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Elementary Processes at Gas/Metal Interfaces^[**]

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Recent years have seen the development of several physical methods for the study of solid surfaces under ultrahigh vacuum conditions, of which the most important are discussed in this progress report. Contemporary views of the chemisorption bond and the factors affecting it are discussed against the background of the adsorption of hydrogen and of carbon monoxide on single crystal surfaces of face-centered cubic transition metals. Catalytic oxidation of CO over palladium and the interaction of oxygen with nickel serve as examples of chemical surface reactions.

1. Introduction

An atom located in the surface layer of a solid occupies an intermediate position between a free atom and an atom in the bulk of a crystal in that a proportion of the chemical valency (otherwise utilized in cohesion) is unsaturated. Suitable particles impinging on the surface from the vapor phase can engage not only in the usual van der Waals interaction (= physical adsorption) but also in chemical bonding. This phenomenon, known as chemisorption, appears to be the primary step of all chemical surface processes.

Reactions on the surface of metals have eminent practical significance; it will suffice to recall the processes of heterogeneous catalysis or corrosion. In spite of tremendous scientific effort in these areas the fundamental elementary steps remain largely unknown and in the absence of reliable predictions work remains mainly empirical. The principal difficulty encountered when dealing with "real" surfaces lies in the multitude of generally uncontrollable parameters (crystallographic orientation, structural defects, impurities, substrate effects, *etc.*) affecting their chemical behavior, which are accessible only poorly, if at all, to the experimental techniques presently available.

The situation is greatly simplified if single-crystal surfaces are used having a uniform orientation which contains a minimum of foreign atoms. The latter requirement can be satisfied only under ultrahigh vacuum (UHV) conditions^[1], *i.e.* at residual gas pressures of about 10^{-10} torr. In the past few years several experimental procedures have been developed for the study of such model systems, which provide highly detailed information in some cases. A parallel development has been the very recent intensification of efforts to arrive at a theoretical understanding of surface phenomena.

2. Experimental Methods

A complete description of surface processes includes the following information: The qualitative and quantitative chemical composition of the interface (including the molecular nature of adsorbed species), the geometrical structure, the energy of binding between the surface and the adsorbed particles, dipole moments of adsorption complexes, the energy distribution of electronic states, vibrations, surface diffusion, and the kinetics of ad- and desorption and of surface reactions. The relevant questions can be answered to various degrees of satisfaction with the aid of various modern experimental methods. Complete theoretical analysis of the experimental data still runs into considerable difficulties, however, and in some cases we are still far removed from full exploitation of the information available in principle from an experiment. Comprehensive descriptions of surface processes are clearly

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not to be expected from the use of a single method; this will require combination of various approaches. A selection of the most powerful experimental tools currently available will be presented below.

Thermal Desorption Spectroscopy^[2]

A basically simple experiment is to expose a clean surface for a given time to a given partial pressure of the gas of interest^[*] at a temperature at which no significant desorption takes place, and then to continuously raise the temperature of the sample under UHV conditions while recording the partial pressure with a suitable measuring device (preferably with a quadrupole mass spectrometer). Figure 1 illustrates a series of such thermal desorption spectra from a Ni(111) surface previously exposed to different doses of hydrogen^[3]. Measurements of this kind afford information about adsorption kinetics, the existence of different adsorption states, adsorption energy, the order of reaction of desorption, and (on use of isotope mixtures) the question whether adsorption is accompanied by dissociation of the molecule.

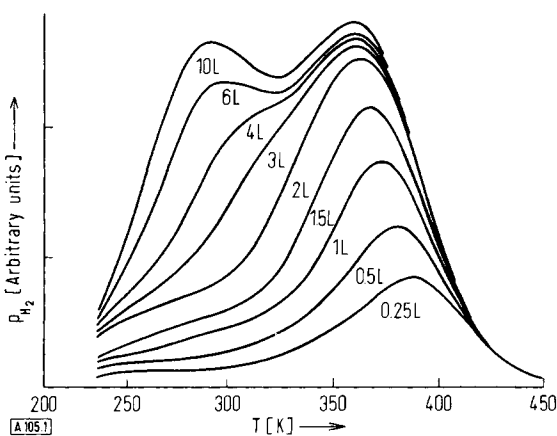


Fig. 1. Thermal desorption spectra for the $H_2/Ni(111)$ system after covering to various extents [3] ($1 L = 10^{-6}$ torr \times s).

Change in Work Function^[4]

The work function of a metal, *i.e.* the minimum energy required to remove an electron from the Fermi level to the vacuum, is modified by the presence of dipole layers on the surface—such as almost invariably arise on formation of adsorbed phases. Various techniques can be used for highly sensitive measurement of this quantity (with an accuracy of about 1 mV). This reveals the dipole moment of the adsorption complex and its possible variation with the degree of coverage. Moreover, such measurements can, after suitable calibration, provide a convenient measure for the surface concentration of adsorbed particles. If there is a reversible equilibrium between the adsorbed layer and the vapor phase, this procedure can be used for plotting adsorption isotherms from which in turn the so-called isosteric adsorption energies can be derived with the aid of simple thermodynamic relationships^[5]. All the adsorption energies reported in the following sections were determined in this way.

[*] The commonest unit employed is 1 L (Langmuir) = 10^{-6} torr \cdot s. This dose will just suffice to completely cover a clean surface with an adsorption layer if each impinging particle is adsorbed.

Secondary Ion Mass Spectrometry (SIMS)^[6]

This relatively common technique involves bombardment of the solid with primary ions (usually noble gases) and mass analysis of the secondary ions or neutral particles generated. By reducing the current density of the primary beam this method can be rendered largely non-destructive while still displaying an extremely high sensitivity. The fundamental individual processes are rather complex, however, thus impeding quantitative conclusions.

