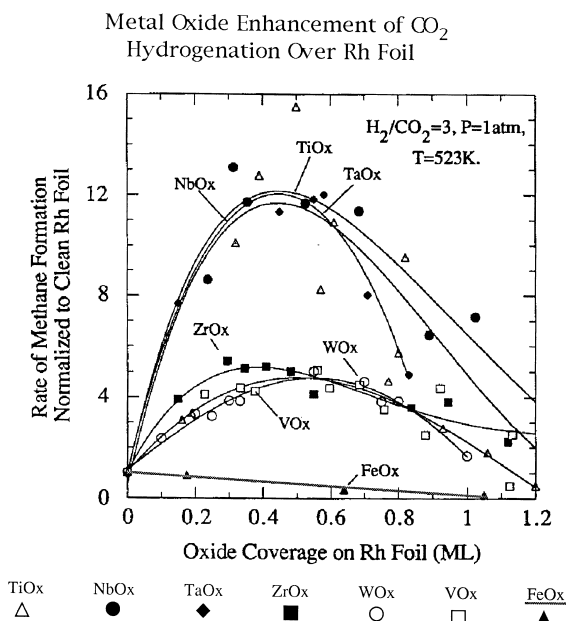


Fig. 10. Plot of rate of methane formation from  $\text{CO}_2$  hydrogenation over rhodium foil promoted by sub monolayer coverages of metal oxide at 523 K. Rates are normalized to that of a clean foil. For various oxides, the rate is highest at  $\sim 1/2$  monolayer coverages indicating the promotional effect.

## 6. Multi-component model catalysts from new controlled fabrication methods

Based on current understanding of heterogeneous catalysis, there is considerable interest in fabricating metal particle on metal oxide model catalysts. One goal is to control the size and structure of these metal particles to directly determine the nature of structure sensitivity for supported systems. Because their high dispersion of surface atoms makes them energetically different from bulk foils and crystals, it is important to determine for nanometer-sized particles the manner in which other components such as the support, promoters and adsorbates effect their structure and reaction kinetics. Interesting structure/activity and structure/selectiv-

ity relationships remain to be understood particularly in the area of chiral selective catalysis.

The industrial catalyst contains the active component, often a metal, that is usually finely dispersed over a support—usually a high surface area metal oxide such as alumina or silica. The catalyst may also include one or more promoters that may effect such properties as the catalysts activity, selectivity or stability. Additional complications in understanding the catalytic chemistry may arise if the catalyst is a multi-metallic or multi-metal oxide system. Synthetic advances in metal and metal oxide film preparation as well as methods borrowed from other areas of scientific endeavor now allow model catalysts with many of these material components to be prepared in a well-defined manner. Each of these types of additional components have been replicated with various sorts of model catalysts, although to date there have been few studies of model systems containing all these components.

Poppa et al. have evaporated metal particles onto alumina covered Transmission Electron Microscopy grids and, by careful control of the preparation parameters, achieved remarkably narrow size distributions of metal particles spread more or less randomly over the support. This system was used in the study of CO oxidation over Pd [40,41]. Xu and Goodman [42,43] and Xu et al. [44] have deposited metal particles (Cu and Pd) over oxide thin films previously grown and characterized on metallic substrates. These model catalysts have been investigated by spectroscopic and probe microscopy techniques and found to be similar in structure to what is expected on a high surface area catalyst. Infrared spectroscopy studies of adsorbed carbon monoxide in the particles reveal that upon annealing the surface of the larger particles is composed of mostly (111) and (110) facets. As a model reaction, carbon monoxide oxidation was carried out over such ultra thin film-supported model catalysts and its rates and activation energies were agreed with those determined for palladium single crystals.

