IV. SURFACE SCIENCE

A. INTRODUCTION

The influence of surface science on catalysis, either directly or indirectly, has been felt since the early work of Irving Langmuir. It has increased over the last decade because of the ready availability of ultrahigh vacuum systems, electron optics, single crystals of pure materials, and the development of various spectroscopic techniques.

Work done over the last decade in surface science has influenced catalysis research by two broad developments; the evolution of surface models and concepts to explain chemisorption and related catalytic phenomena, and the progress in spectroscopic techniques for characterizing catalytic surfaces. Without question, the latter has had the more significant immediate impact on catalysis. Therefore, in this section only a brief overview is given of the experimental and theoretical studies which have dealt with surface phenomena. The primary emphasis is on instrumental techniques.

B. CONCEPTS RELEVANT TO CATALYSIS ON METALS AND ALLOYS

Most of the recent concepts in surface science which have some applicability to catalysis have been developed over the last ten years. This work can be conveniently divided into three areas:

- Catalytic Properties of Surface Overlayers
- Structural Effects on Surface Reactions
- Theoretical Aspects of Surface Composition and Small Clusters

Some examples for each of these areas are given in the following three sections.

1. SURFACE OVERLAYERS

The influence of surface overlayers on catalysis has been a subject of discussion for several years. However, only recently have investigators attempted to define the chemical and physical properties of such overlayers and the effect of these layers on catalytic phenomena. This work has been hastened by the development of flash desorption and surface analysis techniques. An example of this work is provided by the studies of Madix and co-workers (1-9). They have studied the decomposition of formic and acetic acids on well-defined nickel and carbided nickel surfaces, using flash desorption and Auger electron spectroscopy (AES). Their work has shown that surface carbide is selective for H_2 and CO_2 formation, while a clean nickel surface gives predominantly H_2O and CO. The selectivity to CO_2 correlates well with the inability of the surface to adsorb CO_2. The results further suggest that the decomposition of formic acid and the adsorption of CO_2 to produce CO involves similar binding sites. The presence of the ordered surface carbide significantly reduces the binding energy of various gases such as CO, H_2O, CO_2, and H_2. This is expected to have an effect on the activity and selectivity of other catalytic reactions in addition to carboxylic acid decomposition.

In more recent work, Madix and his co-workers have found that small amounts of oxygen tend to modify the surface adsorption and catalytic properties of the surface nickel atoms. It is speculated that the oxygen penetrates the nickel surface to what appears to be the second layer below the surface (9). The oxygen atoms then act as ligands which alter the electronic properties of the surface nickel. Excess oxygen eventually covers the surface and poisons it for further reaction. Other effects of surface overlayers have been observed by Somorjai and co-workers (10) while studying structural effects on surface reactions. These results are discussed in the next section.

The objective of the overlayer studies is to understand more clearly the chemical state of the surface atoms during catalysis and hopefully to be able to modify actual catalysts for improved activity and selectivity. The experiments with a carbided surface may also be relevant for understanding hydrocarbon catalysis over metals because in many instances an actual catalyst operates with a significant surface coverage of carbon during reaction. In addition, surface studies of this type may have application for understanding catalyst deactivation.

2. STRUCTURAL EFFECTS

In trying to understand the influence of the geometric or structural factor on catalysis, many catalytic researchers have studied the change in the turnover number (i.e. the number of reacting molecules transformed into products per second per surface site) with crystal orientation active catalytic surface area. Thus, the whole concept of structure sensitive and structure insensitive reactions has evolved (11). This has been treated in detail in Section III of Part 1. In the area of surface science, Somorjai and co-workers have been particularly active in this respect. For example, they have studied the structure sensitive nature of the dehydrocyclization of n-heptane to toluene (10, 12). By using single crystals prepared to show flat surfaces or surfaces exhibiting steps, and kinks, these workers found that, in the presence of hydrogen, the rate of this reaction is higher on stepped (111) surfaces than on flat (110) surfaces. Carbon-carbon bonds were found to break almost exclusively at the ledges which separate the terraces on the crystal. Hydrogen-hydrogen bonds and carbon-hydrogen bonds were also believed to undergo scission at these same sites, as well as at the steps. It was speculated that bonds do not break as readily on smooth planes than at steps and kink sites. Moreover, a degree of order of carbon overlayer which forms on these surfaces can affect some surface reactions. For example, cyclohexane hydrogenolysis occurs regardless of the structure of the overlayer. However, other reactions such as the conversion of cyclohexene to benzene and n-heptane to toluene require a high degree of ordering in the overlayer (13). The structure of this overlayer can also affect selectivity. Thus, in the dehydrogenation of cyclohexane the overlayer is initially ordered and the dominant product is benzene. However, as reaction proceeds, the overlayer becomes disordered and cyclohexene becomes the main product. Finally, it was found that the difference in the rates of bond breaking between planes and steps has an effect on a number of catalytic reactions. One example is the rate of dehydrogenation of cyclohexane to benzene which is an order of magnitude greater on stepped surfaces than on the smooth planes (13).