Ion Backscattering Spectroscopy^[7]

In this method a monoenergetic ion beam ($E < 10$ keV) is scattered at a surface and the energy of the scattered ions is analyzed. Application of the laws of conservation of energy and momentum shows that the energy spectrum of the backscattered ions is equivalent to a mass analysis of the surface atoms. This mass analysis is restricted to the outermost atoms provided that the ion energy is not too high. In favorable cases the technique also yields structural information about the position of adsorbed particles. Ion backscattering spectroscopy can, in principle, be easily combined with other methods (*e.g.* LEED and AES) but has not yet found wide application.

By far the most important group of methods is based on the analysis of the energy and/or direction of low energy electrons ($E \leq 1000$ eV) emitted from a solid surface on excitation with suitable primary radiation^[8]. The average escape depth of electrons from metals is shown as a function of their energy in Figure 2. It may be seen that this quantity (d) amounts to no more than about two to three atomic layers between 40 and 400 eV, *i.e.* such electrons arise largely from the surface. Among the methods of investigating surfaces which exploit this effect the greatest significance attaches to Auger electron spectroscopy (for elemental analysis), diffraction of low energy electrons (for structural elucidation), and photoelectron spectroscopy (for determination of electronic binding energies and of surface orbitals). The instrumental armamentarium required can be combined in a single apparatus. It should be mentioned that the interaction of electrons with adsorption layers can also lead to chemical changes or desorption. This side effect, while undesirable *per se*, can also be subjected to systematic study as in the method of electron-impact induced desorption (ESD)^[9].

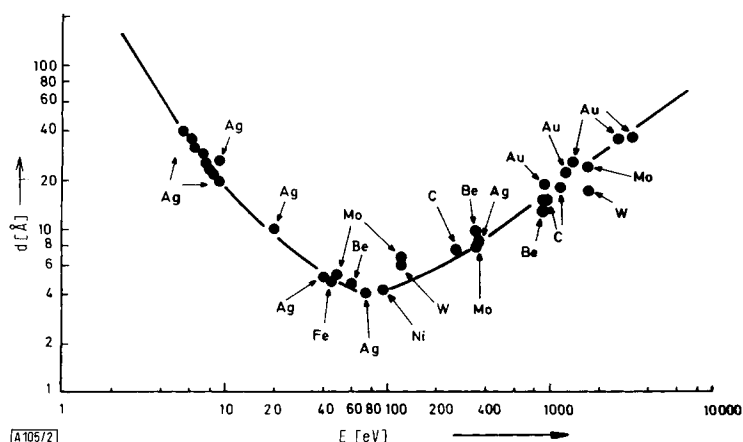


Fig. 2. Average escape depths (d) of electrons from metals as a function of their energy [8].

Auger Electron Spectroscopy^[8, 10]

If an electronic core level of an atom is ionized by suitable primary radiation (preferably an electron beam) then the resulting hole is reoccupied by transition of an electron from a higher level. The liberated energy can be transferred non-radiatively in competition with X-ray fluorescence to another (bound) electron which can then be ejected from the solid with corresponding kinetic energy as a so-called Auger electron. In light elements and at energies less than 1000 eV this effect greatly predominates, thus imparting a high degree of sensitivity to the method. The experimental procedure consists in determination of the energy distribution of the emitted secondary electrons—the second derivative is usually recorded for reasons of expedience. The maxima recorded can be assigned to the elements present in the surface region. The Auger electron spectrum of a contaminated nickel surface is shown as an example in Figure 3a. The area examined is determined by the diameter of the primary electron beam and amounts to about 1 mm². If desired the electron beam can be focused on a much smaller spot. Line scanning of

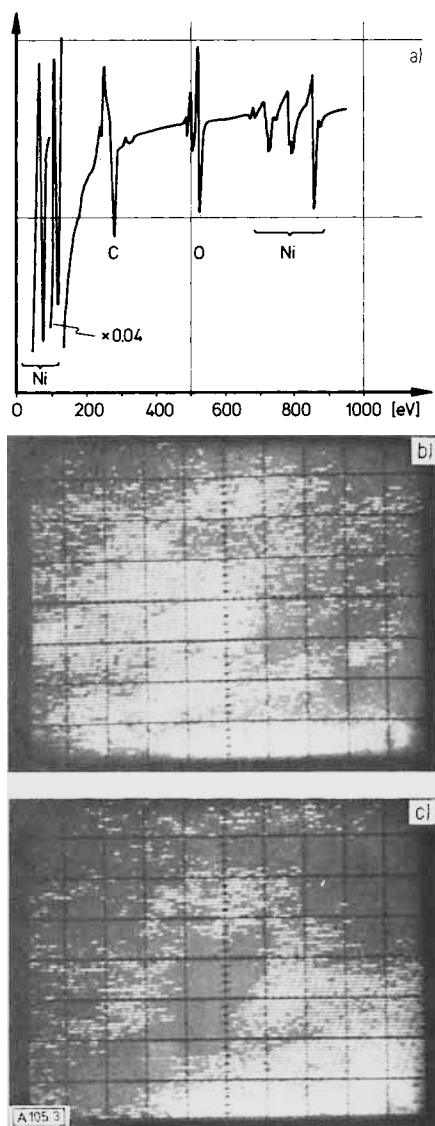


Fig. 3. a) Auger electron spectrum of a nickel surface contaminated with C and O. b) and c) Scanning Auger spectra of the lateral distribution of the elements C and O, respectively, in a surface region measuring 1 × 0.8 mm² (J. Küppers, unpublished).

a given surface region at constant analyzer energy and simultaneous control of the brightness of an oscilloscope image by the intensities of the relevant Auger line permits measurement of the lateral distribution of individual elements on the surface (“scanning Auger”), as illustrated in Figures 3b and 3c.

Provided an element is distributed only in two dimensions on a surface, the intensity of the corresponding Auger signal is proportional to its surface concentration to a good approximation. So far, *absolute* quantitative analysis has been possible only after calibration and is therefore one of the principle unsolved problems of this method.

