8. Effects of Surface Impurities in Chemisorption and Catalysis

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It has long been recognized that the addition of impurities to metal catalysts can produce large effects on the activity, selectivity, and resistance to poisoning of the pure metal [8.1]. For example, the catalytic properties of metals can be altered greatly by the addition of a second transition or Group 1B metal or by the addition of impurities such as potassium or sulfur. On the other hand, catalytic processing is often plagued by loss of activity and/or selectivity due to the inadvertent contamination of catalysts by undesirable impurities. In either case, the catalytic properties are dramatically altered by the modification of the chemistry by the impurity. Although these effects are well recognized in the catalytic industry, the mechanisms responsible for surface chemical changes induced by surface additives are poorly understood. However, the current interest and activity in this area of research promises a better understanding of the fundamentals by which impurities alter surface chemistry. A pivotal question concerns the underlying relative importance of ensemble (steric or local) versus electronic (nonlocal or extended) effects. A general answer to this question will critically influence the degree to which we will ultimately be able to tailor-make exceptionally efficient catalysts by fine-tuning the electronic structure.

If, indeed, low concentrations of surface impurities can profoundly alter the surface electronic structure and thus catalytic activity, then the possibilities for the systematic manipulation of these properties via the selection of the appropriate additive would appear limitless. On the other hand if steric effects dominate the mode by which surface additives alter the catalytic chemistry, then a different set of considerations for catalyst alteration come into play, a set which will most certainly be more constraining than the former. In the final analysis, a complete understanding will include components of both electronic and ensemble effects, the relative importance of each to be assessed for a given reaction and conditions. A major emphasis of our research has been in the area of addressing and partitioning the importance of these two effects in the influence of surface additives in catalysis.
Catalyst deactivation and promotion are extremely difficult questions to address experimentally [8.1]. For example, the interpretation of related data on dispersed catalysts is severely limited by the uncertainty concerning the structural characterization of the active surface. Specific surface areas cannot always be determined with adequate precision. In addition, the knowledge of the crystallographic orientation, the concentration and the distribution of impurity atoms, as well as their electronic states is generally poor. The degree of contamination may vary considerably along the catalytic bed and the impurity may alter the support as well as the metal. Moreover, the active surface may be altered in an uncontrolled manner as a result of sintering or faceting during the reaction itself.

The use of metal single crystals in catalytic reaction studies essentially eliminates the difficulties mentioned above and allows, to a large extent, the utilization of a homogeneous surface amenable to study using modern surface analytical techniques. These techniques allow detailed surface characterization regarding surface structure and composition. Carefully prepared, single-crystal catalytic surfaces are particularly suited to the study of impurity effects on catalytic behavior because of the ease with which impurity atoms can be uniformly introduced to the surface. To date, relatively few studies [8.2-6] have incorporated both surface-science techniques with kinetics at elevated pressures (~1 atm). Kinetics, however, are an essential link between these kind of model catalytic studies and the more relevant practical catalytic systems, establishing the crucial connection between the reaction rate parameters. Although the studies to date are few, the results appear quite promising in addressing the fundamental aspects of catalytic poisoning and promotion.

8.1 Experimental Details

The studies to be discussed were carried out utilizing the specialized apparatus shown in Fig.8.1 and discussed in detail in [8.2,7]. This device consists of two distinct regions, a surface analysis chamber and a microcatalytic reactor. The surface analysis system, with a base pressure of \(< 2 \times 10^{-10}\) Torr, is equipped with two collimated molecular beam dosers which face the front surface of the single crystal disk. The crystal, which can be cooled to 80 K, can be rotated to either doser for adsorption of gases. Temperature programmed desorption (TPD) can be carried out with the crystal in front of a UTI 100C multiplexing quadrupole mass spectrometer.
Fig. 8.1. An ultra-high-vacuum apparatus for carrying out thermal programmed desorption at ultra-high vacuum and kinetic studies at atmospheric pressures on metal single crystals (QMS) using a linear ramp of 10 K/s. The mass spectrometer samples 4 mass peaks every 0.7 s with a sampling time of 0.1 s/amu.

The custom-built reactor, contiguous to the surface analysis chamber, employs a retraction bellows that supports the metal crystal and allows translation of the catalyst in vacuo from the reactor to the surface analysis region. Both regions are of ultra-high-vacuum construction, bakeable, and capable of ultimate pressures of less than $10^{-10}$ Torr. The catalyst samples are typically mounted on tungsten leads and heated resistively. The reactor is operated in a batch mode with sampling subsequent to reaction into an on-line gas chromatograph. Analysis is via a flame ionization detector.

