Catalysis: from single crystals to the “real world”

D. Wayne Goodman
Chemistry Department, Texas A&M University, College Station, TX 77843, USA

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The “pressure and material gaps” separating UHV and technical catalytic investigations have been bridged in recent years by combining in a single apparatus the ability to measure kinetics at elevated pressures on single-crystal catalysts with the capabilities to carry out surface analytical measurements. In these high-pressure/surface analytical studies a well-defined, single-crystal plane is used to model a site or set of sites expected to exist on practical high-surface-area catalysts. This “surface science” approach has been used to study structure sensitivity, the effects of promoters/inhibitors on catalytic activity, and mixed-metal catalysis. In this article, some of the progress made during the last twenty years to integrate modern surface science into fundamental catalytic research will be reviewed, including recent efforts to simulate oxide-supported metal systems using thin oxide films.

1. Introduction

The ultrahigh vacuum (UHV) approach to the study of catalysis offers many advantages over traditional methods in that a variety of modern surface spectroscopies are now available to study in great detail the structure and composition of surfaces and to identify relevant surface species. However, a common criticism of the UHV approach has been that it is too far removed from reality, since catalytic reactions typically are carried out under quite different conditions, namely, at atmospheric (or higher) pressures and with far more complex surfaces.

These so-called “pressure and material gaps” separating UHV and technical catalytic investigations have been bridged in recent years by combining in a single apparatus the ability to measure kinetics at elevated pressures on single-crystal catalysts with the capabilities to carry out surface analytical measurements [1–6]. In these high-pressure/surface analytical studies a well-defined, single-crystal plane is used to model a site or set of sites expected to exist on practical high-surface-area catalysts. This “surface science” approach [6] has allowed a direct comparison of reaction rates measured on single-crystal surfaces with those measured on more realistic catalysts.

These combined methods have also provided detailed studies of structure sensitivity, the effects of promoters/inhibitors on catalytic activity, and, in certain cases, the identification of reaction intermediates by post-reaction surface analysis. These kinds of studies have established the validity of using single-crystal surfaces as models for the more complex technical catalysts for a variety of reactions [6].

In this article, some of the progress made during the last twenty years to integrate modern surface science into fundamental catalytic research is reviewed. Specific examples from our work are used to demonstrate the advantages and relevance of single-crystal studies for modeling the behavior of high-surface-area-supported catalysts. Recent efforts to simulate oxide-supported metal systems using thin oxide films are also described. These thin oxide films offer a wide range of opportunities for investigating the more complex issues of catalysis such as metal–support interactions and quantum size effects in small metal particles using model catalysts that are realistic enough to simulate the nuances of the
more complex “real world” system, yet tractable for typical surface science studies.

2. Clean metal single crystals: structure insensitivity

2.1. CO methanation

The reaction of CO with H₂ is an essential reaction in the production of synthetic natural gas from hydrogen-deficient carbonaceous materials. In addition, this reaction is an obvious starting point in studies of fuel and chemical synthesis from carbon sources. Because of the extensive investigations of the adsorption behavior of H₂ and CO on single-crystal surfaces in the surface science literature, the methanation reaction offers an attractive starting point for elevated pressure investigations using single-crystal catalysts and surface science techniques. Accordingly, this reaction has been the subject of many investigations beginning with monometallic surface studies and, more recently, with studies addressing the effects of surface additives such as poisons, promoters, and dissimilar metals.

For example, in the late seventies the steady-state specific methanation rates (methane molecules/site s⁻¹) were measured on the Ni(111) and Ni(100) surfaces [7,8,1]. (This specific reaction rate is often referred to as a turnover frequency, TOF.) At a given temperature the rate of production of methane over an initially clean single-crystal catalyst was constant, with no apparent induction period. The kinetic data for the close-packed (111) and for the more open (100) crystal plane of Ni were strikingly similar with respect to the specific rates and activation energies. Furthermore, the single-crystal results were virtually identical to data acquired from alumina-supported nickel catalysts [7]. These extraordinary similarities in kinetic data taken under nearly identical conditions demonstrated unequivocally that there is no significant variation in the specific reaction rate or the activation energy in changing from a catalyst consisting of small metal particles to one composed of a bulk single-crystal. These studies provided convincing evidence that the methanation reaction was indeed quite insensitive to the surface structure of nickel catalysts, and established the appropriateness of using single-crystals to model this structure insensitive reaction.