Low Energy Electron Diffraction (LEED)^[8, 11]

A monoenergetic beam of particles having momentum mv is known to be equivalent to a material wave of wavelength $\lambda = h/mv$. For electrons of energy 150 eV, $\lambda = 1 \text{ \AA}$, *i. e.* interference takes place at surfaces of crystals as first demonstrated by *Davison and Germer*^[12]. In several respects the experimental set-up for the LEED technique resembles that for the Laue method for X-ray diffraction: a monoenergetic electron beam impinges normally on a single crystal surface and undergoes partial backscattering in those directions which satisfy the two Laue conditions for lattice periodicity parallel to the surface. Owing to the small depth of penetration of the electrons the third Laue condition (for periodicity in the direction normal to the surface) merely leads to characteristic changes in the intensity of reflections with the wave number of the electrons. After filtering out the inelastically scattered electrons, the elastically diffracted ones are post-accelerated and produce a “diffraction pattern” on a fluorescent screen. Adsorption of gases usually causes the appearance of new diffraction spots. This means that the adsorbed layer forms an ordered structure whose periodicity deviates from that of the substrate. The position of the diffraction spots reveals the unit cell of the surface structure, and in favorable cases also the mutual configuration of the adsorbed particles. Complete structural analysis—and especially determination of distances between the adsorbate and the surface atoms—from the LEED intensities is rendered very difficult by the extensive occurrence of multiple scattering effects. Although an adequate theoretical approach has meanwhile been developed, this formidable task has so far only been accomplished in few cases in which adsorbed atoms form simple superstructures (O, S, Se, Te on Ni^[13], I/Ag(111)^[14]). So far in all instances, the positions with the maximum coordination number (4 on the (100) surface, 3 on the (111) surface) are the adsorption sites occupied.

Photoelectron Spectroscopy^[15]

Irradiation of a sample with monochromatic light of sufficient energy can lead to ionization of the occupied electronic levels (with different probabilities). The emitted photoelectrons have a kinetic energy E_{kin} (disregarding multiple-particle effects), which is given by $E_{\text{kin}} = h\nu - E_{\text{B}}$ (conservation of energy). E_{B} is termed the “binding energy” of the liberated electron relative to the vacuum level. In general, the energy scale is referred to the Fermi level of the solid, which differs

from the vacuum level by the work function Φ . Applying Koopmans' theorem the experimentally determined binding energies are frequently equated to the orbital energies. However, considerable errors may then occur due to neglect of relaxation and correlation effects. Additional effects of this kind will arise compared with the free molecule owing to the presence of a solid surface: their theoretical and experimental treatment remains a largely unsolved problem, and yet a necessary requirement for any quantitative interpretation of changes in orbital energies due to chemisorption bonding.

Photoemission spectra are excited either by soft X-rays (XPS) or by UV light (UPS). The former approach affords mainly information concerning the core levels. Chemisorption levels occurring within the valence band region are better examined by UPS. Excitation is then usually accomplished with He(I) ($h\nu = 21.2 \text{ eV}$) or He(II) ($h\nu = 40.8 \text{ eV}$) resonance radiation. Continuous radiation of even higher photon energy is available from an electron synchrotron; however, this light source is accessible to only few researchers^[16].

While UPS studies have hitherto been mainly concerned with measurements of the energy distribution of photoelectrons over a relatively large emission angle, interesting variations in intensity with the direction of emission have recently been discovered^[17]. The theoretical analysis of these effects is presently undergoing rapid development^[18], and holds promise of some insight into the spatial orientation of the relevant orbitals on the solid surface.

3. Mechanism of Chemisorption

Analysis of the thermal desorption spectra for the $\text{H}_2/\text{Ni}(111)$ system illustrated in Figure 1 reveals, *inter alia*, that desorption corresponds to a second order reaction. Experiments with a mixture of H_2 and D_2 indicated complete equilibration of the isotopes on the surface. Both observations justify the conclusion that hydrogen is adsorbed in atomic form. The energy of the Ni—H bond is only 63 kcal/mol while the dissociation energy of H_2 is 104 kcal/mol. This is certainly a principal reason for the activity of nickel as a hydrogenation catalyst. The dissociative adsorption of the H_2 molecule requires no measurable activation energy, although cleavage of the free molecule needs 104.2 kcal/mol. The way in which this energy threshold is overcome by the surface can be depicted schematically as in the potential energy diagram^[19] of Figure 4: on approaching the metal surface a H_2 molecule passes through a shallow energy minimum, corresponding to physisorption. In contrast, a H atom is capable of chemisorption bonding characterized by a deeper

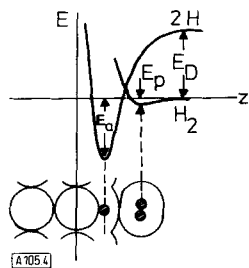


Fig. 4. Potential energy diagram according to Lennard-Jones [19] for adsorption of hydrogen on metals. E_D , dissociation energy of H_2 (104 kcal/mol); E_P , adsorption energy for physical (molecular) adsorption; E_A , adsorption energy for atomic chemisorption.

minimum closer to the surface. Intersection of the two potential energy curves below the zero point leads to dissociative adsorption without activation energy. Adsorption of hydrogen on copper involved measurable activation energy^[20]; the energy curves therefore intersect above the zero energy level.

The occurrence of chemisorption between a H atom and a metal surface is illustrated by the energy-level scheme of Figure 5. The metal is represented as a continuum of electronic states occupied up to the Fermi level E_F . As long as the H atom is located at a long distance from the surface its 1s electron is in a state of sharply defined energy (ionization energy $I = 13.6 \text{ eV}$) lying below the Fermi level of the metal (work function $\Phi \approx 5\text{--}6 \text{ eV}$). A second electron in the 1s level gains only 0.75 eV in energy relative to the vacuum level owing to electron-electron repulsion so that the affinity level A lies above the Fermi level. Therefore only slight transfer of charge will be expected to occur from the metal to the adsorbed H atom, as is manifested in the small dipole moment of about 0.05 D^[3] established experimentally, and the bond should be essentially covalent. On coupling of the H atom to the metal a new chemisorption level will arise which is broadened and shifted relative to the H1s orbital. The broadening of this level can be regarded as a consequence of Heisenberg's uncertainty principle, *i.e.* an electron has only a limited lifetime in the chemisorption level owing to tunneling to and from the metal. A somewhat different (but equivalent) approach ascribes the broadening to the continuous energy distribution of the set of molecular orbitals formed from the orbital of the adsorbed H atom and a suitable set of metal wave functions.