Details of sample cleaning procedures are given in the references accompanying the corresponding data. All reactants were initially of high purity and further purification procedures are generally used to improve the gas quality. These typically include multiple distillations for condensables and/or cryogenic scrubbing using a low-conductance glass-wool packed trap at 80 K.

The sulfur coverages S(ads) were deposited by dosing H$_2$S at ~ 600 K until the desired level of S(ads) was obtained [8.8,9]. Coverages of S(ads) were calibrated as described previously [8.8-10]. Coverages of Cl(ads), P(ads), C(ads), and N(ads) were deposited from Cl$_2$, PH$_3$, ethylene, and hydrazine, respectively [8.8,9,11,12].

Copper [8.13] and silver [8.14] were evaporated from a resistively heated tungsten wire wrapped with high-purity wire. The metal sources were thoroughly outgassed prior to metal evaporation, and the deposition rates were accurately controlled by monitoring the voltage drop across the tungsten fila-
ment. The metal flux from the evaporator was also checked routinely via a quartz microbalance mounted off-axis to the sample.

8.2 Discussion

8.2.1 Electronegative Impurities

Impurities whose electronegativities are greater than those for transition metals generally poison a variety of catalytic reactions, particularly those involving H₂ and CO. Of these poisons, sulfur is the best known and technologically the most important [8.1]. The first step in the systematic definition of the poisoning mechanism of this category of impurities is the study of the influence of these impurities on the adsorption and desorption of the reactants.

(a) Chemisorption

The effect of preadsorbed electronegative atoms Cl, S, and P on the adsorption-desorption of CO and H₂ on Ni{100} has been extensively studied [8.8, 11,12,15-18] using TPD, low-energy electron diffraction (LEED), and Auger electron spectroscopy (AES). It has been found that the presence of electronegative atoms causes a reduction of the sticking coefficient, the adsorption bond strength, and the adsorption capacity of the Ni{100} surface for CO and H₂. The poisoning effect becomes more prominent with increasing electronegativity of the preadsorbed atoms [8.9].

Adsorption of Cl, S, and P on nickel causes a reduction in both hydrogen and CO adsorption and a shift of the TPD peak maxima to a lower temperature [8.9]. The effect of preadsorbed Cl, S, and P on the CO TPD behavior is shown in Fig.8.2 and on the H₂ TPD in Fig.8.3. Coverages of impurities are expressed in terms of monolayers (ML) or the ratio of surface impurity atoms to the surface metal atoms. The TPD desorption curves represent the total adsorbate desorption for different impurity coverages after an exposure sufficient to reach the saturation adsorbate coverage. Both CO and H₂ adsorption decrease markedly in the presence of surface impurities. The effects of P, however, are much less pronounced than for Cl or S.

Figure 8.4 shows the observed dependence of the total CO adsorption on impurity coverage. Similarly, Cl, S, and P cause a reduction of hydrogen adsorption and a shift of the TPD peak maxima to a lower temperature [8.9]. At higher impurity levels a lower temperature state for H₂ emerges. The extent of this effect increases in the sequence P, S, Cl. As seen in Fig.8.5, the
reduction of $H_2$ coverage is most apparent in the presence of Cl atoms. The similarity in the atomic radii of Cl, S, and P (0.99, 1.04, and 1.10 Å, respectively [8.19]) suggests a relationship between electronegativity and the poisoning of chemisorptive properties by these surface impurities. Related studies [8.11] have been carried out in the presence of C and N. These impurities have the same electronegativities as S and Cl, 2.5 and 3.0, respectively. The comparison between the results for C and N and those for S and Cl is entirely consistent with the interpretation that electronegativity effects dominate the poisoning of chemisorption by surface impurities with similar atomic size, and with occupy the same adsorption sites. In the case of ad-
Fig. 8.3. Effect of varying Cl, S, and P precoverage on H₂ TPD from Ni{100}. The H₂ exposure = 10 L

Fig. 8.4. Dependence of total CO adsorption on additive precoverage

sorbed impurities with the same electronegativity, but with different atomic radii (S and C, Cl and N), the effect becomes less pronounced with decreasing atomic radius.

Particularly noteworthy in the above studies is the general observation that those impurities strongly electronegative with respect to nickel, Cl,
Fig. 8.5. Dependence of total \( H_2 \) adsorption on additive precoverage

N, and S, modify the chemisorptive behavior far more strongly than would result from a simple site-blocking model. The initial effects of these impurities as shown in Figs. 8.4 and 5 suggest that a single impurity atom successfully poisons as many as ten nickel atoms. This result supports an interaction that is primarily electronic in nature.