Having validated the model, post-reaction surface analysis provided unique insights into the details of the reaction mechanism. For example, Auger electron spectroscopy (AES) following the reaction showed a low level of a carbonaceous species and the absence of oxygen [7]. The Auger lineshape for the carbonaceous residue was similar to that of nickel carbide, indicating that the surface carbon was of a “carbidic” type [7]. Further experiments were carried out to study the interaction of CO with Ni(100) at different temperatures [9]. AES data showed the deposition of carbon on the surface and the absence of oxygen. Two kinds of carbon were formed on the surface from CO: a carbidic type identical to that found following a H₂/CO reaction, which formed at temperatures < 650 K, and a graphitic type, which formed at temperatures > 650 K. The carbidic type saturated at 0.5 monolayers and could be readily removed from the Ni(100) surface by heating the crystal to 600 K in 1 atm of H₂; methane was formed as product. In contrast, the graphitic type was completely unreactive toward hydrogen and led to deactivation of the catalyst. The deposition of an active carbon residue and the absence of oxygen on the nickel surface following heating in pure CO is consistent with the well-known disproportionation reaction, the Boudouard reaction,

\[ 2 \text{CO}_{\text{ads}} \rightarrow \text{C}_{\text{ads}} + \text{CO}_2. \]

On Ni(100), the carbon formation data from CO disproportionation indicates a rate equivalent to that observed for methane formation in a H₂/CO mixture. Therefore, the surface carbon route to product was shown to be sufficiently rapid to account for all methane production [9].

Thus, the proposed reaction mechanism involving the dissociation of CO and the subsequent hydrogenation of the resulting carbon species (C_{ads}) accounts quite satisfactorily for the effect of pressure on the methanation rate, for the variation in the measured surface carbon
level as reaction parameters are changed, and for the formation at characteristic temperature–pressure conditions of a catalyst-deactivating graphitic carbon [10,11].

Studies similar to the methanation studies outlined above for nickel have also been carried out on two faces of ruthenium: the zig-zag, open (110) and the close-packed (001) planes [12–14]. These studies confirm that CO methanation on ruthenium surfaces is structure insensitive as well, and occurs via the same mechanism as observed for nickel.

2.2. CO oxidation

The relative simplicity of CO oxidation makes this reaction an ideal model for a heterogeneous catalytic reaction. Each of the mechanistic steps (adsorption and desorption of the reactants, surface reaction, and desorption of products) has been studied extensively using surface science techniques [15]. Because many of the reaction parameters determined in UHV can be applied directly to the kinetics at higher pressures [16], CO oxidation to date best illustrates the continuity between UHV and elevated pressure kinetic studies.

The rates of CO oxidation measured on single-crystals of Rh have been measured and compared with those observed on supported Rh/Al₂O₃ catalysts [16,17]. The data show remarkable agreement between the model and supported systems with respect to the specific reaction rates and apparent activation energies. These results indicate that the kinetics of CO oxidation on Rh is insensitive to changes in catalyst surface morphology. Under the conditions of the reaction near stoichiometry, the surface of the catalyst is predominantly covered with CO so that the reaction is limited by the adsorption of oxygen [16,17]. As the temperature is increased, the reaction rate increases as more vacant sites become available for oxygen adsorption due to the higher CO desorption rate. Accordingly, the CO oxidation rate typically increases with temperature and exhibits an apparent activation energy very similar to that for CO desorption.

The behavior of the reaction has been analyzed by using a kinetic model established from UHV surface science studies of the interactions of CO and O₂ with Rh [16]. By using the rate constants for adsorption and desorption of CO and O₂ measured at UHV conditions, the kinetics of CO oxidation over Rh can be very accurately predicted at elevated pressures. The results of this model are virtually indistinguishable from the measured data, and thus represent an exceptional example of the continuity between UHV surface science and “real world” catalysis.