In other work by Kahn with Petersen and Somorjai, the hydrogenation of cyclopropane over platinum single crystals was studied at atmospheric pressure. The turnover number was similar to that measured for highly dispersed supported platinum catalysts (14). This work is significant because it is the first time that specific reaction rates were demonstrated to be similar for single crystals and highly dispersed catalysts at conditions comparable to those used for testing actual catalysts. It also confirms that the hydrogenation of cyclopropane is a structure insensitive or facile reaction.

Another contribution from surface science and one which could be important in catalysis, especially with respect to poisoning, sulfiding, and activity maintenance, is a phenomenon called corrosive chemisorption. An example is given by the work of Domange and Oudar (15) who studied the adsorption of sulfur on copper single crystals. A reconstruction of the outermost layer of copper atoms to form a two-dimensional sulfide layer was observed. Low energy electron diffraction showed that at saturation a monolayer of sulfur contains the same number of sulfur atoms on each of the three low index planes. Thus, the idea of specific sites becomes more diffuse and the same reconstructed surface layer is formed irrespectively of the crystallographic orientation of copper.

Other metals behave differently. For example, as was mentioned in Section VI of Part 1, platinum and nickel appear to show a specific interaction of certain crystal planes with sulfur, thereby altering selectivity as well as activity. It has been suggested (16) that this is due to a reconstruction of the surface of the catalyst. This is thought to be a consequence of the difference in surface energy of the various low-index planes of the metal. It is speculated that the adsorption of small amounts of H_2S modifies the surface energy balance and leads to a new equilibrium distribution of surface planes with different catalytic activity. Such an explanation has important consequences for the types of reactions that are affected by poisoning or reconstruction by H_2S. Thus, as mentioned in Section III of Part 1, reactions which are structure sensitive such as hydrogenolysis and isomerization would be affected to a much greater degree by this type of poisoning compared to structure insensitive reactions such as hydrogenation. This type of work may begin to give some insight as to how sulfur and other moderators or poisons interact with catalytic surfaces.

However, not enough work has been done yet to quantify the contribution of structural changes.

The studies in surface science concerning surface overlayers, structural effects, or surface reconstruction have led to a better understanding of some of the factors which can be important for guiding the reaction paths of catalytic reactions. It is possible that continued efforts will give the catalytic scientist guidance for the modification of catalytic selectivity and improvement of catalyst activity maintenance. However, more work needs to be done to be able to better relate the data of well defined single crystal systems to those for practical catalysts.

3. THEORETICAL ASPECTS

The impact of theoretical surface science on catalysis has been less extensive than the experimental work discussed above. Two exceptions are the prediction of surface composition of alloys and the theory of small clusters.

Because of the importance of alloy catalysis research over the last decade (Section I, Part 1), a number of thermodynamic studies have been directed at predicting surface and bulk composition for dispersed bimetallic systems. The most notable are those by Ollis (17), Hoffman (18), Williams (19), and Sachtler and co-workers (20). These studies predict changes in the composition of a surface as a function of temperature, chemical environment, and crystallite size. Many of these studies are based on regular solution theory, and therefore predict that the component with the lowest surface free energy will predominate at the surface. According to these models, this difference between bulk and surface compositions decreases exponentially with increasing temperature. Thus, with NiCu alloys, Cu which has a lower surface energy than Ni is present in excess at the surface. Chemical environment is also important. As discussed later, the presence of strongly adsorbed gases can significantly alter the equilibrium surface composition. These models, while not in total agreement with each other, provide a valuable semi-quantitative picture for the surface composition of bimetallic systems. They have also stimulated much research in the area of surface characterization. Some of these studies involving various spectroscopic techniques will be discussed later.

The surface composition of an alloy catalyst during operation can also be determined by the reactive environment with which it is in equilibrium. Examples of this are the work by Williams and Boudart (21), Bartholomew and Boudart (22) and Sachtler and co-workers (23, 24). Williams and Boudart (21) found that the chemisorption of O_2 on Ni-Au alloys increased the surface concentration of Ni. Similar results were found by Bartholomew and Boudart (22) for O_2 chemisorption on Pt-Fe alloys where Fe increased in concentration at the surface, and also by Sachtler and co-workers (23, 24) for the chemisorption of CO on Pd-Ag, Pt-Ag and Pt-Ru alloys. The latter work showed "chemisorption-induced" enhancement in the surface concentration of Pd, Pt in these bimetallic alloys. No effect was observed for the Pt-Ru system. These studies suggest that alloy characterization data such as selective chemisorption measurements of surface composition at ambient conditions should be used with caution for interpreting catalytic results.