\section*{b) Catalytic Activity}

Kinetic studies have been carried out for several reactions as a function of sulfur coverage over single crystals of nickel [8.8,20], rhodium [8.14], and ruthenium [8.21]. For the methanation reaction over Ni(100) [8.8], the sulfided surface (Fig. 8.6a) shows behavior remarkably similar to results for the clean surface at a considerably reduced hydrogen partial pressure. For clean Ni(100) [8.2] a departure from Arrhenius linearity is observed at 700 K. Associated with the onset of this nonlinearity or "rollover" is a rise in the surface carbon level. This rise in carbon level continues until the carbon level reaches 0.5 ML, i.e., the saturation level. This behavior of the Arrhenius plot has been interpreted [8.2] as reflecting the departure of atomically adsorbed hydrogen from a saturation or critical coverage. For a sulfur surface coverage of 4\%, the reaction rate at identical conditions departs similarly from linearity at 600 K, some 100 K lower in reaction temperature. Here too, an increase in surface carbon level is associated with this deviation from linearity. This behavior indicates that the sulfur is very effective in reducing the steady-state surface atomic hydrogen coverage which results in an attenuation of the rate of surface carbon hydrogenation. These results are consistent with the chemisorption results [8.9] discussed above for \( H_2 \) on sulfur-poisoned Ni(100) surface. Similar results
Fig. 8.6 a, b. An Arrhenius plot of the rate of methanation over sulfided (a) Ni(100) and (b) Ru(0001) catalysts at 120 Torr and a H/CO ratio of 4. Coverages (θs) are expressed as fractions of a monolayer. NCH₄ is the turnover frequency (TF) or the number of methane molecules produced per surface nickel atom per second.

(Fig. 8.6b) have been seen [8.21] for sulfur poisoning of a Ru(0001) surface toward CO hydrogenation.

Both the kinetics and the TPD studies show that the poisoning effects of sulfur are very nonlinear. Figure 8.7a shows the relationship between the sulfur coverage on a Ni(100) catalyst and the methanation rate catalyzed by this surface at 600 K. A precipitous drop in the catalytic activity is observed for low sulfur coverages. The poisoning effect quickly maximizes with little reduction in the reaction rate at sulfur coverages exceeding 0.2 monolayers. The activity attenuation at the higher sulfur coverages is in excellent agreement with that found for supported Ni/Al₂O₃ by Rostrup-Nielsen and Pedersen [8.22]. The initial change in the poisoning in Fig. 8.7a suggests that more than ten nickel atom sites are deactivated by one sulfur atom.

Similar behavior has been observed for sulfur-poisoned Ru(0001) [8.21] and Rh(111) [8.14] catalysts. Results for these studied are shown in Figs. 8.7b, c. A result common to these studies is that sulfur effectively poisons catalytic activity at coverages less than 10% of the surface metal concentration.
Fig. 8.7 a-c. Methanation rate as a function of sulfur coverage on (a) Ni(100), (b) Ru(0001), and (c) Rh(111) catalyst. Pressure = 120 Torr, \( \text{H}_2/\text{CO} = 4 \), Reaction temperature = 600 K.

b) Catalytic Selectivity

For methanation, sulfur is seen to significantly attenuate the surface activity. In those cases where multiple products are possible, dramatic modifications in the distributions of these products have been observed [8.25]. Figure 8.8 shows the effect that progressive sulfiding of a Ni(111) catalyst has on the cyclopropane/hydrogen reaction. A small amount of sulfur (< 0.1 ML) exponentially lowers the rate of methane formation, the dominant product formed on the clean surface. Similarly, the rate of ethane formation falls in concert with the methane suggesting, as is expected, a close correlation between these hydrogenolysis products. In contrast to the methane and ethane products, the production of propane/propylene (C_3) product actually increases with the sulfur addition. Qualitatively, the increase in the C_3 product corresponds to the decrease in the methane rate. These results show rather directly that the initial sulfiding promotes the ring-opening reaction.
by reducing the tendency of the surface to break more than one carbon-carbon bond.

In contrast to the clean Ni(111) surface where no ethylene was observed as a reaction product, significant amounts of ethylene are found [8.20] for the sulfided surface. In addition to reducing the tendency of the surface to break carbon-carbon bonds, sulfur also lowers the hydrogenation activity. This tendency has been confirmed by measuring directly the attenuation of the hydrogenative character of Ni(111) versus sulfur coverage by monitoring the ethylene/hydrogenative reaction [8.23].

The effect of sulfiding a Ni(111) catalyst for the cyclopropane reaction is threefold: (a) A reduction in the carbon-carbon bond-breaking activity; (b) an increase in the relative propane/proplylene product yield; and (c) the appearance of significant amounts of olefin (ethylene) product. The cumulative result of these changes is a dramatic alteration of the measured selectivity of the modified surface compared with the clean surface.