Further examples of the correspondence between model single crystals and supported metal catalysts have been found for Pt, Pd, Ir, and Ru [18,19]. In the case of Ru [19], post-reaction surface analysis indicates that the optimum rate of CO oxidation on Ru(001) is observed when the surface is covered by almost a monolayer of oxygen. This surface condition contrasts with that of Rh, where the optimum activity is obtained for surfaces essentially free of oxygen adatoms [17].

Although many questions remain unanswered regarding the origin of the so-called “structure insensitivity” of methanation and CO oxidation, the single-crystal results are impressive with respect to their ability to reproduce the detailed kinetic behaviors of the corresponding supported “real world” catalysts. Furthermore, the spectroscopic tools of surface science coupled with reaction kinetics on single-crystals have provided valuable new insights into the mechanisms of these reactions.

3. Clean metal single-crystals: structure sensitivity

3.1. Alkane reactive sticking on single-crystal surfaces

In contrast to methanation and CO oxidation, there are reactions whose reactivity and selectivity depend markedly on the surface geometry or the metallic particle size of the catalyst. The reactive sticking of alkanes as well as the hydrogenolysis or “cracking” of alkanes are important examples of “structure sensitive” reactions [20].
The dissociative sticking of methane has been seen to increase in the order Ni(111) < Ni(100) < Ni(110) [21]. Initial reaction rates for the Ni(110) and Ni(100) surfaces are very similar, and are ~ 7 to 10 times greater than the initial rate for the Ni(111) surface at 450 K. A comparison of these results with data of molecular beam studies suggests that the sticking probabilities of molecules with very low normal kinetic energies must be accurately known when attempting to model high-pressure processes using molecular beam techniques [21–23]. Furthermore, while dissociation of methane on Ni(111) and other close-packed transition-metal surfaces likely proceeds via the “direct” channel to dissociation, results for the reactive sticking of methane [24], ethane, propane, and butane on Ni(100) [22] show that dissociation of these molecules on this more “open” Ni surface proceeds primarily via a trapped molecular “precursor”.

These so-called “bulb” experiments on alkane reactive sticking on nickel single-crystal surfaces were carried out at high incident flux conditions. Elevated pressures, in general, are required to produce measurable products, not because of the greater abundance of molecules with higher kinetic energies, but rather because of the competition that is inevitably present between desorption from the precursor, or accommodated adsorbed molecular state, and dissociation. Since activation energies for desorption of many reactants of interest (particularly saturated hydrocarbons) are usually considerably smaller than the activation energies for reaction, desorption dominates and reaction probabilities are quite small, often too small to measure at UHV conditions. For these reactants, the greater number of adsorption/desorption events at higher pressures simply serves to overcome this limitation. This behavior is common to many surface-catalyzed reactions and is the essence of the so-called “pressure gap” [25].

By extrapolating the rates of dissociative adsorption of alkanes measured in “bulb” experiments to the pressure and temperature conditions used in hydrogenolysis and steam reforming studies, it has been shown that alkane dissociation rates on the clean surface are one to two orders of magnitude larger than the rates of alkane hydrogenolysis and reforming under comparable conditions [21]. Since the alkane dissociation rates determined in the “bulb” experiments are initial rates at the limit of zero carbon coverage, these rates represent a theoretical upper limit to the rates of hydrogenolysis and steam reforming of these alkanes on unpromoted nickel catalysts.

The above studies have shown a direct relationship between the atomic corrugation of a surface and its activity toward the dissociative sticking of alkanes. Since dissociative sticking is the key initial step in the hydrogenolysis of alkanes, then a similar correlation between the atomic “roughness” and activity for hydrogenolysis reactions might be anticipated. This indeed is the case as discussed in the following section.