The theory of small atomic clusters is another area which has grown in importance. It has been stimulated by an intense interest in the physics of small particles, primarily because of the applicability of these materials in catalysis. For example, Johnson (25) has applied the $X\alpha$ scattered-wave method to metal clusters. This quantum mechanical procedure was originally developed for treating polyatomic molecules and solids. It allows one to calculate highly accurate ground and excited electronic states of polyatomic clusters as functions of cluster size, composition, geometry, and environment. Its primary advantage is that it requires only moderate amounts of computer time compared to other approximation procedures. The application of this computational procedure to chemisorption on transition-metal surfaces and to metal aggregates has recently been described (25), however, not enough work has been done to fully assess its potential.

Baetzold and co-workers (26-28) have also developed quantum mechanical computational procedures for determining the electronic and atomic structure of metal clusters. They have studied Cu-Ni and Pd-Ag and shown that d holes exist on the Group VIII metal atom for compositions up to and greater than 60% Ib metal (26), in contrast to what one would expect from rigid band model calculations. In this same area, work by Wertheim (29) and Spicer (30, 31) has shown that the Anderson model or virtual bound state treatment for bimetallic systems is a better approximation than that provided by rigid band theory. In this model a bound d-state is associated with each transition metal atom. The width of the band associated with this state depends upon alloy composition. For example, for Ni metal one starts with a broad d band which has 0.6 holes above the Fermi level. As copper is added to form a NiCu alloy, the band narrows and reduces in intensity. As it narrows, the Fermi level effectively "moves" to the edge of the d band. It reaches the edge of the band at about 60% Cu which is precisely where ferromagnetism disappears. This model is in contradistinction to the rigid band model which pictures the addition of Cu as donating electrons to the empty d band with subsequent pairing and loss of magnetism.

The above mentioned thermodynamic and quantum mechanical studies concerning surface composition and the structural and electronic properties of clusters have value in that they stimulate the experimentalist. However, it is clear that alteration or refinement of these theories requires more intense experimental feedback than has occurred to date.

C. PHYSICAL TECHNIQUES

A number of physical techniques have been developed in surface science and applied to catalysis. Most of these have recently been reviewed elsewhere (32). Table IV-1 is reproduced from reference 32, and gives a summary of these techniques and their application.

Those techniques which have been developed over the last decade and have had the most significant impact in catalysis fall in two categories, electron and ion spectroscopies. Among electron spectroscopies, ultraviolet photoelectron spectroscopy (UPS), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) are prevalent. Ion spectroscopies of interest are secondary ion mass spectroscopy (SIMS), ion scattering spectroscopy (ISS), and ion neutralization spectroscopy (INS). These techniques are briefly reviewed, with emphasis on the application and limitations of each technique.

1. ELECTRON SPECTROSCOPIES

In this section, a brief description of the experimental techniques is given, followed by some examples of their application to catalysis.

a. Description of Techniques

In x-ray photoelectron spectroscopy (XPS) (33) an x-ray of known energy, $h\nu$, is absorbed by a sample, ejecting electrons with kinetic

TABLE IV-1. TECHNIQUES FOR MATERIALS ANALYSIS

Input Energy Source	Observation	Name Of Technique	Information				Applicability			Maturity	Interpret.	R&D In Catalysis Needed
			Surf.	Bulk	Struc.	Bond.	Catalytic Reactions	Catalytic Materials	Degree Of Generality			
γ-Rays	Absorption	Mössbauer Effect	No*	Yes	Yes	Yes	Sometimes	Yes	Restricted	Developed	Simple To Complex	Yes
X-Rays	Absorption	EXAFS	No*	Yes	Yes	Yes	No	Yes	Broad	New	Complex	Yes
	Fluorescence	--	No*	Yes	No	Yes	Yes	Yes	Broad	New	Simple	Yes
	Diffraction	--	No	Yes	Yes	No	Questionable	Yes	Broad	Highly Developed	Routine	No
	Small Angle Scattering	SAXS	No	Yes	Yes	No	Questionable	Yes	Broad	New	Complex	Yes
	Electrons	XPS/ESCA	Yes	Yes	No	Yes	Questionable	Yes	Broad	New	Complex	Yes
Ultraviolet Radiation	Electrons	UPS	Yes	Yes	No	Yes	Possibly	Yes	Broad	New	Under Development	Yes
Visible Radiation	Reflection	--	No*	Yes	No	Yes	Yes	Yes	Broad	Undeveloped	Complex	Yes
	Reflection (Polarized Light)	--	No*	Yes	No	Possibly	Possibly	Possibly	Unknown	Undeveloped	Complex	Possibly
Infrared Radiation	Attenuated Total Reflectance	ATR	Yes	No	No	Yes	Yes	No	Restricted	New	Simple To Complex	Possibly
	Absorption	--	No*	Yes	No	Yes	Yes	Yes	Broad	Highly Developed	Simple	No

TABLE IV-1. TECHNIQUES FOR MATERIALS ANALYSIS (cont.)