Results which correspond directly to the steady-state kinetics mentioned above have been found in TPD experiments following the adsorption of cyclopropane onto a clean and sulfided Ni(111) surface [8.23]. Figure 8.9 curve a shows a H₂ TPD following the adsorption of a saturation exposure of cyclo-
Fig. 8.9. Hydrogen TPD following the adsorption of a saturation exposure of cyclopropane onto (a) a clean and (b) a 0.05 ML sulfided Ni(111) surface.

propane onto a clean Ni(111) surface. The small peak at 130 K corresponds to H₂ formed in the QMS during the cracking of the parent cyclopropane, indicating molecular physisorption of cyclopropane. The H₂ desorption at the higher temperatures corresponds to the recombination of atomic hydrogen formed from the decomposition of cyclopropane, or hydrocarbon fragments thereof, to carbon and adsorbed atomic hydrogen. The area under this peak relative to the area measured following a saturation H₂ exposure on the clean Ni(111) surface allows the assessment of the absolute coverage of cyclopropane adsorbed. [8.23]. This coverage corresponds to a closed-packed arrangement of cyclopropane molecules lying flat on the surface. Thus, on the clean surface all the adsorbed cyclopropane undergoes decomposition to carbon (carbidic) and hydrogen (atomic).

The addition of small amounts of sulfur affects significantly the adsorption and dehydrogenation of cyclopropane as measured by TPD. Figure 8.9 curve b shows a repeat of the experiment on the clean surface, however, with the addition of 5% of a monolayer of sulfur. This small addition of sulfur is seen to reduce the activity of the surface toward breaking carbon-carbon bonds such that only 20% of the subsequently adsorbed cyclopropane decomposes to carbon and hydrogen. The remaining cyclopropane either desorbs molecularly or rearranges to propylene [8.23].

A series of TPD measurements following cyclopropane adsorption with successively larger sulfur coverages [8.23] allows the quantitative assessment
of the change in the ability of the surface to break carbon-carbon and/or carbon/hydrogen bonds with sulfur coverage. This relationship is shown in Fig.8.10. It is noteworthy that the precipitous drop in the carbon-carbon bond breaking ability with sulfur coverage is strikingly similar to the fall in the methane formation rate with sulfur coverage in the steady-state reaction rate measurements of Fig.8.8.

At first glance, one might interpret these results as the simple poisoning of minority or defect sites on the surface and that these sites are crucial to the TPD decomposition and the reactivity at steady-state reaction conditions. However, this is a very unlikely explanation given that numerous studies [8.2,4,10,24-27] have shown a close corresponding between the steady-state rates measured for single-crystal catalysts and those rates found for supported, small-particle catalysts. That the defect densities on these two very different materials would be precisely the same is highly unlikely. It is much more likely that these reactions are not defect controlled and that the surface atoms of the single crystals are uniformly active.

There are two other possible explanations for this result: (1) an electronic or ligand effect as discussed at the beginning of this chapter or (2) an ensemble effect (the requirement that a certain collection of surface atoms are necessary for the reaction to occur). Experimentally, these two possibilities can be distinguished [8.4,12]. If an ensemble of more than ten nickel atoms is required for methanation, then altering the electronic character of the impurity should produce little change in the degree to which the impurity poisons the catalytic activity. That is, the impurity serves
merely to block a single site in the reaction ensemble, nothing more. On the other hand, if electronic effects play a significant role in the poisoning mechanism, then the reaction rate should respond to a change in the electronic character of the impurity. Substituting phosphorus for sulfur (both atoms are approximately the same size) in a similar set of experiments results in a marked change in the magnitude of poisoning at low coverages as shown in Fig. 8.11. Phosphorus, because of its less-electronegative character, effectively poisons only the four nearest-neighbor metal atoms sites.

Effective poisoning of catalytic activity at sulfur coverages of less than 0.1 ML has been observed for other reactions, including ethane and cyclopropane hydrogenolysis [8.20], ethylene hydrogenation [8.23], and \( \text{CO}_2 \) methanation [8.27]. The results of several studies on nickel are summarized in Fig. 8.12.
These studies indicate that the sensitivity of the above reactions to sulfur poisoning are generally less than that for poisoning by sulfur of CO methanation. The rate attenuation is, nevertheless, strongly nonlinear at the lower sulfur levels. A direct consequence of the differing molecular sizes of the reactants (CO, ethylene, ethane, cyclopropane) involved in the reactions investigated is that electronic effects, rather than ensemble requirements, dominate the catalytic poisoning mechanism for these experimental conditions.