### 3.2. Hydrogenolysis of alkanes on single-crystal surfaces

The reactivity for the conversion of ethane to methane over nickel catalysts has been shown to depend critically on the particular geometry of the surface. The specific reaction rates for methane formation from ethane on the Ni(100) and Ni(111) surfaces clearly show that the more open (100) surface is far more active than the close-packed (111) surface [20]. For the Ni(100) surface, the data yield an activation energy of 100 kJ/mol. In contrast, the kinetic data for the Ni(111) surface correspond to an activation energy of 192 kJ/mol, implying that a different reaction mechanism is operative for Ni(111). It should be noted that surface analysis following reaction showed the (111) and (100) surfaces with comparable submonolayer quantities of carbon. Therefore, preferential surface carbon formation, or self-poisoning, on the (111) surface does not contribute to its lower activity [20].

The (111) surfaces are encountered more prevalently in fcc materials as the particle size is increased via successively higher annealing temperatures [20]. The results of this study then are consistent with rate measurements on supported nickel catalysts [20] which show hydrogenolysis
activity to be a strong function of particle size, the larger particles exhibiting the lower rates.

The selectivity of ethane production from the hydrogenolysis of \textit{n}-butane over iridium single-
crystals has been demonstrated to scale with the concentration of low-coordination-number metal
surface atoms \cite{26,27}. The Ir(110)-(1 \times 2) surface, which has a stable “missing-row” structure \cite{26,27},
has been found to produce ethane very selectively. This contrasts with the results for the
close-packed Ir(111) surface, where only the statistical scission of C–C bonds has been observed.
The results of this study correlate qualitatively with the observations made previously for selective
hydrogenolysis of \textit{n}-butane to ethane on supported iridium catalysts as a function of iridium
particle size \cite{28}. The results for Ir(110)-(1 \times 2) model very well the small-particle limit, whereas
the results for Ir(111) relate more closely to the data for the corresponding large particles (> 10
nm). By assuming particle shapes the general behavior of declining selectivity with larger parti-
cle size could be modeled accurately.

The stoichiometry of the surface intermediate leading to high ethane selectivity, based on kinet-
ics and surface carbon coverages subsequent to reaction, is suggested to be a metallocyclopent-
tane \cite{26,27}. The Ir(110)-(1 \times 2) or “missing-row” structure results in rows of highly coordinatively
unsaturated “\text{C}_7” sites. These sterically unhindered \text{C}_7 sites can form a metallocyclopentane
species (e.g., a 1,4-diadsorbed hydrocarbon species) which has been proposed as an interme-
diate in the central scission of butane to ethane \cite{29,30}. Based on analogous chemistry reported in
the organometallic literature \cite{29,30}, the mecha-
nism responsible for the hydrogenolysis of \textit{n}-butane on the Ir(110)-(1 \times 2) surface is postu-
lated to be the reversible cleavage of the central C–C bond in this metallocyclopentane interme-
diate. On the other hand, butane hydrogenolysis on the Ir(111) surface appears to operate via a dif-
f erent mechanism. First, dissociative chemisorption of butane and hydrogen occurs followed by
irreversible cleavage of the terminal carbon–carbon bond of the adsorbed hydrocarbon. Fur-
ther C–C bond cleavage prior to product desorp-
tion leads to the methane and ethane observed as initial products.

Although many of the atomic-level details with respect to the origin of the “structure sensitivity”
of alkane hydrogenolysis still remain unresolved, this work shows clearly that a large component of this important catalytic effect is a structural one and relates to the partitioning of particular reaction sites or to facet re-distribution as a function of particle size. Most importantly, the results summarized above correlate very well with measurements on supported “real-world” catalysts and emphasize the important role that single-
crystal studies can play in defining relationships between surface structure and catalytic activity/ selectivity.

4. Chemically modified surfaces: poisons and promoters

The addition of impurities to a metal catalyst can produce dramatic changes in the activity, selectivity and resistance to poisoning of the cata-
ylist. For example, the selectivity of some transition metals can be altered greatly by the addition
of additives such as potassium, and the activity can be reduced substantially by the addition of
electronegative species such as sulfur. Although these effects are well recognized in the catalytic
industry, the mechanisms responsible for chemical changes induced by surface additives are
poorly understood. An important question concerns the underlying relative importance of en-
semble (steric or local) versus electronic (non-local or extended) effects. A general answer to
these questions will enhance our ability to im-
prove existing catalysts and perhaps lead to the
design of more efficient catalytic materials.