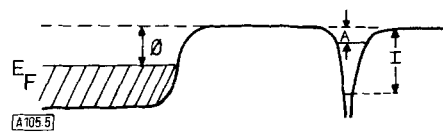


Fig. 5. Energy diagram for interaction of a H atom (right) with a metal surface (left).

The shift results from several contributory factors, *i.e.* the drop in energy due to the chemical bond, an increase due to intraatomic Coulomb interaction, and a further increase arising from the attractive interaction of the ionized atom with its image charge in the metal. A useful concept that can be introduced at this stage is that of the so-called local density of states $\rho(E)$ defined by overlap of the adatom wave function with the metal wave function at a given energy E , *i.e.* describing the energy distribution of the states generated by the chemisorption bond. To a first approximation this local density of states is directly apparent from the energy distribution measured by UV electron spectroscopy (UPS)—or more precisely in the additional emission relative to the pure metal as a result of chemisorption^[21]. It should be pointed out, however, that the quantitative analysis of such spectra is still beset by serious theoretical difficulties^[8, 15b].

Figure 6 shows the UPS spectra of a pure Ni(111) surface (curve a) and one covered with hydrogen (curve b)^[22]. In curve a) a pronounced maximum about 2 eV wide is seen immediately below the Fermi level which arises from the emission from the Ni d band with its high density of states. (The increase on going to lower energy is attributable to the emission of secondary electrons and not to the existence

of further (lower-lying) valence states of high density of states.) After adsorption of hydrogen an additional, relatively broad maximum appears *ca.* 6 eV below E_F (*ca.* 12 eV below the vacuum level) which is identified as the above mentioned chemisorption level. The broadening may possibly also be affected by other (many-particle) effects^[23].

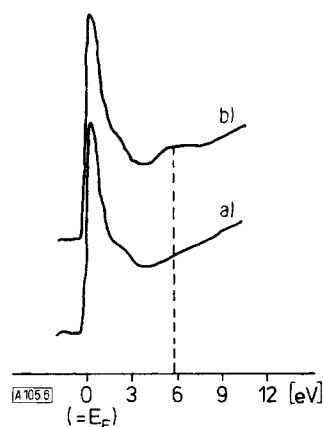


Fig. 6. UV photoelectron spectra ($h\nu=21.2$ eV) of a) a clean Ni(111) surface and b) one covered with hydrogen.

The first quantitative theory of chemisorption of hydrogen on transition metals was developed by *Newns*^[24] within the framework of the so-called Anderson formalism (see below), and considered only coupling of the H1s level with the metal d band. Fitting the adsorption energy to the experimental value affords a chemisorption level at *ca.* 6 eV below E_F , thus corresponding exactly to the additional maximum in the photoemission spectrum. A subsequent EH calculation (extended Hückel theory) for a small cluster of metal atoms showed, however, that the sp band should also play an important role in the chemisorption of hydrogen^[25]. Recent confirmation has come from an extension of the formalism used by *Newns* with inclusion of the Ni sp band and of non-orthogonality effects^[26]. The chemisorption level should accordingly be centered about 7 eV below E_F .

The theory of chemisorption is presently in a state of flux. It unites essential elements of the quantum chemistry of molecules with those of solid state theory^[27]. An important aspect is that the metal represents an open system, *i.e.* provides an inexhaustible supply of electrons. The simplest approach is based on an LCAO-MO model utilizing a Hartree-Fock approximation. A relevant formalism was originally set up by *Anderson*^[28] for the treatment of dilute alloys and later applied to the chemisorption problem^[24, 26, 29]. Such calculations reveal the tendency for formation of a "surface molecule" in the case of strong chemisorption; this species is composed of the adsorbed particle and a small number of neighboring metal atoms. The latter participate directly in bonding with electronic states split off from the band of the metal utilized (as is seen to be the case in the H/Ni(111) system). The chemisorption bond thus assumes a markedly local character, suggesting a comparison with similar molecular compounds (*e.g.* in the case of CO adsorption described in Section 4 with corresponding polynuclear carbonyl complexes). Furthermore this also provides some justification for confining the theory of chemisorption to the treatment of small clusters. A particu-

larly suitable approach is the SCF- X_α procedure developed by *Slater* and *Johnson*^[30] which has already been applied with considerable success to the calculation of ionization energies in a number of systems^[31].

A serious problem common to all LCAO-MO procedures is the neglect of correlation effects. These can be included in an extended Anderson model^[32]. Another attempted approximation starts from the Heitler-London (VB) method (in which correlation effects are of course overemphasized)^[33]. The computational effort involved in such theoretical models is much greater, however, and abandonment of the concept of one-electron states makes direct comparison with orbital-spectroscopic data difficult. The reader is referred to available surveys^[27] concerning the points in favor of and against the various procedures.

4. Chemisorption of CO

Carbon monoxide is the molecule whose adsorption properties have been studied most thoroughly so far. The following discussion will be confined to a few cubic face-centered metals. The more complex CO/tungsten system was recently described by *Gomer*^[34]. *Ford* has reviewed the results available up to 1970^[35].