Input Energy Source	Observation	Name Of Technique	Information				Applicability			Maturity	Interpret.	R&D In Catalysis Needed
			Surf.	Bulk	Struc.	Bond.	Catalytic Reactions	Catalytic Materials	Degree Of Generality			
Infrared Radiation (continued)	Absorption/ Emission (Fourier Transform)	FTS	Yes	Yes	No	Yes	Yes	Yes	Broad	New	Simple	Yes
	Laser Raman Scattering	LRS	No*	Yes	No	Yes	Possibly	Possibly	Broad	New	Simple To Complex	Yes
Microwaves	Absorption	NMR (Wide Band)	No*	Yes	No	Yes	Possibly	Sometimes	Restricted	Developed	Simple To Complex	Yes
	Absorption	NMR (High Resolution)	No*	No	No	Yes	Possibly	Possibly	Restricted	New	Under Development	Yes
Radiowaves	Absorption	EPR	No*	Yes	Sometimes	Yes	Possibly	Yes	Restricted	Developed	Complex	Possibly
Magnetic Fields	Magnetization	Magnetic Suscept.	No*	Yes	Sometimes	Yes	Possibly	Yes	Restricted	Highly Developed	Moderately Complex	No
Moderate Electric Fields	Electric Potential	Surface Potential	Yes	No	No	Sometimes	No	Yes	Restricted	Developed	Simple	No
	Resistivity	Electrical Conductiv.	No*	Yes	No	No	Possibly	Yes	Restricted	Developed	Simple	No
	Electric Potential	Hall Effect	No*	Yes	No	No	Possibly	Yes	Broad	Undeveloped	Simple	No
High Electric Fields	Field Emitted Ions	FEIM, FIM	Yes	No	Yes	Yes	Doubtful	No	Restricted	Moderately Devel.	Complex	Yes
	Field Emitted Electrons	FEEM, FEM	Yes	No	Yes	Yes	Doubtful	No	Restricted	Developed	Complex	No
	Field Emitted Electrons	FEED	Yes	No	No	Yes	No	No	Restricted	New	Under Development	No

TABLE IV-1. TECHNIQUES FOR MATERIALS ANALYSIS (cont.)

Input Energy Source	Observation	Name Of Technique	Information				Applicability			Maturity	Interpret.	R&D In Catalysis Needed
			Surf.	Bulk	Struc.	Bond.	Catalytic Reactions	Catalytic Materials	Degree Of Generality			
High Energy Electrons	Diffraction	HEED	No	Yes	Yes	No	No	No	Restricted	Developed	Under Development	No
	Energy Loss	ELS	Yes	No	No	Yes	No	Possibly	Broad	New	Under Development	Yes
	X-Rays	APS	Yes	Yes	No	Yes	No	Possibly	Broad	New	Under Development	Possibly
Low Energy Electrons	Diffraction	LEED	Yes	No	Yes	No	No	No	Restricted	Developed	Under Development	No
	Scattering	ILEED LEES	Yes	No	No	Yes	No	No	Unknown	New	Under Development	No
Ions	Electrons	INS	Yes	No	No	Yes	No	No	Unknown	New	Complex	No
	Ions	EIS	Yes	No	No	No	No	Yes	Broad	New	Simple	Yes
	Ions	SIMS	Yes	No	No	No	No	Possibly	Unknown	New	Simple	No
Heat At Programmed Rate	Gas Desorption	TPD	Yes	No	No	Yes	No	Yes	Broad	New	Simple	Yes
	Reaction Produces Desorption	TPK	Yes	No	No	Yes	Yes	No	Broad	Undeveloped	Simple	Yes
None	Heat	Micro-Calorimetry	No*	Yes	No	Yes	Yes	Yes	Broad	Developed	Simple	No

* Surface information can be obtained from these techniques for well dispersed catalysts or when the interaction of the input energy occurs with species that are primarily on the surface.

DEFINITION OF ACRONYMS USED IN TABLE IV-1

EXAFS	Extended X-ray Absorption Fine Structure
SAXS	Small Angle X-ray Scattering
XPS/ESCA	X-ray Photoelectron Spectroscopy
UPS	Ultra Violet Photoelectron Spectroscopy
ATR	Attenuated Total Reflectance
FTS	Fourier Transform Spectroscopy
LRS	Laser Raman Spectroscopy
NMR	Nuclear Magnetic Resonance
EPR	Electron Paramagnetic Resonance
FEIM/FIM	Field Emission Ion Microscopy
FEEM/FEM	Field Emission Electron Microscopy
FEED	Field Electron Energy Distribution
HEED	High Energy Electron Diffraction
ELS	Energy Loss Spectroscopy
AES	Auger Electron Spectroscopy
APS	Appearance Potential Spectroscopy
LEED	Low Energy Electron Diffraction
ILEED	Inelastic Low Energy Electron Diffraction
LEES	Low Energy Electron Scattering
INS	Ion Neutralization Spectroscopy
EIS/ISS	Elastic Ion Scattering Spectroscopy
SIMS	Secondary Ion Mass Spectroscopy
TPD (TDS)	Temperature Programmed Desorption (Thermal Desorption Spectroscopy)
TPK	Temperature Programmed Kinetics

