CATALYSIS BY METALS: FROM EXTENDED SINGLE CRYSTALS TO SMALL CLUSTERS

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Model oxide-supported metal cluster catalysts have been prepared by evaporating the corresponding metal (e.g., Cu, Pd, Ni) onto a oxide thin film (~100 Å), which in turn is supported on a refractory metal (Mo, W, Ta) surface. The deposited metal films, upon annealing, form small metallic clusters on the oxide surface whose size are dependent upon the initial metal film thickness. The surface structures and cluster morphologies have been characterized using scanning probe microscopies, temperature-programmed desorption, X-ray, and ultraviolet photoemission; and high-resolution electron energy loss spectroscopy/infrared reflection-absorption spectroscopy of adsorbed carbon monoxide. The catalytic properties of these clusters have also been investigated with respect to several reactions including CO/O₂ and CO/NO. The chemical and electronic properties of the metal clusters with respect to size are compared to the analogous properties of extended single crystal surfaces.

1. Introduction

A focus of catalytic research has been to understand how the atomic structure, composition, and electronic properties of a surface relate to catalytic activity and selectivity. Over the last three decades, an array of ultrahigh vacuum (UHV) surface techniques has been developed allowing surfaces to be precisely defined at the atomic level. Accordingly, considerable effort has been directed toward integrating these UHV methods into basic catalytic research. Clearly an integrated approach, one that combines modern surface techniques with traditional methods, can enhance significantly our understanding of a broad range of phenomena that can occur on metal surfaces relating to catalytic reactivity and selectivity.

UHV surface science offers many new opportunities in catalytic research, in that a variety of modern spectroscopies are available to study the detailed structure and composition of surfaces and to identify stable surface species. However, a criticism that has been made frequently of the UHV approach is 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.

The so-called “pressure gap” which has separated UHV and technical catalytic investigations has 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
of carrying 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 approach 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 for a variety of reaction categories to model the more complex technical catalysts.

Despite these successes in modeling catalysts with single crystals, there is a clear need to develop models with higher levels of complexity to address those important issues specifically related to very small metal particles and to interactions between the metal particle and the support. In this article, recent efforts to simulate oxide-supported metal systems using thin oxide films are described. These thin oxide support materials offer a wide range of opportunities for studying the more complex issues of catalysis such as metal-support interactions using a model catalyst that is realistic enough to simulate the nuances of the more complex "real world" system, yet tractable for typical surface science probes. The ultimate goal of this work is the preparation of well-defined, supported metal particles with known morphologies.

The first challenge in this work is the preparation and characterization of a suitable oxide catalyst support. Unfortunately, oxide surfaces such as those frequently encountered as catalyst supports are insulating materials and 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 used primarily to study 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) and Al₂O₃(0001). 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; however, this method is less than ideal.

Recently the difficulty associated with surface charging has been eliminated in our laboratory by preparing an ultrathin, highly ordered, oxide film on the surface of a metal substrate. 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 vibrational 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, a new approach has been developed to acquire 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 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\textsuperscript{20,21} has addressed the preparation and characterization of ultrathin silicon dioxide films on a Mo(110) surface. The SiO\textsubscript{2} films, following an anneal to 1400 K, have properties very similar to vitreous silica as shown by reflection-absorption infrared spectroscopy (RAIRS).\textsuperscript{20} Because silica supports are so widely utilized in practical catalytic applications, these SiO\textsubscript{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. For example, model silica-supported copper\textsuperscript{22-24} and palladium\textsuperscript{25} 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.\textsuperscript{23,24} As in the studies described in the previous section, the silica films are supported on a Mo(110) substrate.\textsuperscript{20} The structure of the model silica-supported copper catalysts has been investigated with RAIRS and scanning tunneling microscopy (STM).\textsuperscript{22,23} 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.\textsuperscript{22-24} The STM studies show several types of copper clusters on silica and reveal images of metal clusters on the amorphous support with atomic resolution.\textsuperscript{22}