The adsorption energies of CO on nickel are 26.5 kcal/mol for the (111)-face^[36] and 30 kcal/mol for the (100)-^[37] and the (110)-face^[38]. These values are close to the dissociation energy for Ni(CO)₄, *i.e.* 35 kcal/mol^[39]. The analogy between carbonyl compound and adsorption complex is also apparent in other properties: adsorption of CO on nickel raises the work function of the metal by about 1.3 eV^[36], which is synonymous with partial transfer of electronic charge from the metal to the adsorbate. In Ni(CO)₄ *ab initio* SCF-MO calculations likewise revealed an electron transfer to the ligands, producing a positive charge of about 0.5 e_0 at the nickel atom^[40]. This electron transfer is ascribed to partial population of the $2\pi^*$ MO of the CO molecule, manifested in the IR spectrum as a shift of the CO stretching frequency to lower wave numbers^[41]. Finally, comparison of the photoelectron spectra of Ni(CO)₄^[42] and CO adsorbed on nickel^[43], as shown in Figure 7 together with the spectrum of gaseous CO^[44], appears remarkable. The three maxima are assigned (in order of increasing ionization energy) to the 5σ , 1π , and 4σ orbitals of CO_g. For Ni(CO)₄ the first maximum is due to the Ni d electrons, the following broad band corresponds to overlap of orbitals derived from the 5σ and 1π MOs of the ligand, and the third maximum arises from the CO 4σ orbital^[42].

In 1964 *Blyholder* proposed^[45] a donor-acceptor mechanism analogous to that responsible for bonding in carbonyl compounds to account for the adsorption of CO on metals (see Fig. 8). According to this model, an electron transfer takes place from the occupied 5σ orbital to the metal and a back-donation of metal d electrons into a chemisorption level derived from the antibonding (initially unoccupied) $2\pi^*$ MO. As a consequence, the energy of the 5σ orbital should be lowered relative to that of the 1π orbital, so that the two levels cannot be resolved in the UPS spectrum and give rise to the broad maximum observed about 8 eV below E_F . Although another interpretation was originally given for the spectroscopic data^[43a], this assignment of the UPS maxima

has meanwhile been confirmed by recent theoretical^[26,46] and experimental studies^[43c,47].

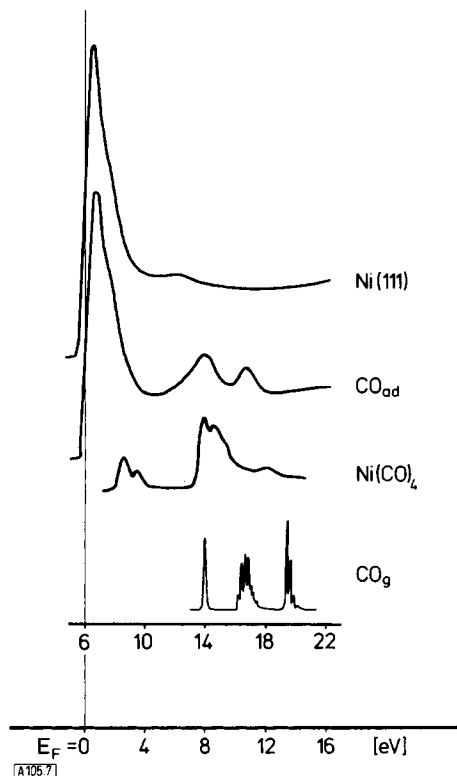


Fig. 7. UV photoelectron spectrum of CO adsorbed on Ni(111) compared with the spectra of Ni(CO)₄ and gaseous CO.

A theoretical study^[26] has indicated that some 50% of the adsorption energy of CO on a Ni(111) surface (*i.e.* 13 kcal/mol) should arise from coupling of the 5σ orbital to the metal sp bands. In the case of the corresponding surface of the neighboring element copper, coupling of the d electrons to the 2π* orbital should play only a very minor role, as

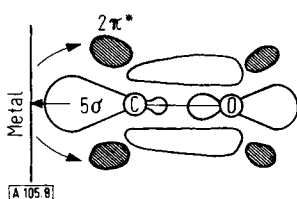


Fig. 8. Donor-acceptor mechanism for the adsorption of CO on metal surfaces.

is confirmed by the far lower adsorption energy of about 12 kcal/mol^[43d] and by the reverse sign of the dipole moment (*i.e.* negative excess charge on the metal side)^[48]. Table 1 lists the CO adsorption energies for the (111)-faces of various cubic face-centered transition metals. It should be noted that

Table 1. Adsorption energies [kcal/mol] for CO on the (111) faces of cubic face-centered metals [49].

	Ni	Cu
	26.5	12
	Pd	Ag
	34	6.5
Ir	Pt	
33	35	

in all cases except silver the adsorption structures are characterized by identical LEED superstructures, *i.e.* identical surface configurations. The differing adsorption energies are therefore due primarily to the “electronic” factor, *i.e.* the influence of the electronic properties of the solid.

The difference between Pd and Ag is particularly striking. In this context, interesting points arise in connection with the use of alloys. Figure 9 shows the variation of CO adsorption energy as a function of the change in work function (which is a measure for the degree of coverage) for Ag/Pd alloys having various surface compositions^[50]. It is seen that for all samples E_{ad} attains the value for pure Pd at very low coverages but at higher surface concentrations even low amounts of Ag bring about a drastic reduction of the adsorption energy, *i.e.* the surfaces become energetically heterogeneous. A qualitative explanation of these findings results from the electronic properties of such alloys, according to which the components essentially retain their electronic structure^[51] (thus in Cu/Ni alloys there are still unoccupied d states at the Ni sites, even at high Cu contents^[52]) and do not form a “collective” d band, in contrast to former views. Of course it should always be borne in mind in all experiments on alloys that the composition of the surface can deviate considerably from that of the bulk and therefore requires specific careful examination^[53].

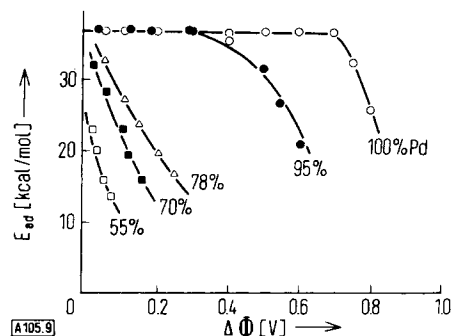


Fig. 9. Adsorption energy for CO on (111) surfaces of Ag/Pd alloys of various surface composition as a function of the change in work function $\Delta\Phi$ [50].