energies given by $E_k = h\nu - E_B - \phi$, where E_B is the binding energy of the electrons with respect to the Fermi level, and ϕ is the work function of the sample. Since the sample is in contact with the spectrometer, ϕ is also the work function of the spectrometer. Therefore, the technique provides direct measurement of E_B, the energy level of the core electrons or the valence band of the solid. The former yields atomic identification. In addition, chemical shifts are frequently observed for these energies. This topic has received considerable attention and several methods have been proposed for interpreting shifts in terms of changes in the distribution of the valence electrons in a solid (33-36). These methods enable one, in theory, to obtain a description of bonding in terms of the partial charges on the atoms

For ultraviolet photoelectron spectroscopy (UPS) (37, 38) photon excitation energies are not high enough to eject core electrons, and therefore only valence electrons are studied. The advantages of using this technique for valence electron studies are higher resolution and greater signal intensity compared to XPS. The increased resolution occurs because vacuum uv light source linewidths are only a few meV, whereas soft x-ray linewidths (XPS) are of the order of 1eV. The reason for increased intensity is complex, but it is primarily related to the high photon fluxes and larger ionization cross section for the valence electrons with uv radiation. A drawback of high photon fluxes is the possible damage by photodesorption of the surfaces under examination. As with XPS, chemical shifts are also observed.

Auger electron spectroscopy (AES) (39, 40) involves an energy analysis of secondary electrons (Auger electrons) which are ejected when a core hole relaxes. The initial hole can be produced by several excitation sources including x-rays or electrons. Auger transitions which do not involve valence electrons readily identify the atom as is the case for XPS and UPS. Chemical shift data are more difficult to interpret because three energy levels are involved. Thus, AES has been used primarily for atomic identification or surface analysis (39, 40).

All three of these spectroscopies are considered to be surface analysis techniques because most of the information obtained comes from the first several atomic layers. One of the limitations of XPS, UPS, and AES is that the sampling depth can vary with excitation energy and the form of the sample (e.g. powder, flat crystal, etc.). A recent review (41) shows that the sampling depth is in general about a factor of two smaller for AES than XPS (primarily because of lower kinetic energies of escaping electrons) and that UPS escape depths may vary considerably. Typical ranges are 2-24 Å for AES, 7-40 Å for XPS, and 3-50 Å for UPS. This variation in sampling depth makes it difficult to make quantitative measurements. AES has been used predominantly and more successfully than the other two techniques for this purpose. It should be possible to use XPS for quantitative measurements if the proper energy lines are chosen. UPS, on the other hand, is not as adaptable for this purpose. This is because the spectra do not lend themselves to direct identification of elements and also because they usually consist of broad peaks superimposed on a scattered electron background (41).

A major problem with these techniques has been the effects of sample charging which can be significant for insulators. A large number of catalyst supports are insulators (e.g. Al_2O_3), and therefore charging must be considered when studying such systems. For surface analysis, charging may not be important. However, for investigating the chemical state of surface atoms (chemical shifts), this phenomenon can have a marked effect on interpretation of the spectra. Many workers have tried to "dope" insulator samples with various standards such as gold, and therefore to compensate for shifts with a known spectrum. However, this has also presented problems, and does not appear to give reproducible data in many cases. Most of the surface science work in this area has been done with metals, and therefore charging has not been a major consideration.

In spite of the above mentioned limitations, progress has been made in studying the surface and chemisorption properties of metals. Application of the studies to catalysis will be discussed next.

b. Applications to Catalysis

Because of low pressure (perhaps ultimately up to 10^{-2} Torr) requirements, it is unlikely that industrial catalytic reactions can be effectively studied with any of the above three electron spectroscopies. The major use of these techniques appears to be in characterizing a surface before and after reaction, or in the study of chemisorption. As mentioned previously, AES has been applied primarily for surface analysis, while UPS and XPS have been used to study the chemical state of surface atoms or the nature of the interaction of chemisorbed species. The following examples are representative of this work.

Using AES, Szalkowski and Somorjai (42) studied the surface composition of vanadium oxides (on vanadium single crystals). They observed chemical shifts of the order of 0.6 eV per unit nominal oxidation number for the inner shell Auger transitions. From relative intensities of the oxygen and vanadium Auger peaks, these workers determined the surface composition of the different oxides. Using both chemical shifts, and the oxygen to vanadium Auger peak intensity ratios for the various vanadium oxides ($VO_{.92}$, V_2O_3, V_3O_5, and VO_2), they were able to follow the oxidation of vanadium metal to V_3O_5.