Recent studies [8.28] using high-resolution electron energy loss and photoelectron spectroscopy to investigate the effect of sulfur on the CO/Ni(100) system are consistent with an extended effect by the impurity on the adsorption and bonding of CO. Sulfur levels of a few percent of the surface nickel atom concentration were found sufficient to significantly alter the surface electronic structure as well as the CO bond strength.

8.2.2 Electroneutral Impurities

Interest in bimetallic catalysts has risen steadily over the years because of the commercial success of these systems. This success results from an enhanced ability to control the catalytic activity and selectivity by tailoring the catalysts' composition [8.29-40]. A key question in these investigations, as with other impurities, has been the relative roles of ensemble and electronic effects in defining the catalytic behavior [8.41-44]. In gathering information to address this question, it has been advantageous to simplify the problem by utilizing models of a bimetallic catalyst such as the deposition of metals on single-crystal substrates in the clean environment familiar to surface science. Many such model systems have been studied but a particularly appealing combination is that of copper on ruthenium. Copper is immiscible in ruthenium which facilitates coverage determinations by TPD [8.13] and circumvents the complication of determining the three-dimensional composition.

a) Copper Overlayer Structure

The adsorption and growth of copper films on the Ru(0001) surface have been studied [8.13,45-56] by work function measurements, LEED, AES, and TPD. The results from recent studies [8.53-56] indicate that for submonolayer depositions at 100 K the copper grows in a highly dispersed mode, subsequently forming two-dimensional islands pseudomorphic to the Ru(0001) substrate upon annealing to 300 K. Pseudomorphic growth of the copper indicates that the Cu-Cu bond distances are strained approximately 5% beyond the equilibrium bond distances found for bulk copper. This behavior is seen to continue to
the 1 ML level. Additional copper deposition to 2 ML shows a similar two-
dimensional island growth but with an epitaxial, or relaxed, Cu(111) struc-
ture. Subsequent annealing to 900 K, in both these cases enhances the two-
dimensional islanding of the films but does not affect the overall structure. Results from AES and LEED [8.56] show that a 900 K anneal of copper films in excess of 2 ML leads to three-dimensional Cu(111) island formation expon-
sing areas of the surface covered by the original copper bilayer - one pseudomorphic and one epitaxial.

b) Chemisorption

Recent work [8.13,54] has shown that a subtle modification of the preparation techniques of the Cu film on the Ru(0001) substrate can lead to significant changes in the system's chemisorptive properties. For example, in early studies the attenuation of hydrogen chemisorption by copper on Ru(0001) was observed to be quite precipitous by Shimizu et al. [8.46] following copper deposition at 1080 K. More recent work [8.13,54] has shown that preparation of the Cu overlayer at 100 K, with or without an anneal to 1080 K, leads to simple site blocking of H2 chemisorption, that is, poisoning of the hydrogen dissociation on a one-to-one (copper-to-ruthenium) basis. These results to-
gerther suggest that the degree of the two-dimensional character could differ substantially in the Cu overlayer resulting from these two preparation tech-
niques. In our studies [8.13,54,56] the presence of a distinct "monolayer" and a "multilayer" feature in the copper TPD provides a convenient and defin-
itive method for measuring absolute copper coverage [8.13,54].

A comparison of CO desorption from Ru [8.56], from multilayer Cu (~ 10 ML) on Ru and 1 ML Cu on Ru is shown in Fig.8.13. The TPD features of the 1 ML Cu

![CO Thermal Desorption](image)

**Fig.8.13.** Results of TPD for CO adsorbed to saturation lev-
els on the clean Ru(0001), on multilayer Cu, and on a 1ML
Cu covered Ru(0001).
(peaks at 160 and 210 K) on Ru are at temperatures intermediate between Ru and bulk Cu. This suggests that the monolayer Cu is electronically perturbed and that this perturbation manifests itself in the bonding of CO. An increase in the desorption temperature relative to bulk Cu indicates a stabilization of the CO on the monolayer Cu suggesting a coupling of the CO through the Cu to the Ru. The magnitude of the CO stabilization implies that the electronic modification of the Cu by the Ru is significant and should be observable with a band-structure probe. Recent angularly resolved photo-emission studies [8.57] indeed show a unique interface state which is probably related to the altered CO bonding on Cu films intimate to Ru.