The “geometric” factor embraces the change in adsorption properties, on the one hand with the position of the adsorbate relative to the position of the metal atoms for a given single crystal face, and on the other with the crystallographic orientation, inclusion of structural defects representing a natural extension. These aspects will now be considered with the aid of adsorption of CO on palladium^[54].

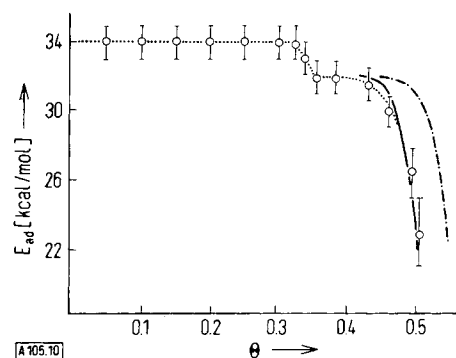


Fig. 10. CO/Pd(111). Adsorption energy as a function of a degree of coverage Φ [55].

Figure 10 shows the variation in the isosteric adsorption energy for CO on Pd(111) as a function of the degree of coverage Θ ^[55]. E_{ad} is seen to remain constant up to $\Theta=1/3$, and then suddenly falls by 2 kcal/mol as the degree of coverage further increases. At $\Theta=1/3$ the LEED diffraction pattern contains additional spots of a superstructure whose pertinent structural model is reproduced in Fig. 11 a. Up to that coverage, all CO molecules can apparently occupy energetically

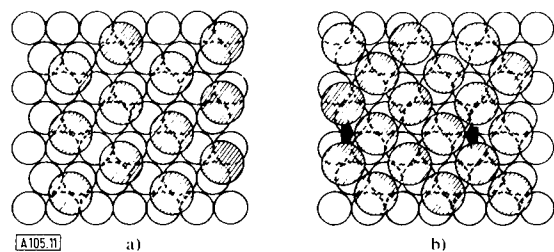


Fig. 11. Structural model for the configuration of adsorbed CO molecules on a Pd(111) surface. a) $\Theta=1/3$; b) $\Theta=1/2$; this structure arises by continuous compression of the unit cell shown in a) [55].

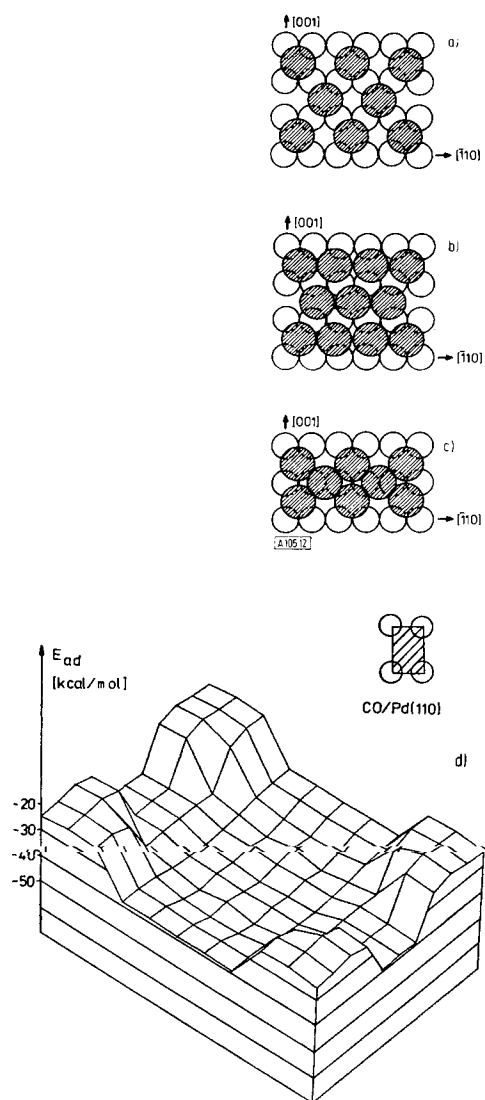


Fig. 12. a)–c) Structural models for the configuration of adsorbed CO molecules on a Pd(110) surface [54]: a) $\Theta=1/2$; b) $\Theta \approx 3/4$; c) $\Theta=1$.—d) Theoretical energy profile for the variation of the CO adsorption energy within the unit cell of the Pd(110) surface [26].

favorable sites without engaging in mutual interactions. (Whether these adsorption sites correspond to the “bridging positions” drawn or should be assigned to points between three Pd atoms cannot yet be decided but is immaterial for the present discussions.) As soon as the degree of coverage exceeds the value $1/3$ the unit cell of the adsorbate structure is continuously compressed (cf. Fig. 11 b). Surface saturation is characterized by a kind of densest packing of the adsorbed molecules, their “size” corresponding to a diameter of about 3 \AA in the present case; this value agrees fairly well with the van der Waals diameter of the CO molecule in the gaseous state^[56]. The dot-dash curve in Figure 10 representing the decrease in E_{ad} with increasing Θ was calculated from these data and shows fairly good agreement with experimental data.

Similar behavior was noted for adsorption of CO on a series of other surfaces^[36, 38, 49b, 49c, 54, 57]. As a further example, Figure 12 depicts the structural models for the three ordered structures of CO on Pd(110) which are successively formed with increasing degree of coverage^[54]. In addition, this figure also shows a theoretically derived energy profile for the variation of the adsorption energy with the position of the CO molecule with respect to the Pd atoms^[26]. (This energy profile deviates slightly from a previously published version^[29b] owing to the subsequent introduction of coupling between the 5σ orbital and the metallic s electrons.) The position of most favorable energy is accordingly seen to lie between four Pd atoms. However, the area required by the CO molecules precludes occupation of each one of these positions, and an initial closing up of the adsorbed particles along the grooves in the $[\bar{1}10]$ -direction will take place up to about $\Theta=0.75$. On further increase of the degree of coverage, the less favorable bridging positions will also be occupied until saturation is reached (Fig. 12 c).