On the other end of the metal particle size spectrum, Gates et al. have synthesized true metal carbonyl clusters (2–6 atoms) and deposited them within zeolites and on other supports to study their activity [45,46]. The metal carbonyls are either deposited on the surface in cluster form or they are formed by reaction with CO from adsorbed single metal atom precursors. They are then decarbonylated while the structural framework metal cluster remains intact, as can be determined by EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy.

Toluene hydrogenation, a reaction considered to be structure insensitive, was performed as a trial reaction over Ir<sub>4</sub> and Ir<sub>6</sub> clusters. The clusters proved to be stable catalysts as evidenced by constant activity over several hours and no apparent structural changes were induced in the metal framework as determined by EXAFS. Significantly, the rates of reaction over the clusters were almost an order of magnitude lower than over larger iridium aggregates and crystallites. As the reaction rates are so low and the clusters too small to be adequately described by any surface plane, these results call into question the meaning of the term structure sensitivity at such small particle sizes. The electronic structure of these nanoclusters may be very different from particles of larger size.

## 7. Lithographically fabricated model catalysts

Other scientific fields have made use of lithography techniques for many years. Microcircuit design and fabrication is based on lithography. More recently, mechanical and bioengineering have taken up microlithography as a means of developing ultra miniature sensors and machines. In catalysis, lithography offers the opportunity to access chemically relevant length scales (3–1000 nm) in a controlled and well-defined manner. The size of metal particles generally found in industrial catalysts is within this

length scale as is the average distance between the particles.

Synthetic methods, as opposed to lithography, are limited by what chemistry will allow. With careful attention to preparation conditions, one can gain control over the metal particle size distribution for many systems. However, the preparation method is always slightly different and some particle/support systems defy easy synthesis.

Lithography is a general process which allows the possibility of not only controlling particle size for a wide range of systems but also allows control of spatial distribution of particles on support, and it does so for a wide range of particles and support materials. The essential requirement is that the support be flat and somewhat conductive. These two properties are generally important in model catalyst studies as well and so they do not apply any additional restrictions on the sorts of systems that can be studied. The particle size and spatial distribution may be important variables in metal support interactions where the amount of interface between the metal and the metal oxide is important and spillover of surface species between the particle and support.

There are several lithographic methods available to selectively deposit metals on a substrate. All of them use the same basic process (Fig. 11). One starts with a source of energetic particles to pattern a polymer-based resist-covered surface. The chemical nature of the polymer is altered so that one can selectively remove the resist according to the pattern. Afterwards, one deposits a thin film of metal (or whatever material is called for) over the surface. Then, the remaining resist is removed leaving behind metal only in the area had no resist previous to the metal deposition.

The advantage electron beam lithography has over other lithographic methods, such as optical, X-ray and ion beam lithographies, is its resolution [47,48]. Light-based lithographies and some ion beam techniques have the advantage of parallel exposure; a mask can be used to expose

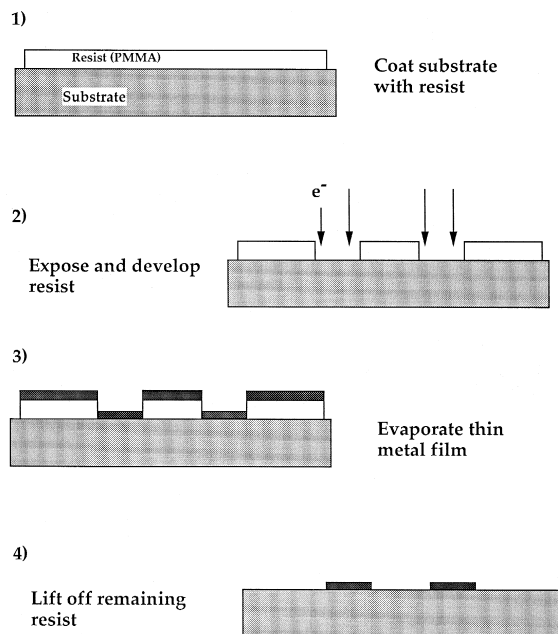


Fig. 11. Procedure for electron beam lithography. Coat flat substrate with polymer resist ( $< 0.250 \mu\text{m}$  thick). Expose resist to electron beam ( $\sim 10\text{--}100 \text{ kV}$ ) at every point where a particle is to be deposited. Selectively develop resist in alcohol/ketone solution to remove polymer only in the exposed areas. Evaporate a thin metal film over everything. Strip remaining resist with stronger developing solution, leaving metal only in the areas previously exposed by the beam.