Figure 8.14 shows the results [8.56] of CO chemisorption on the Cu/Ru(0001) system as a function of the Cu coverage. Copper deposition was at 100 K, followed by an anneal to 900 K. This preparation, as discussed above, is expected to produce significant two-dimensional copper island formation. In each case the exposure (approximately 10 L or 10^{-5} Torr s) corresponds to a saturation coverage of CO. Most apparent in Fig.8.14 is a monotonic decrease upon addition of Cu of the CO structure identified with Ru (peaks at 400 and 480 K) and an increase of the CO structure corresponding to Cu (peaks at 200 and 275 K). The buildup of a third feature at ~300 K (indicated by the dashed line) is assigned to CO desorbing from the edges of copper islands. Integration of the 200, 275, and 300 K peaks provides information regarding island sizes, that is, perimeter to island area ratios, at various copper

![Image](image_url)

**Fig.8.14.** Results of TPD corresponding to CO adsorbed to saturation levels on the clean Ru(0001) surface, and from this same surface with various coverages of Cu.
coverages. For example, at $\Theta_{\text{Cu}} = 0.66$ we estimate the average island diameter to be approximately 50 Å. This island size is consistent with an estimate of the two-dimensional island size corresponding to this coverage of 40-60 Å derived from the width of the LEED beam profiles [8.56].

These results demonstrate that significant structural perturbations of Cu occur at the Cu/Ru interface and that these changes lead to large effects on the chemistry of the altered copper. Such chemical effects are certain to play a role in the enhanced catalytic properties of Cu/Ru bimetallic catalysts.

c) Catalytic Activity

Model studies of the Cu/Ru(0001) catalyst have been carried out [8.21] for methanation and hydrogenolysis reactions and are shown in Fig.8.15. These data suggest that copper merely serves as an inactive diluent, blocking sites on one-to-one basis. A similar result has been found in an analogous study [8.14] introducing silver onto a Rh(111) methanation catalyst.

SINFELT et al. [8.58] have shown that copper in a Cu/Ru catalyst is confined to the surface of ruthenium. Results from the model catalysts discussed here then should be relevant to those on the corresponding supported, bimetallic catalysts. Several such studies have been carried out investigating the addition of copper or other Group 1B metals on the rates of CO hydrogenation [8.41,59,60] and ethane hydrogenolysis [8.60-62] catalyzed by ruthenium. In general, these studies show a marked falloff in activity with addition of the Group 1B metal suggesting a more profound effect of the Group 1B metal on ruthenium than implied from the model studies. A critical parameter in the supported studies is the measurement of the active ruthenium surface using hydrogen chemisorption techniques. Haller and co-workers [8.61,62] have recently suggested that hydrogen spillover during chemisorption may occur from ruthenium to copper complicating the assessment of surface Ru atoms. Recent studies in our laboratory [8.55] have shown directly that spillover from ruthenium to copper can take place and must be considered in the hydrogen chemisorption measurements. Hydrogen spillover would lead to a significant overestimation of the number of active ruthenium metal sites and thus to significant error in calculating ruthenium specific activity. If this is indeed the case, the results obtained on the supported catalysts, corrected for the overestimation of surface ruthenium, could become more comparable with the model data reported here.

Finally, the activation energies observed on supported catalysts in various laboratories are generally unchanged by the addition of a Group 1B metal.
Fig. 8.15 a,b. Relative rate of (a) CO hydrogenation and (b) ethane hydrogenolysis as a function of Cu coverage on a Ru(0001) catalyst. Reaction temperature is (a) 575 K and (b) 550 K.

[8.61-63], in agreement with the model studies. A crucial test of the relevance of modeling bimetallic catalysts using single crystals will be the ability of the model systems to alter the selectivity of the catalyst towards dehydrogenation reactions as is generally observed on supported systems [8.64]. These experiments are currently underway in our laboratory.
In general, we find that electroneutral impurities, in contrast to electronegative impurities such as sulfur, tend to act as blocking agents for adsorption and reaction. This is likely a result of minimal perturbing effects on the substrate by the overlayer due to the similarities in electronegativities. Quite clearly, at monolayer and near-monolayer coverages, overlayer metals are perturbed by the substrate and exhibit special chemical properties that are unlike those of the bulk metal. The latter effects are likely to be major contributors to the special properties of multimetallic catalysts.