The general conclusion drawn from these observations is that the CO molecules do not seem to be fixed at specific adsorption sites. Instead, relatively slight differences exist in the adsorption energy over a surface, which permit a relatively high mobility of adsorbed molecules on the one hand, but also lead to a tendency to seek out a compromise between a densest packing and the periodicity of the substrate lattice, which determines the energy minima, for the arrangement of molecules on approaching the saturation limit. An analogy is observed with the polynuclear carbonyl compounds where the maximum number of ligands is likewise determined by their spatial requirements. Moreover, dynamic ^{13}C -NMR studies showed that geometric fixation of the CO molecules already gives way to fast site exchange phenomena at relatively low temperatures^[58]. There is no longer any tendency to close packing for small adsorbed particles such as H, O, or N, where the great demand on surface valences for chemisorption bonding limits maximum coverage.

The variation in the initial adsorption energy (*i. e.* the value obtained by extrapolation to $\Theta=0$) for CO on a series of variously oriented Pd single crystal surfaces is shown in Table 2. Remarkably, this quantity varies by only about 15% although the number of nearest neighbors of the metal atoms varies between 9 [(111)-face] and 6 [(311)-face]. Similar observations have also been recorded *e. g.* for the CO/Ni^[36], H_2/Ni ^[3], and H_2/Pd systems^[59], but the experimental data still appear too sparse to justify any general conclusions. Nevertheless, an interesting parallel can be drawn with the finding that numerous reactions occurring on “real” catalysts are not

affected by particle size, *i.e.* are largely insensitive to the structure of the catalyst surface^[60].

Table 2. Adsorption energies [kcal/mol] for CO on variously oriented single crystal faces of Pd.

Face	(111)	(100)	(110)	(210)	(311)
E_{ad}	34	36.5	40	35	35.5

One possible way of conferring a closer resemblance to "real" surfaces upon the single crystal surfaces employed as models consists in introducing periodic arrangements of atomic steps which can be conveniently analyzed by the LEED method^[61]. No measurable changes in bond energy were recorded for the adsorption of CO on a stepped Pd(111)-surface^[54], while a (relatively slight) effect was established on adsorption of hydrogen^[59]. Drastic differences between "flat" and stepped Pt(111)-surfaces were found by *Somorjai et al.*^[62] for the kinetics of reactions with hydrocarbons.

Hitherto, only the adsorption of the undissociated CO molecule has been discussed. In spite of its high dissociation energy this molecule decomposes fairly easily above 200°C on nickel surfaces, and even at room temperature on iron surfaces. Studies on the CO/Ni(110) system^[63] showed that the carbon atoms eventually unite to form thin layers of graphite which can be reoxidized to CO by oxygen; on the other hand the adsorbed oxygen atoms can react with CO to give CO₂. This rationalizes the mode of action of these metals as catalysts for establishing the Boudouard equilibrium.

5. Interactions between Adsorbed Particles and Surface Reactions

The surface configurations of adsorbed CO molecules mentioned in the previous section can be largely understood in terms of direct through-space interactions owing to the incipient mutual interpenetration of electron shells and dipole-dipole repulsion. However, other long-range interactions frequently also occur (especially with strongly bound small atoms like H, O, or N) which are of an indirect nature (through bond) and are attributable to a coupling *via* the metal electrons involved in the chemisorption bond. Theoretical treatments of this problem^[64] have shown that such interactions have an oscillatory character, *i.e.* they may be attractive or repulsive. The adsorbed particles then preferably occupy highly symmetric adsorption sites determined by the periodicity of the substrate lattice. Use of a lattice-gas model of this kind and assuming certain interaction energies permits simulation of thermal desorption spectra^[65], the formation of defined LEED superstructures^[66], and the appearance of order-disorder transitions^[67]. The last-named phenomena represent the two-dimensional analog of phase transitions, such as are known for ordered alloys or ferromagnetic substances, and can be monitored by means of the change in the LEED intensities with temperature^[68]. Available data would indicate such interaction energies between adjacent adsorbed particles are several kcal/mol at maximum.

If two different kinds of species A and B are present on the surface then, by analogy with the "normal" thermodynamics of mixed phases, two limiting cases can be discerned,

which are likewise basically due to intermolecular interactions^[69]:

1) A and B form an ordered mixed phase (*cooperative adsorption*), the surface configuration and binding energies possibly being different from those of the pure single component adsorption phases. Such an example is provided by the system of H + CO on Ni(111)^[70].

2) A and B are completely immiscible (*competitive adsorption*), *i.e.* the surface exhibits separate domains of the two adsorbed species.

The second case has been observed, *e.g.* in the interaction of oxygen and carbon monoxide with a Pd(111) surface^[55] and rationalizes the kinetics of steady-state CO₂ formation. The individual steps of this reaction^[71] are listed in Table 3.

Table 3. Steps involved in catalytic oxidation of CO on palladium.

CO	+	*	\rightleftharpoons	CO _{ad}	
O ₂	+	*	\rightleftharpoons	2 O _{ad}	
O _{ad}	+	CO _{ad}	\rightarrow	CO ₂	Langmuir-Hinshelwood
O _{ad}	+	CO	\rightarrow	CO ₂	Eley-Rideal
CO _{ad}	+	1/2 O ₂	\rightleftharpoons	CO ₂	

The O₂ is adsorbed dissociatively with an adsorption energy of about 60 kcal/mol (CO, 34 kcal/mol) on regions not yet occupied by CO_{ad}. CO molecules impinging from the gas phase onto a surface occupied by O_{ad} react very rapidly, even below room temperature, to give CO₂ which immediately desorbs (Eley-Rideal reaction). Conversely, a surface covered with CO_{ad} ($\theta_{CO} > 2/3$ max. CO coverage) completely inhibits adsorption or reaction with O₂ although a gain in energy would be associated with displacement of CO_{ad}. If both kinds of particle are located on the surface, then they occupy separate domains having diameters of at least 50–100 Å. The reaction between O_{ad} and CO_{ad} (Langmuir-Hinshelwood reaction) proceeds somewhat slower than that between O_{ad} and CO, and requires an activation energy of 7 kcal/mol^[72]. As a consequence of these steps, a steady state formation of CO₂ is only expected if sufficient surface sites are made available for adsorption of O₂ as a result of thermal desorption of CO. The reactant CO thus inhibits the reaction and its desorption becomes rate determining. Figure 13 illustrates this situation with the aid of measurements of the steady state rate of formation of CO₂ and the surface concentration of CO_{ad} as a function of temperature^[72].