all of the features at one time. Electron beam lithography is a serial process where each pixel of each feature must be exposed individually. However, electron beam lithography has been shown to produce feature sizes less than 10 nm, while the state-of-the-art of the other techniques such as optical and ion beam lithographies is usually in the 100 nm size range. It was selected for this reason by researchers in this laboratory to fabricate metal particle arrays on oxide supports.

A sample of platinum particles on an oxidized silicon wafer was prepared by Dr. Shalom Wind at IBM, Yorktown Heights (Fig. 12). The particles were arranged in a square array of 200 nm periodicity, each particle being 50 nm in diameter and 15 nm in height as measured by Atomic Force Microscopy (AFM). The array covered an area of  $5 \text{ mm} \times 8 \text{ mm}$ , consisting of  $\sim 10^9$  such platinum particles.

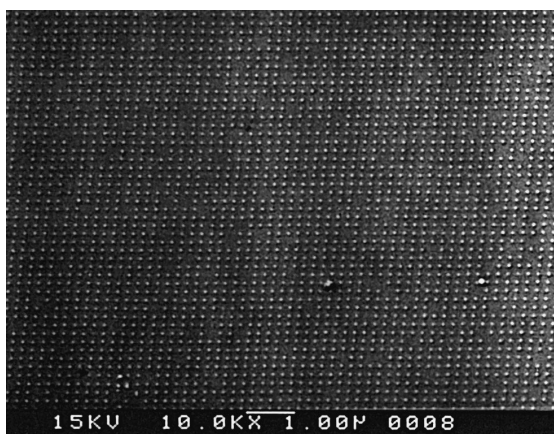


Fig. 12. Scanning Electron Microscopy image of Pt/Silica array produced by e-beam lithography. The distance bar is 1  $\mu\text{m}$ . Array contains  $\sim 10^9$  particles each 50 nm in diameter and 15 nm high. The particles are arranged in a square array with 200 nm between the centers. The total platinum surface area is 0.04  $\text{cm}^2$ .

### 7.1. Chemical characterization and catalytic activity of nanoparticle arrays

The particle array exhibits remarkable stability to annealing and exposure to electron and ion beams. The catalysts surface was cleaned of carbonaceous contaminants by a sequence of low energy ion sputtering. Such cleaning is necessary to activate the sample. AFM and carbon monoxide thermal desorption experiments show that the structure of the array remains intact after such cleaning procedures [49].

Ethylene hydrogenation was selected as a test reaction for this array and was run at high pressure in a conjoining reaction cell. Ethylene turnover rates are in good agreement with those previously measured over single crystals, high surface area-supported catalysts and a platinum foil run as a standard in the same system.

Thermal desorption experiments were performed with deuterium and isotopically labeled carbon monoxide in order to investigate the chemical nature of the silicon oxide support. It was seen that ratio of  $\text{D}_2$  desorption from the particle array to  $\text{D}_2$  desorption from a reference platinum foil was 2–4 times greater than the same ratio for  $^{13}\text{C}^{18}\text{O}$ . This extra adsorbed deuterium is explained by spillover from the metal

to the silicon oxide support as is known to occur on high surface area, dispersed catalysts.

Recently a state-of-the-art electron beam lithography machine has been installed at LBNL (Lawrence Berkeley National Laboratory). This new instrument, called the ‘nanowriter’, is designed to have  $< 3$  nm resolution and the speed and sample capability to prepare arrays covering several square centimeters. As a result, there is the possibility of fabricating useful supported metal model catalysts with the sub- $10$  nm feature sizes necessary to exactly mimic industrial catalysts.