8.2.3 Electropositive Impurities

A direct consequence of interpreting the poisoning effects of electronegative impurities in terms of electronic surface modification is that additives with electronegativities less than that of the metal should promote a different chemistry reflecting the donor nature of the additive. For example, alkali atoms on a transition metal surface are known to exist in a partially ionic state, donating a large fraction of their valence electron to the metal, resulting in a work function decrease. This additional electron density on the transition metal surface atoms is thought to be a major factor in alkali atoms altering the chemisorptive bonding of molecules such as \( \text{N}_2 \) [8.65] or \( \text{CO} \) [8.66], and in promoting the catalytic activity in ammonia synthesis [8.67]. These results are consistent with the general picture that electron receptors tend to inhibit \( \text{CO} \) hydrogenation reactions whereas electron donors typically produce desirable catalytic effects, including increased activity and selectivity. Recent chemisorption and kinetic studies have examined quantitatively the relationship between the electron donor properties of the impurity and its effect on the catalytic behavior.

a) Chemisorption

The addition of alkali metal atoms to Ni\((100)\) results in the appearance of more tightly bound states in the \( \text{CO} \) TPD spectra and to an increase in the degree of \( \text{CO} \) dissociation [8.66]. The dissociation probability increases in the sequence \( \text{Na} \), \( \text{K} \), \( \text{Cs} \), indicating a correspondence between the donor properties of the impurity and its ability to facilitate \( \text{CO} \) dissociation. On iron [8.68], \( \text{CO} \) absorbs with a higher binding energy on the potassium-promoted Fe\((110)\) surface than on the corresponding clean surface. The \( \text{CO} \) coverage increases and the sticking coefficient decreases with increasing potassium coverage. The probability for \( \text{CO} \) dissociation increases in the presence of potassium [8.68]. Analogously, NO is more strongly adsorbed and dissociated to a greater
extent on sodium-covered Ag[111] than on clean Ag[111] [8.69]. The addition of potassium to iron increases the dissociative adsorption of N₂, isostructural with CO, by a factor of 300 over that for the clean surface [8.70]. Recent studies of CO adsorption on potassium-promoted Pt[111] [8.71-73] and Ni[100] [8.74] are consistent with this general picture of donor-enhanced metal-CO bonding. For H₂ chemisorption, Erth et al. [8.75], using TPD techniques, have observed an increase in the adsorption energy of hydrogen on iron. They suggest that the empty state above the Fermi level created by the pronounced electron transfer from potassium to the d-band of iron may possibly be involved via interaction with the H 1s level.

b) Carbon Monoxide Dissociation Kinetics

Adsorbed potassium causes a marked increase in the rate of CO dissociation on a Ni[100] catalyst [8.76]. The increase of the initial formation rate of "active" carbon or carbide carbon via CO disproportionation [2 CO → C(ads) + CO₂] is illustrated in Fig.8.16. 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 rates shown in Fig.8.16 are the observed rates of carbon formation extrapolated to zero carbon coverage. The carbide buildup kinetics at various temperatures for the clean surface [8.77] and for a potassium coverage of 10% of a monolayer are compared in Fig.8.17 [8.76]. Of particular significance in these studies is the reduction of the activation

![Graph](image)

**Fig.8.16.** The relative initial rate of reactive carbon formation from CO disproportionation as a function of potassium coverage. P₀ = 24 Torr, T = 500 K
energy of reactive carbon formation from 23 kcal/mole for the clean Ni(100) surface to 10 kcal/mole for a 10% potassium-covered surface [8.76].

a) Methanation Kinetics

Kinetic measurements [8.76] over a Ni(100) catalyst containing well-controlled submonolayer quantities of potassium show a decrease in the steady-state methanation rate under a variety of reaction conditions. These results are summarized in Fig.8.18. The presence of potassium did not alter the apparent activation energy associated with the kinetics of Fig.8.19; however, the po-
Fig. 8.19. A comparison of the rate of methane synthesis over a clean single-
crystal Ni{100} catalyst to the corresponding rate over a potassium-doped
catalyst. Total reactant pressure is 120 Torr, H₂/CO = 4

Fig. 8.20. A comparison of the product distributions (weight percentage) ob-
served for a clean and a potassium-doped catalyst at T = 500 K, H₂/CO = 4,
and a total pressure of 120 Torr. Potassium coverage = 0.10 ML
tassium did 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% on the potassium-covered catalyst.

d) Promotion of Higher Hydrocarbon Formation
As shown in Fig. 8.20, adsorbed potassium causes a marked increase in the
steady-state rate and selectivity of nickel for higher hydrocarbon synthesis
[8.76]. At all temperatures studied, the overall rate of higher hydrocarbon
production was faster on the potassium-dosed surface showing that potassium
is a promoter with respect to Fischer-Tropsch synthesis. This increase in
higher hydrocarbon production is attributed to the increase in the steady-
state active carbon level during the reaction, a factor leading to increased
carbon polymerization. Potassium impurities on a nickel catalyst, then, cause
a significant increase in the CO dissociation rate and a decrease in the ac-
tivation energy for CO dissociation at low carbon coverages. These effects
can be explained in terms of an electronic effect, whereby the electropositive
potassium donates extra electron density to the nickel surface atoms, which
in turn donate electron density to the adsorbed CO molecule. This increases
the extent of π-backbonding in the metal-CO complex, resulting in an increased metal-CO bond strength and a decrease in C-O bond strength. This model satisfactorily explains the decrease in the activation energy for carbide buildup brought about by potassium.