4.1. Electronegative impurities

Kinetic studies \cite{31–33} have been carried out for CO methanation over Ni(100) surfaces cov-
ered with sulfur and phosphorus impurities. The rates of CO methanation as a function of sulfur
and phosphorus coverage over a Ni(100) catalyst show a non-linear relationship between the sulfur
coverage and the methanation rate. A sharp decrease in catalytic activity is observed at low sulfur coverages, and the poisoning effects of the sulfur are rapidly maximized. Such is the case for the attenuation of the methanation activity by sulfur for alumina-supported nickel catalysts [34]. The initial attenuation of the catalytic activity by sulfur suggests that ten or more equivalent nickel sites are deactivated by a sulfur atom. These results can be interpreted in either of two ways: (1) an electronic effect that extends to the next-nearest-neighbor sites; or (2) an ensemble effect that requires a certain number of surface atoms to facilitate the reaction sequence. If extended electron effects are significant, then the reaction rate is expected to be a function of the relative electronegativity of the poison. On the other hand, if an ensemble of ten nickel atoms is required for the critical steps of methanation, then altering the electronegative character of the poison should produce little change in the attenuation of activity by the additive.

Substituting phosphorus for sulfur results in a marked change in the magnitude of the poisoning effect at low coverages. Phosphorus, because of its reduced electronegative character, is much less effective as a poison and influences only the four nearest-neighbor nickel atom sites. These results then support the argument that extended electronic effects, rather than ensemble or site-blocking effects, are dominant in catalytic deactivation by sulfur. Similar poisoning effects by sulfur have been observed for methanation over ruthenium and rhodium single-crystal catalysts [35,36].

4.2. Electropositive impurities

The role of electronegative impurities in poisoning Ni(100), Ru(001), and Rh(111) toward methanation activity has been discussed above. These results have been ascribed as arising, to a large extent, from an electronic effect. In the context of this interpretation it is expected that an electropositive impurity might have the opposite effect, i.e. to increase the methanation activity of a metal surface. A study of CO hydrogenation over potassium-covered Ni(100) [33,37] has shown that this is not the case, although certain steps in the reaction mechanism are strongly accelerated by the presence of the electropositive impurity.

Kinetic measurements of CO methanation over a Ni(100) catalyst containing submonolayer quantities of potassium adatoms [37] indicate a decrease in the steady-state rate of methanation with an increase in the potassium coverage. The presence of potassium does not alter the apparent activation energy associated with the kinetics; however, potassium does change the steady-state coverage of active carbon on the catalyst. This carbon level changed from 10% of a monolayer on the clean catalyst to 30% of a monolayer for a catalyst covered with 0.1 monolayers of potassium [37].

Adsorbed potassium caused a marked increase in the steady-state rate and selectivity of Ni(100) for higher hydrocarbon synthesis [37]. At all the temperatures studied, the overall rate of higher hydrocarbon production was faster on the potassium-dosed surfaces, so that potassium may be considered a true promoter with respect to this reaction, Fischer–Tropsch synthesis. The effects of potassium upon the kinetics of CO hydrogenation over Ni(100) (i.e. a decrease in the rate of methane formation and an increase in the rate of higher hydrocarbon production) are similar to those reported for high-surface-area supported nickel catalysts [38,39]. This agreement between single-crystal nickel and supported nickel indicates that the major mechanism by which potassium additives alter the activity and selectivity of industrial catalysts is not related to the support material, but that it is rather a consequence of direct potassium–nickel interactions.

Adsorbed potassium causes a marked increase in the rate of CO dissociation on a Ni(100) catalyst [37]. There is a dramatic increase in the initial formation rate of “active” carbon or carbonic carbon via CO disproportionation as a function of potassium coverage. The relative rates of CO dissociation were determined for the clean and potassium-covered surfaces by observing the growth in the carbon Auger signal with time in a CO reaction mixture, starting from a carbon-free surface. The presence of potassium adatoms leads
to a reduction of the activation energy of reactive carbon formation from 96 kJ/mol on clean Ni(100) to 42 kJ/mol on a 10% potassium-covered surface [37].