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 crystal and small particles and as well between the kinetics of CO oxidation at low and high pressures.\textsuperscript{25,26} IR spectra of adsorbed CO on model silica-supported Pd catalysts are displayed in Fig. 1 for Pd coverages of 1.0, 7.0, and 15 ML. The Pd overlayers on the thin silica films were annealed to 900 K prior to the CO adsorption experiments. This thermal treatment has been shown to produce small metal particles in the range 30 to 500 Å, with larger particles being formed for the higher palladium coverages. The IR spectra of adsorbed CO on model Pd/SiO\textsubscript{2} cata-

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1.png}
\caption{A comparison of infrared reflection-absorption spectra of CO on Pd(111), Pd(100), and silica-supported palladium surfaces. The spectra were collected at 100 K with a CO pressure of $1 \times 10^{-6}$ Torr.}
\end{figure}

lysts with different Pd coverages show three distinct absorption features corresponding to CO adsorbed onto threefold hollow (1880 cm\textsuperscript{-1}), bridging (1990 cm\textsuperscript{-1}), and atop (2110 cm\textsuperscript{-1}) configurations. At $\theta_{\text{Pd}} = 1.0$ ML the dominant absorption feature corresponds to CO adsorbed onto an atop position, while the peaks originating from threefold hollow and bridging CO are broad, suggesting a nonhomogeneous distribution of these adsorption sites. Increasing the Pd coverage to 7.0 ML and then to 15 ML results in the sharpening of the absorption features and the dominance of the peak originating from CO adsorbed in the bridging positions. These results demonstrate that the larger particles have well-defined crystal orientations whereas the smaller particles have a wide distribution of adsorption sites. A comparison of the IR spectra of equilibrated CO overlayers obtained from the Pd_{15 ML}/SiO\textsubscript{2} sample, Pd(100),
and Pd(111) single crystals reveals striking similarities. As Fig. 1 shows, the stretching frequencies of adsorbed CO on the model Pd/SiO₂ catalyst are identical to the combined features observed for Pd(100) and Pd(111). The agreement among the IR spectra of the model supported catalysts and the metal single crystals suggests that the metal particles formed on the thin SiO₂ film have facets consisting primarily of (100) and (111) orientation. This is anticipated in that the formation of metal particles with Miller indices is thermodynamically favored.

The oxidation of CO on these model systems has been studied as well. Figure 2 shows the low dependencies of specific CO₂ formation rates on the reaction temperature. The specific activities of the single crystal and the supported catalysts for CO oxidation are essentially identical. The apparent activation energies for the relatively large particles (θPd > 2 ML) are similar (~ 27 kcal/mol), but somewhat lower (~ 25 kcal/mol) for the smaller particles (0.6, 0.3 ML). The apparent activation energies for each of the three Pd single crystals with different orientations are similar but distinctive [29.4 ± 0.3 kcal/mol for Pd(100), 28.1 ± 0.4 kcal/mol for Pd(111), and 30.7 ± 0.5 kcal/mol for Pd(110)]. An excellent correspondence is found among the results obtained for the model silica-supported Pd catalysts and the Pd single crystals for the oxidation of CO.

The effect of palladium particle size on the catalytic properties was investigated utilizing the decomposition of chemisorbed NO (Fig. 3) and reactions of NO with CO in flowing conditions (Fig. 4). ^1⁵NO was used in order to differentiate N₂ from CO and N₂O from CO₂ with mass spectrometry. During temperature programmed reaction on the large particles following a saturation ^1⁵NO exposure, ^1⁵NO desorbs in three peaks centered at 315, 515, and 595 K; ^1⁵N₂ is produced in peaks at 545, 595, and 690 K; and ^1⁵N₂O is evolved in a peak at 545 K [Fig. 3(A)]. The 545 K N₂ peak is

![Arrhenius plot of CO oxidation rate on Pd(111), Pd(110), and Pd(100) and silica-supported palladium. P₀₂ = 0.50 Torr](image)

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*Fig. 2. The Arrhenius plots of CO oxidation rate on Pd(111), Pd(110), and Pd(100) and silica-supported palladium. P₀₂ = 1.00 Torr; P₀₂ = 0.50 Torr*
attributed to the fragmentation of N₂O. On small palladium particles (∼ 50 Å), ¹⁵N₂O is not produced; ¹⁵NO desorbs in two peaks at 310 and 515 K, and N₂ is evolved at 530 and 670 K [Fig. 3(B)]. The relative yield of N₂ with respect to ¹⁵NO desorption (above 400 K) decreases as the particle size grows (from ∼ 50% for 30 Å to ∼ 20% for 250 Å particles), suggesting less NO decomposition on the larger particles. In addition, the formation of N₂O on the larger particles correlates with the appearance of the NO desorption peak at 595 K. There is no detectable O₂ evolution below 1000 K for all sizes of palladium particles. However, O₂ desorption is observed in a peak at ∼ 1250 K, concurrent with the desorption of palladium. Therefore, the oxygen from nitric oxide decomposition is apparently dissolved into the bulk of the palladium particles.