More recently, Takeuchi et al. (43) studied the relationship of catalytic activity for selective hydrogenation of alkynes with surface composition of nickel sulfide catalysts. In this work the surface composition was only estimated. These workers found that a nickel sulfide catalyst having an atomic ratio of S/Ni = 0.6 had good activity for selective hydrogenation of acetylene to ethylene, while a nickel sulfide catalyst with S/Ni = 0.9 had no measurable activity. The purpose of this study was to understand the effect of sulfidation on catalyst selectivity for partial hydrogenation reactions. A model was developed in which a nickel atom is surrounded by four sulfur atoms in Ni_3S_2 and by six sulfur atoms in NiS. Therefore, it was reasoned that in contrast to NiS, nickel atoms on the surface of Ni_3S_2 have the appropriate coordinative unsaturation for the chemisorption of hydrocarbons like acetylene. Partial hydrogenation was speculated to be controlled by reversible formation of coordinatively unsaturated nickel atoms. These results are in qualitative agreement with work by Kirkpatrick (44) who showed that NiS is inactive for the partial hydrogenation of polyenes to corresponding monoolefins, but becomes active with time due to the reduction of the sulfide to Ni_3S_2.

In another study using AES, Williams and Baron (45) studied the poisoning of platinum and palladium oxidation catalysts by lead, phosphorous, and sulfur contaminants in automotive exhaust. They found that the noble metal surface first saturates with lead without any deposition of sulfur or phosphorous. The initial accumulation of Pb on Pd is different than that for Pt. At low exposures, Pb is depleted from the Pd surface. These workers feel that the Pb diffuses as PbO from the surface into the bulk of the Pd. The latter is in the oxide form during operation, the diffusion resulting from the solubility of PbO in PdO. On Pt, however, this cannot occur because PtO is not formed at these conditions. Continued exposure to S, P, and Pb leads to the deposition of $PbSO_4$ and $Na_4P_2O_2$.

It has also been found by means of AES that a gaseous environment can change the surface composition of an alloy. For example, Williams and Boudart (21) observed that the surface composition of Ni-Au alloys over a wide range of compositions was predominantly Au. However, with exposure of these alloys to O_2, no surface Au could be detected, as oxygen drew nickel to the surface.

The above examples illustrate the type of studies which have been done with AES. Most of this work has involved surface composition studies. The use of UPS and XPS, on the other hand, has been primarily directed at the nature of the surface orbitals and the molecular orbitals of chemisorbed molecules (47, 48). For example, for heteronuclear diatomic molecules, characteristic photoemission from either atom in the adsorbed molecule may be studied (38). Oxygen lines have been used to identify the two types of adsorbed CO species on tungsten, the α and β form. The O (1s) chemical shifts from the XPS technique have been used to follow the desorption of α-CO species from the CO monolayer. Similar work at the National Bureau of Standards (38, 47) with N_2, NO, O_2, H_2CO, and CO indicates that the 1s binding energies of adsorbate atoms decrease as the strength of adsorption increases. This is in qualitative agreement with some physical models (49).

Recent UPS studies of C_2H_2, C_6H_6, and CH_3OH have been reported (49, 50) which are thought to show the nature of surface σ and π bond formation and dissociation. For C_6H_6 adsorbed on Ni (111), for example, both π and σ levels of the hydrocarbon have been observed in the chemisorbed layer. With CH_3OH on a W(100) surface, UPS indicates that dissociation occurs at low coverages to yield adsorbed CO and H atoms. As coverage increases, more complex species, possibly CH_3O are observed (50-52). The advantage of UPS for these chemisorption studies is that the adsorbate is not as affected by the excitation beam as it is for XPS and AES. This is primarily due to the fact that photodissociation and photodesorption cross sections (probabilities) are very small for most adsorbed species, including many organic molecules (52). However, as with most of these studies of chemisorbed species, interpretation of such results is difficult, especially when overlap of metal d-levels with molecular levels is involved.

Similar work by Spicer et al. (53) using UPS looked at the change in surface electronic structure (valence band) for MoS_2, Cu, Pt, and Si upon physisorption and chemisorption of gases such as O_2, CO, H_2, and N_2. When only physisorption occurs, negligible electronic change is observed for the surface. However, a significant drop in surface emission occurred with chemisorption which was attributed to hybridization of the surface orbitals with the adsorbing gas orbitals. With Pt, in particular, the marked drop in emission is suggested to indicate which metallic orbitals participate in bonding. With Cu this hybridization is reported to produce new orbitals located within or above the d-band. It would be interesting to interpret these results by means of recent theories for chemisorption, particularly that by Schrieffer (54, 55).

Another area where UPS has been used recently is in probing the surface electronic structure of metals and alloys. For example, Helms et al. (56) studied the surface electronic structure, composition, and CO binding energy for Cu-Ni alloys. Individual peaks in the surface electronic structure were assigned to Ni and Cu. This is in contrast to what would be expected from rigid band theory. The binding energy of CO on the alloy was found to vary in a quasi-continuous manner with surface composition from that of

Ni to that for Cu. It was concluded that the binding energy is, thus, determined by the local configuration of the adsorption site. This is in contrast with a model which would depend upon the average surface electronic structure.