These studies of promoters and poisons on surfaces illustrate the suitability of single-crystal model catalysts for studying the effects of surface modifiers in catalysis. Further work addressing these important issues will most surely aid in the understanding of this particular important aspect of practical catalysis.

5. Alloy surfaces: bimetallic catalysts

Considerable effort has been expended in recent years to address the chemical and physical properties of mixed-metal solids. This interest, to a large extent, has been motivated by the extensive technological applications that mixed-metal systems have in catalysis. The two basic questions in these studies are: (i) what is the nature of the heteronuclear metal–metal bond?; (ii) how does the formation of this bond affect the physical and chemical properties of metals? The answers to these questions are a challenge to modern science and a prerequisite for a non-empirical design of multi-metallic catalysts for industrial applications.

For solid metals, a reduction in the atomic coordination number produces a narrowing of the valence band at the surface. As a consequence, charge must flow between the surface atoms and the bulk so that the composite system maintains a common Fermi level [40–42]. This phenomenon suggests that the properties of a bond in a bimetallic surface can be very different from those of the corresponding bond in a 3D alloy, stressing the need to investigate the nature of the surface metal–metal bond.

In the study of surface metal–metal bonds, it has been advantageous to use model bimetallic systems generated by vapor depositing one metal onto a crystal face of a second metal [43–45]. These well-defined bimetallic surfaces offer the possibility of correlating electronic and chemical properties of a system with atomic-level surface structure. The results obtained by using these well-defined models have significantly altered the way in which the metal–metal bond in bimetallic surfaces is viewed.

For example, X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS) have been extensively used to investigate the core and valence levels of transition metal films supported on dissimilar transition-metal substrates [46–56]. The results of these studies show quite clearly that formation of a heteronuclear metal–metal bond can induce large changes in the electron density about a metal. These modifications in the electronic structure, in turn, affect the cohesive energy of the bimetallic bond.

Furthermore, the results of numerous studies dealing with the chemisorption of CO on well-defined bimetallic surfaces indicate that the electronic perturbations described above also modify the chemical properties of the metal overlayers. A striking correlation between changes in the CO desorption temperatures and the relative shifts in the surface core-level binding energies for supported monolayers of Pd, Ni, and Cu has been observed recently [43]. Strong electron donor–electron acceptor interactions in bimetallic bonding in these systems deactivate Pd and Ni adatoms toward CO chemisorption, whereas the same type of phenomena activate Cu adatoms. Bimetallic surfaces with the strongest Pd–substrate bonds have the weakest Pd–CO bonds. In contrast, surfaces with the strongest Cu–substrate bonds show also the strongest Cu–CO bonds [43].

In many respects, the behavior seen for the 2D metal overlayers is different from that expected for bulk metals. Results of X-ray [43] and ultraviolet [57] photoemission, work function measurements [58,59], and CO chemisorption [43,60], for pseudomorphic monolayers of Ni and Pd on W(110) show that the surface electronegativity of Pd is much lower than that of Ni. This trend is contrary to that found in several scales of bulk electronegativities [61], where Pd is more electronegative than Ni. Data reported for monolayers of Ni, Cu, and Pd on Ru(0001) [48,49,53], also indicate a sequence of surface electronegativities (Pd < Ni < Cu) opposite to that found for bulk electronegativities [61].
The experimental evidence mentioned above indicates that the nature of a metal–metal bond in a bimetallic surface is very different from that of the corresponding bond in a bulk 3D alloy. Formation of a surface metal–metal bond produces a flow of electron density toward the element with the larger fraction of empty states in its valence band. The resulting electronic modification of the interacting metals can dramatically alter the chemical (catalytic) properties of the bimetallic system [43].

The effects on catalytic activity of adding one metal to a second one have been illustrated recently via the addition of Cu to Rh(100) with respect to CO oxidation [62]. The overall rate of the reaction was observed to increase by an order of magnitude above the rate for either rhodium or copper at a Cu coverage of 1.3 monolayers. Above this coverage the rate decreases to an activity approximately equal to that of Cu-free Rh(100), a result caused by the 3D clustering of the Cu multilayers. The rate enhancement observed for submonolayer Cu deposits likely is related, to some extent, to the electronic modification of the Cu overlayer due to its interaction with the Rh(100) substrate. The interaction of overlayer Cu with Rh(100) is known to significantly increase the bonding of CO with the overlayer Cu [63], a result consistent with the enhanced catalytic properties of the overlayer for CO oxidation.