The reaction of CO with NO under flowing conditions further demonstrates a particle size effect (Fig. 4). The relative rate of product evolution was monitored with a quadrupole mass spectrometer during reaction with flowing ¹⁵NO and CO (1:1) at 1 × 10⁻⁶ Torr. The reaction rate increases with the catalyst temperature, reaching a maximum at ∼ 580 K, then declines. On the large palladium particles [Fig. 4(A)], the maximum rate of ¹⁵N₂O evolution occurs at 570 K, 10 K lower than the maxima for CO₂ and N₂ production. On the small particles (< 50 Å), ¹⁵N₂O is not produced during the steady-state reaction of a 1:1 mixture of ¹⁵NO and CO [Fig. 4(B)]. N₂ is produced by NO dissociation and atomic nitrogen recombination, and CO₂ is produced from the oxidation of carbon monoxide. There is a temperature (∼ 580 K) at which the product formation rate is maximized, since the residence time for CO and NO decreases with temperature whereas the reaction rates increase with temperature.

Both the decomposition of NO and the reaction of NO and CO show that the reaction channel for N₂O formation is not available on the small particles (< 50 Å). The N₂O formation requires the simultaneous presence of adsorbed NO and atomic nitrogen at sufficient coverages. The temperature programed reaction spectra of Fig. 4 show that the dissociation of NO occurs along the trailing edge of the main NO desorption peak at 515 K. The formation of N₂O correlates with the appearance of the NO desorption peak at 595 K. The higher adsorption energy of the 595 K state increases the NO surface residence time and thus enhances the probability of N₂O formation by
NO combination with atomic nitrogen. It is noted that on extended single crystal surfaces, \( \text{N}_2\text{O} \) is also formed during the decomposition of NO.\textsuperscript{27-29} However, the decomposition of NO and the formation of \( \text{N}_2\text{O} \) correlate with the presence of step/defect (low-coordination) sites on the single crystal surfaces.\textsuperscript{27-30} Accordingly then, it is likely that there are surface sites with low coordination and varying reactivities on the large particles and extended surfaces. On the perfect (111) and (100) facets, NO desorbs at \(< 520 \, \text{K},\textsuperscript{29,30} \) whereas on particles with a variety of low-coordinated sites, NO can be decomposed to atomic nitrogen and oxygen on some sites, or can be more strongly adsorbed (595 K desorption state) on other sites. The presence of both sites on the large Pd particles, a strong adsorption site for NO and a second that promotes decomposition, provides a mechanism for the formation of \( \text{N}_2\text{O} \). The absence of the \( \text{N}_2\text{O} \) on the small palladium particles, on the other hand, can be explained by the lack of the high temperature NO adsorption state (595 K) which is, in turn, related to the reactivity of the surface sites. The surface of the small particles is more reactive as indicated by the increased amount of NO dissociation (\( \sim 50\% \) for 30 Å and \( \sim 20\% \) for 250 Å particles), so that all NO molecules on the low-coordinated sites are likely decomposed to atomic oxygen and nitrogen at lower temperatures. The presence of atomic oxygen and nitrogen in the near-surface region will likely further decrease the NO adsorption energy.

These kinds of model supported catalytic studies allow the so-called "pressure and material gaps" to be bridged simultaneously. Further investigations 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.

2. Conclusions

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. These kinds of investigations offer unprecedented opportunities to address the molecular details of the chemistry at oxide surfaces. Furthermore, 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 an array of surface science techniques can be utilized to study catalysis by metals in systems with well-defined particle sizes and morphology. These more complex systems provide a convenient intermediate model between the traditional extended single crystals and the profoundly complex technical catalysts.

Acknowledgments

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References