Finally, the XPS studies by Ratnasamy et al. (57-60) of commercial cobalt molybdate catalysts should be mentioned as an indication of future possibilities. This work indicates that there are at least three states for cobalt on the surface, Co^{+2} in a $CoAl_2O_4$ environment, Co^{+2} in a CoO phase, and Co^{+2} in coordination with strongly bound water molecules. The molybdenum is also thought to exist in several environments, however, the corresponding peaks are not resolvable in the spectra. The molybdenum peaks simply broaden. This broadening is reported to represent molybdenum in at least three phases; phase A where chemical interaction with the support is so strong that the Mo ions cannot be reduced in hydrogen even at high temperatures, phase B which has minimal interaction with the support and is easily reduced to a sub-oxide or metal, and phase C which is partially reduced in the presence of cobalt metal. The presence of these three phases of Mo was deduced from the XPS work as well as reduction, sulfidation, and hydrodesulfurization studies (57, 60).

2. ION SPECTROSCOPIES

Ion spectroscopies have been applied much less to catalytic problems than have electron techniques. Therefore, this section is primarily devoted to the two ion techniques which have been given the most attention, namely secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS). As with the treatment of electron spectroscopy, this section is divided into a description of the techniques and applications to catalysis.

a. Description of Techniques

Ions have been used for many years to clean surfaces by bombardment. Recently, two techniques have been used to obtain information concerning surfaces by making use of the ion bombardment process. By coupling the system to a mass spectrometer, one can identify the emitted (secondary) ions which are removed from the surface. This forms the basis for SIMS (61, 62). Alternatively, one can measure the energy of the incident ions which are scattered elastically by collision with surface atoms. This is the basis for ISS (63-66). If the incident ion beam is neutralized on the surface, measurement of the energy of electrons emitted from the sample in an Auger type relaxation gives the basis for ion neutralization spectroscopy (INS). However, the latter has not received the attention of SIMS or ISS, and therefore will not be discussed here.

For all of these ion techniques the incident beam is a noble gas ion. Energies range from 1 to 50 kev. In the low energy region of this range, the probability for neutralization is very high (greater than 99.99% for He^+ ions (63)). However, sufficient scattering of ions occurs to allow detection. In fact, the high neutralization probability assures that those ions which are detected in ISS result from single scattering events. For these particles a simple two body collision model adequately describes the mechanics of the system. It leads to a relationship between incoming and outgoing energies, the scattering angle, and the masses of the incoming ion and that of the surface atoms. It is therefore possible to identify the surface atoms by mass. By the principle of conservation of energy and momentum for a binary elastic collision between an energetic noble gas ion of mass M_1 and a surface atom of mass M_2, the following relationship is easily derived:

$$M_2 = M_1 \frac{1 + (E_1/E_o)}{1 - (E_1/E_o)}$$

In this derivation, the scattering angle is taken as 90^o and E_o and E_1 are the energies of the ion beam before and after scattering, respectively.

When the energy of the incoming ions is increased, the scattering event becomes more complex. Multiple scattering occurs. Since this scattering is a function of the relative position of the surface atoms, analysis of the energy spectrum can, in principle, provide information on the short range structure of these surfaces. Some work has been done in this area, however, the details are very complex and difficult to interpret (63).

The primary complication of any of the techniques which use high energy ions is the possibility of disturbing the surface of the impact of ions. Furthermore, sputtering of surface atoms may not proceed uniformly, thereby leading to surface concentration changes which did not exist in the original sample. However, the ion techniques are not significantly affected by the conductivity of the solid and therefore the sample charging encountered for electron spectroscopies is not a problem. Also, ion techniques are sensitive to the presence of hydrogen, which cannot be detected by electron spectroscopic techniques such as AES, XPS, or UPS. Hydrogen detection, for example, could be important in the determination of the composition of C-H residues on catalyst surfaces. Work in this area is underway at the University of California at Berkeley by Somorjai and co-workers (67).

A number of detailed papers describing SIMS, ISS, and other ion spectroscopies can be found in reference 68.

b. <u>Applications to Catalysis</u>

The application of SIMS and ISS to catalytic materials has not been extensive, with more work having been done with thin films and electronic devices. However, the following two studies illustrate the potential of these techniques.