These results for mixed-metal systems have provided new information regarding the nature of the metal–metal bonding in mixed-metal interfaces (alloy catalysts). Although many subtleties of the surface chemistry of alloys remain to be addressed, model studies using surface science methods offer a new approach for elucidating many of these issues.

6. Oxide surfaces

Insulating surfaces such as those frequently encountered as catalysts or catalyst supports present problems of varying degrees to many charged-particle surface probes. For example, high-resolution electron-energy-loss spectroscopy (HREELS) is a principle technique for surface vibrational studies. However, this technique has been restricted to conducting substrates (metals and semiconductors) because of surface-charging problems encountered with insulators. Only limited studies have been carried out on highly insulating surfaces, e.g. MgO(100) [64] and Al₂O₃ (0001) [65]. In some cases, the effects of surface charging during charged-particle measurements have been compensated or stabilized with the aid of a neutralization electron gun [64,66].

Recently, the difficulty associated with surface charging has been eliminated by preparing an ultrathin, highly ordered, oxide film on the surface of a metal substrate [67]. Any charging induced in the thin film during charged-particle measurements is dissipated via the conducting substrate.

In the application of HREELS to adsorbates on ionic substrates, a second difficulty encountered is that the accompanying vibrational spectra are dominated by losses due to excitation of surface optical phonons. Since the intense multiple phonon losses generally extend over a wide vibrations frequency range of the HREELS spectra, it is not practical to observe directly adsorbate losses (which are several orders of magnitude smaller in intensity than the phonon losses) in the 0–4000 cm⁻¹ spectral range.

In recent studies [68–70], a new approach has been developed to acquiring HREELS data in order to circumvent the difficulties associated with these phonon losses. By utilizing a high-energy incident electron beam in combination with an off-specular scattering geometry, this new approach enables the direct observation of weak loss features due to the excitation of adsorbates without serious interference from intense multiple surface optical phonon losses. HREELS data indicate that carboxylic acids, methanol, and water undergo heterolytic dissociation, whereas ethylene and ethane are found to adsorb associatively on MgO. However, an increase in the surface basicity of MgO, achieved by thermal treatment, results in the dissociation of ethane. Further studies [71–73] on NiO show this surface to be far less basic with respect to the dissociation of various probe molecules with acid strengths
ranging from those of carboxylic acids and alcohols to alkenes and alkanes.

Very recent work \[74,75\] has addressed the preparation and characterization of ultrathin silicon dioxide films on a Mo(110) surface. The SiO\(_2\) films following an anneal to 1400 K have properties very similar to vitreous silica as shown by reflection–absorption infrared spectroscopy (RAIRS) \[74\]. Because silica supports are so widely utilized in practical catalytic applications, these SiO\(_2\) films offer an interesting starting material for constructing a more realistic supported-metal-particle catalyst, intermediate in complexity between metal single-crystals and the supported “real world” catalysts. Examples of model silica-supported metal catalysts are described in the following section.

These thin film oxide preparations can serve as convenient model catalysts as well. For example, recent work \[76–79\] has demonstrated their utility in studying the oxidative methane coupling reaction:

\[
4 \text{CH}_4 + \text{O}_2 \xrightarrow{\text{Li/MgO, } 1000 \, \text{K}} 2 \text{C}_2\text{H}_6 + \text{H}_2\text{O}.
\]

The kinetics of this reaction have been measured on thin MgO(100) films doped with Li. These studies show an excellent correlation between the absolute rates and activation energies of the model thin films and the corresponding rates and activation energies observed for the “real world” Li/MgO powdered catalysts \[77\]. Furthermore, electron energy loss studies have demonstrated a correlation between the density of F-centers at the Li/MgO surface (oxygen defect with a trapped electron pair) and the reactivity of that surface toward the above methane coupling reaction. This correlation suggests a new mechanism by which this class of materials can activate methane, the critical step in this potentially important methane coupling reaction.