## 8. New directions

The rich chemistry exhibited by multi-component industrial catalysts has always provided a driving force to understand the surface chemistry of more complex model systems under industrially relevant conditions (high pressure and temperature). Towards this end, new methods of model catalyst preparation have been developed to expand catalyst complexity without sacrificing molecular level control over structure and composition. In addition, there is a continued need for surface specific analytical techniques that are capable of operating in situ.

As always, model catalyst studies derive their importance from the molecular level information they offer about the surface chemistry of catalytic systems. The outstanding questions in catalysis dictate where the advances will need to be made to further develop the field.

How do the microscopic structure and morphology of the catalyst effect the surface and catalytic chemistry? Further work will continue to be done to bridge the gap in material complexity that exists between model and industrial catalysts. These efforts will have to take into account the increasing complexity of industrial catalysts in which multi-component systems with multiple phases are becoming more important [50]. The interaction between these phases

is something that model catalyst studies will have to address.

The ability to construct complex model catalysts will be instrumental in the understanding of the surface chemistry of promoters and co-catalysts. Information concerning such issues as the location, structure and chemical state of these compounds will be necessary for a complete understanding of their roles in catalyst activity, selectivity and stability.

Catalytic processes often occur over short time scales, especially at high temperatures where the lifetime of surface intermediates is very short. Different surface chemistry may occur at high temperatures above the desorption temperature of most surface species. A molecule that impinges on a hot surface, clean of relatively static adsorbed species, may have sufficient energy to very quickly react and desorb as an excited species. These processes occur at sub-millisecond time scales and if the desorbing species are indeed unstable, then the possibility of addition gas phase reaction exists. The role of the surface chemistry in a catalytic reaction with both heterogeneous and homogeneous components is an open question having ramifications in short contact time oxidations and other important reactions [51,52]. Model catalyst studies will almost certainly need to include short time scale techniques in order to investigate these reactions.

Liquid phase catalysis is a growing field in which studies of model systems stand to play an important role. Here, again, scanning probe microscopies and surface specific spectroscopies figure to be the major techniques allowing in-situ investigations of model catalyst surfaces. Scanning Tunneling Microscopy and nonlinear optical spectroscopies have already been shown to be useful in the studies of the solid–liquid interface. Adsorbate surface chemistry may be different at the solid–liquid interface where the density of the fluid is orders of magnitude greater than at the solid–gas interface. In an analogous manner to the study of the solid–gas interface, more complicated multi-component

models of the solid–liquid interface will need to be fabricated as the field progresses.

An understanding of the root causes of catalyst selectivity is an important challenge. A major hurdle in this endeavor to prepare single site model heterogeneous catalysts in order to directly investigate and perhaps tune their catalytic nature. Preparation schemes have been developed to modify model catalyst surfaces to produce particular active sites [46,53,54].

Enantiomer selective catalysis of organic molecules is a field of growing importance where the ability to control a specific site is paramount. Advances in nonlinear optical spectroscopic techniques such as SFG bring the opportunity to study chiral chemistry at the surface. One of the most important stereoselective industrial processes is the Ziegler–Natta synthesis of isotactic polypropylene. The industrial Ziegler–Natta system is complex, consisting of titanium chloride supported on ball-milled magnesium chloride which is then treated with a co-catalyst (generally an aluminum trialkyl) and a Lewis base for stereoselectivity. Surface science techniques have been used to prepare model catalysts for this system that are capable of polymerizing ethylene with rates comparable to the industrial systems [55]. The combination of advanced model catalyst preparation techniques with in-situ characterization techniques capable of discerning differences in chirality promises to be a powerful tool in understanding heterogeneous chiral catalysis.

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