In recent work by Shelef (69) et al., the surface composition of oxides (particularly spinel structures such as $CuAl_2O_4$, $CoAl_2O_4$, and $NiAl_2O_4$) was examined using ISS. The results of this work were correlated with NO chemisorption (see Section IV of Part 1), also developed for the same purpose. Their data showed no cobalt on the surface of $CoAl_2O_4$. However, in the case of $CuAl_2O_4$ and $NiAl_2O_4$, considerable amounts of the transition metals were found at the surface. This correlates well with NO adsorption where $CuAl_2O_4$ adsorbs as much NO as CuO, $CoAl_2O_4$ a negligible amount, and $NiAl_2O_4$ only 1/4 of the amount taken up by NiO. These results are important because they explain why Co_3O_4, which is a very active oxidation catalyst, loses activity when supported on Al_2O_3. It forms a spinel, the surface of which is completely covered with oxygen, and therefore leads to low activity. CuO and NiO, on the other hand, although lower in oxidation activity than Co_3O_4, retain greater fractions of this activity when supported on Al_2O_3 even though spinel formation occurs. For these oxides the active constituents, presumably Cu^{+2} and Ni^{+2} cations, are still accessible to adsorbing gases, and are not covered by oxygen anions. These facts are in qualitative agreement with various solid state models (70) for these three spinels where $CoAl_2O_4$ is considered a "normal" spinel with Co^{+2} ions in tetrahedral positions, while Ni^{+2} ions for example, have an octahedral site preference. Cations in the tetrahedral sites are more electrically unsaturated if one anion is missing on the surface from their coordination sphere. These cations will tend to diffuse below the surface and be shielded by oxygen anions more than cations in the octahedral sites. Similar, but more complex arguments involving distorted mixed structures can be made for the Cu spinels (70, 71).

Other work by Wheeler and Bettman (72) used both ISS and SIMS to study the poisoning of Co_3O_4 by Al_2O_3 and MgO. The specific oxidation activity of Al_2O_3-doped Co_3O_4 for hydrocarbon oxidation was found to decrease by a factor of about 4-5, while the MgO-doped Co_3O_4 was poisoned by a factor of about 8. The ISS spectra indicated that the Al_2O_3-doped sample had a surface which was enriched in aluminum, relative to the bulk. The ISS results for the MgO-doped sample were difficult to interpret, however, the surface was found to be depleted of cobalt, and therefore assumed to be enriched in magnesium. These results correlated reasonably well with the poisoning phenomenon. Similar results were found for $MgAl_2O_4$-supported Co_3O_4, where it was speculated that MgO and Al_2O_3 were leached out of the support during catalyst preparation and then doped and poisoned the Co_3O_4. This was thought to be due to the very acidic condition of the $Co(NO_3)_2$ impregnating solution. Other experiments where the solution was neutralized with NH_3 support these contentions.

Further work was done with the MgO-doped Co_3O_4 catalyst using SIMS. The results were qualitatively similar to those obtained by ISS, in that the Mg signal stayed approximately constant, while the Co signal rose with time (i.e. as successive layers were sputtered away). This again suggested that cobalt was depleted at the surface relative to the bulk.

It is clear that SIMS and ISS may have some application to catalyst characterization, especially where profiles of composition are required. However, there are a number of limitations such as variations in sputtering rate with environment or species. More work needs to be done to assess these physical techniques.

D. SUMMARY AND CONCLUSIONS

Work in surface science has led to the development of novel concepts and spectroscopic techniques which have had some impact in catalysis. By far the more significant of the two areas appears to be the latter because it has led to improved methods for catalyst characterization. Both electron spectroscopies (mainly AES, XPS, and UPS) and ion spectroscopies (SIMS and ISS) have played a prevalent role. However, as previously discussed, all of these techniques have limitations which need to be overcome before they can offer broad applicability.

In looking to the future, it is clear that there may be solutions to some of these limitations. For example, recently Wagner (73-76) has reported a new way to use XPS using core Auger lines which may obviate the severe problem of sample charging, and thereby give data which would be universally reproducible. In terms of other techniques, Lytle and co-workers (77-79) have done extensive development of a new x-ray technique called extended x-ray absorption fine structure spectroscopy (EXAFS). Preliminary research shows that this technique may be able to identify surface atoms and also give a handle on the local structural and electronic environment of these atoms. It has already been applied to some catalysts such as $CuCrO_3$ (80), Au/MgO (81), and Pt/Al_2O_3 (81, 82). An added feature of this technique is that it uses x-ray excitation and measures x-ray absorption, and therefore may be readily applied to catalysts during reaction. There are already workers beginning to explore this new area (83, 84), however, the results are yet forthcoming.

Finally, it should be mentioned that there are those who question the applicability of the results of surface science to catalysis because much of this work, by necessity, has been done on well defined clean surfaces. Therefore, it has frequently been argued that the direct translation of such results to "real" catalysts is questionable. Although caution is most certainly warranted in such cases, this is perhaps an extreme viewpoint.

Indeed, another view (85) has been that the impact of surface science is not likely to be revolutionary in that it is difficult to expect that a novel catalyst will be discovered and developed as a result of pioneering work in surface science as it is presently understood. What is more probable is that catalytic scientists will adopt and adapt the methods of surface science to help understand various catalytic phenomena as well as the nature of catalytic materials.

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