These initial studies for model MgO, NiO, and SiO\(_2\) catalysts are very promising with respect to the future possibilities of modeling with thin oxide films a variety of adsorption and catalytic processes that take place over oxide surfaces.

### 7. Metal/oxide surfaces

Recently, model silica-supported copper \[80,81\] and palladium \[82\] catalysts have been prepared by evaporating the appropriate metal onto a silica thin film. The preparation conditions define the corresponding metal-particle dispersions or average size \[81\]. As in the studies described in the previous section, the silica films are supported on a Mo(110) substrate \[74\].

The structure of the model silica-supported copper catalysts has been investigated with RAIRS and scanning tunneling microscopy (STM). The RAIRS studies of adsorbed CO indicate that there are several types of copper clusters with surface structures similar to (111), (110), and other high-index planes of single-crystal copper \[80\]. The STM studies show several types of copper clusters on silica and reveal images of metal clusters on the amorphous support with atomic resolution \[80\].

The adsorption and reaction of CO on model silica-supported palladium catalysts over a wide range of temperatures and pressures have demonstrated a continuity between the catalytic chemistry of single-crystals and small particles, as well as between the kinetics of CO oxidation at low and high pressures \[82\].

These kinds of model-supported catalytic studies allow the so-called “pressure and material gaps” to be bridged simultaneously. Further studies of this nature offer unprecedented opportunities to connect in a direct way studies on single-crystals at UHV conditions with analogous investigations of catalytic processes on “real world” catalysts at elevated pressures.

### 8. Conclusions and future prospects

An approach that combines ultrahigh vacuum surface analytical methods with an elevated pressure reactor can provide new information about the molecular details that define and control the mechanism of reactions at the gas/solid interface. Using these techniques, basic concepts of heterogeneous catalysis such as structure insensitivity and structure sensitivity can be directly ad-
dressed. For structure insensitive reactions excellent agreement can be obtained between studies on single-crystal surfaces and studies on the corresponding high-surface-area-supported catalysts, demonstrating the relevance of kinetics measured on well-ordered single-crystal surfaces for modeling the behavior of practical catalysts. For structure sensitive reactions, the activity of a particular site or set of sites can be examined and the effects of surface structure explored in atomic detail.

Model studies on single-crystal surfaces are also helpful in developing a better understanding of the effects of surface impurities, e.g. poisons and promoters, on the catalytic activity and selectivity of metals. The influence of modifiers on the surface chemistry of adsorbed reactants, products, and intermediates can be studied using UHV techniques. Such investigations have shown that this information can be related to the effects of the impurities on the catalytic behavior. Of particular interest is the possibility that these kinds of studies will help to clarify the relative importance of electronic and geometric contributions in determining the role of surface modifiers.

Combined surface science and kinetic studies have probed the nature of the metal–metal bond in mixed-metal catalysts. These investigations indicate that charge transfer is an important component in surface metal–metal bonds that involve dissimilar elements. The larger the charge transfer, the stronger the cohesive energy of the bimetallic bond and the greater the perturbation of the chemical properties of the interacting metals.

Recent studies have shown that model oxide surfaces can be prepared in thin-film form, a preparation that readily enables their exploration with a wide array of charged-particle surface techniques. Techniques have now been developed to facilitate the application of high-resolution electron-energy-loss spectroscopy to adsorbates on oxides directly. These kinds of investigations offer unprecedented opportunities to address the molecular details of the chemistry at oxide surfaces.

Finally, the addition of metals to the above oxides as supports provides a convenient method to model important aspects of supported-metal catalysts such as support particle interactions and quantum size effects of supported-metal particles. Using such models a host of surface science techniques can be utilized to study catalysis by metals in systems with well-defined particle sizes and morphology.

Clearly great progress has been made during the last twenty years with respect to establishing continuity between the world of surface science and the “real world” of catalysis. These two disciplines are complementary, each playing an essential role in guiding the inquiry of the other. Cooperation and synergism between these two disciplines most surely will continue to lead to new insights into the amazingly complex world of heterogeneous catalysis.

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