Since a local effect by the potassium is sufficient to account for the kinetics, the spatial extent of the effect of potassium in these experiments cannot be assessed. However, recent high-resolution electron energy loss spectroscopy (HREELS) of CO on potassium-doped platinum [8.72] and ruthenium [8.78] indicate an alkali influence significantly larger than a simple potassium radius. These results, taken together suggest that extended electronic perturbations are effectively altering the surface chemistry via a similar mechanism to that invoked for the poisoning results discussed above.

e) Electronic Compensation Effects
Intrinsic to interpreting catalytic poisoning and promotion in terms of electronic effects is the inference that adsorption of an electronegative impurity. Recent experiments have shown this to be true in the case of CO₂ methanation [8.27]. As shown in Fig. 8.21, the adsorption of sulfur decreases the rate of methane formation significantly. The adsorption of potassium in the presence of sulfur shows that the potassium can neutralize the effects of sulfur.

![Graph](image)

**Fig. 8.21.** Methane production from a CO₂/H₂ reaction mixture over (a) a clean, (b) a sulfided, (c) a potassium-covered, and (d) a potassium-and-sulfur-covered Ni{100} catalyst.
8.2.4 Related Theory

Theoretical work has been undertaken to address directly the predicted magnitude of the near-surface electronic perturbations caused by impurity atoms. Early work by Grimley and co-workers [8.79,80] and Einstein and Schrieffer [8.81] concentrated on the indirect interactions between adsorbates which occur via the surface conduction electrons. These calculations suggested that atom-atom interactions through several lattice spacings can occur. More recently, Peipeim et al. and Hamann [8.82] and Joyner et al. [8.83] have calculated the change in the surface one-electron density of states due to the adsorption of an electropositive or electronegative atom. Such changes are assumed to affect the interaction of an adsorbing atom or molecule with the surface. The lateral range of these changes is then a measure of the range of the interactions.

The calculations of Peipeim et al. and Hamann have expressly addressed the surface electronic perturbation by sulfur [8.82] as well as by chlorine and phosphorus [8.84]. The sulfur-induced total charge density vanishes beyond the immediately adjacent substrate atom site. However, the Fermi-level density of states, which is not screened and which governs the ability of the surface to respond to the presence of other species, is substantially reduced by the sulfur even at nonadjacent sites. Finally, the results for several impurities indicate a correlation between the electronegativity of the impurity and its relative perturbation of the Fermi-level density of states, a result which could be very relevant to the poisoning of $\text{H}_2$ and $\text{CO}$ chemisorption by $\text{S}$, $\text{Cl}$, and $\text{P}$ [8.9], as discussed above.

Theoretical treatments taking into account the direct interaction between adsorbates due to an overlap between their orbitals have also been reported [8.85,86]. Considerations are given to the energy cost of orthogonalization of the orbitals to one another, a factor which dominates at very short adsorbate-adsorbate distances.

In addition, the direct electrostatic interaction between adsorbates has been treated [8.87-89]. At intermediate distances of the order of a surface lattice constant, Nørskov et al. report [8.88] that this interaction can give rise to substantial ( $> \sim 0.1 \text{ eV}$) interaction energies, when both adsorbates in question induce electron transfer to or from the surface or have a large internal electron transfer.

Both sets of theories, that is, "through bond" or "through space", are consistent with adsorbate perturbations sufficiently large to effect chemically significant changes at next-nearest-neighbor metal sites. This perturbation length is sufficient to explain adequately the observed poisoning of
chemisorptive and catalytic properties by surface impurities reported in the above discussion.

8.3 Conclusions

Model studies using metal single crystals and ultra-high-vacuum surface techniques are profitable in developing an understanding of the mechanisms by which poisons and promoters alter catalytic performance. Kinetic measurements in conjunction with these studies are particularly useful in linking the surface analytical measurements to practical catalysts. Because of the importance of surface chemical modification in catalysis and many related technological areas, much more work should and will be invested in defining in detail the physics and chemistry associated with the changes induced by surface impurities. Of particular interest are the specific bonding sites on and the electronic interaction of the impurity with the substrate. Also, the influence of the impurity on the chemisorptive behavior of the reactants as well as the bond strengths of the reactants are key pieces of information needed. These kinds of data are currently accessible using an array of modern surface techniques. These studies, in parallel with studies on supported catalysts, promise to be most revealing regarding the basic mechanisms of surface chemical modification.

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