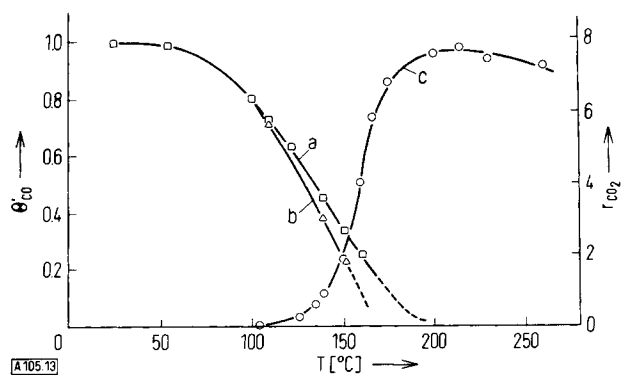


Fig. 13. Catalytic oxidation of CO on a Pd(111) surface: Steady state formation rate r_{CO_2} of CO₂ and relative degree of CO coverage $\theta_{CO} = \theta_{CO}/\theta_{CO,max}$ as a function of temperature. Curve a, θ_{CO} for $p_{CO} = 8 \times 10^{-9}$ torr in absence of O₂; curve b, θ_{CO} in a reaction mixture with $p_{O_2} = p_{CO} = 8 \times 10^{-9}$ torr; curve c, r_{CO_2} (in relative units) at $p_{O_2} = p_{CO} = 8 \times 10^{-9}$ torr [72].

A similar situation applies to the catalytic oxidation of CO on single crystal surfaces of Pt^[73], Ru^[74], and Ir^[49b]; modifications are attributable to differing strength of the M—O bond, which renders the reaction O_{ad} + CO rate determining in the case of nickel^[75].

Interaction between oxygen and nickel represents another kind of surface reaction leading to formation of three-dimensional compounds (oxide). During the action of O₂ on pure Ni(111) or Ni(100) surfaces formation of chemisorption structures is first observed whose unit cells are related in a simple manner to the periodicity of the metal lattice^[76, 77]. In the case of the c2 × 2 structure on Ni(100) the LEED intensities were subjected to detailed theoretical analyses^[13]. Each O atom was accordingly found to be located between four Ni atoms at a perpendicular distance of 0.9 Å. The increase in the work function reveals a slight excess negative charge at the oxygen atom. The UPS spectrum^[78] (curve b in Fig. 14) exhibits an additional maximum about 5.5 eV below the Fermi level, shown by cluster calculations^[79] to arise from chemisorption levels derived from O 2p states. The energy distribution of the Ni d electrons remains largely unaffected at this stage.

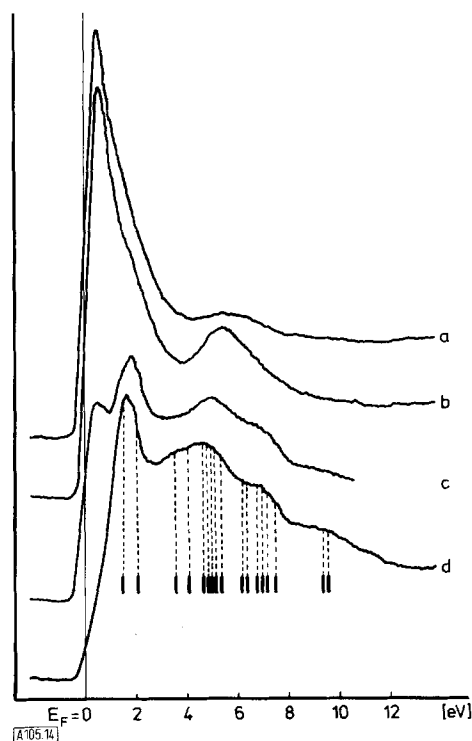


Fig. 14. UV photoelectron spectra ($h\nu = 40.8 \text{ eV}$) pertaining to the interaction between O₂ and a Ni(111) surface [78]. a, clean surface; b, with a chemisorbed oxygen layer; c, transition to oxide; d, after formation of an epitaxial NiO layer.

After saturation of the chemisorption layer further uptake of oxygen is much slower and leads to formation of an epitaxial NiO layer just a few atomic layers thick^[77, 78]. The UPS spectrum (curve c) now also displays drastic changes in the region of the Ni d band. Continuous growth of a thick NiO layer then represents the third stage of this reaction. In the UPS spectrum (curve d) the emission from the metallic d band has completely disappeared, being replaced by a maximum at about 1.7 eV which is assigned to the d states of the Ni²⁺ ions in NiO. Furthermore, a fundamental change

observed in the remaining spectrum is in good agreement with the excitation energies calculated for a NiO₆¹⁰⁻ cluster^[80]. Transition to the oxide is also observed in a discontinuous change in the binding energy of the Ni 2p electrons^[81]. As an overall conclusion, it follows that the oxygen chemisorption complex and the oxide are two clearly distinguishable phases whose transformation is not associated with a continuous variation of the valence state or structure.

6. Conclusion

The examples presented in this survey are merely a fraction of the information available and are intended mainly to illustrate the insights into chemical processes occurring on metal surfaces provided by present-day techniques. Apart from further development of experimental and theoretical methods, the main task of the future will be to throw a bridge from the model systems to the situations encountered in practice.

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