Chapter 3

CATALYST CHARACTERIZATION: STRUCTURE/FUNCTION

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3.1 INTRODUCTION

The fundamental concepts of electronic structure and bonding that are at the basis of all chemistry are also at the root of understanding the structure and reactivity of catalyst sites. A specific aspect of catalysis by solids is, however, that we are less interested in their bulk structure than in the interfaces between two phases. Novel theoretical and experimental methods have opened the gates to this new two-dimensional world which includes solid/gas, solid/liquid, and solid/solid interfaces. Often one solid phase consists essentially of small clusters, each comprising only a few atoms but interacting simultaneously with another solid, the support, and with molecules of the surrounding fluid. The ability of coordinatively unsaturated atoms at this interface to quickly form chemical bonds which are also swiftly broken again, is an essential criterion for catalysis.

The main classes of catalysts used in energy applications are: zeolites, metals, and transition metal oxides. Crudely speaking, we can say that the chemical functions associated with these catalysts are acidity, oxidation, and reduction, from which it will be surmised that the chemical and physical techniques needed to characterize these classes of materials will be quite different. Thus, one way in which this discussion might be organized would be along the lines of the kind of material being characterized. Instead, we have chosen to use a more conceptual organization, illustrated with examples of materials and techniques, the selection of which may be more indicative of our personal experience than the relative importance in the field of catalysis.

It will be the objective of this chapter to present some examples of catalyst characterization which are on the frontier of what we can do, which reveal apparent contradictions between findings of well characterized surfaces and practical catalysts, or which are illustrative of where progress is needed in instrumentation or concepts of characterization. From these, we will arrive at some recommendations for catalyst characterization which will be important in the future. These will not necessarily be associated with any particular catalyst or reaction, but will seek lines of research to develop new concepts, approaches, or techniques which will have some generality. It would not be useful to attempt to catalogue techniques of surface characterization, but representative examples will be used to focus on the problems of catalyst characterization and attributes that will be required for progress.

It will be presumed that the ultimate goal of all catalyst characterization is to identify and describe Taylor's active centers (Taylor, 1925), *i.e.*, the catalytically active sites. Several rather obvious corollaries follow. Identification would best be accomplished *in situ* under the conditions of temperature and pressure in the range where the catalyst would be used. Moreover, as the performance of any catalyst is mainly of interest during the *steady-state* of the catalyzed reaction, catalyst characterization should, ideally, be done in the presence of all reactants, products, and intermediates. For instance, we see little value in studying clean transition metals or their oxides as potential catalysts for HDS if it is certain that under HDS conditions these metals or oxides will be quantitatively converted to metal sulfides. Likewise, the surface composition of numerous metal alloys is known to change in the presence of a reacting gas. It should also be kept in mind that surface reconstruction in the presence of a reacting gas is a very common phenomenon for small particles; consequently, the structure and the shape of supported particles will often change when the catalyst is exposed to the reacting gas or fluid. Quite generally, it is important to distinguish between the *catalyst precursor* and the *true catalyst*; the transformation of the former into the latter often occurs during the first stages of the catalyzed reaction.

To assure kinetic significance of the site or adsorbed intermediate associated with the site, the spectroscopy used should be capable of time resolution that allows transients on the time scale of reaction to be followed, and the kinetic response of a reactant and/or product should be followed simultaneously (Tamaru, 1978). Because catalytic reactions may always be assumed to be more sensitive probes for the site than are physical techniques, we also need to think of new chemisorptive and model reaction probes for catalyst characterization to complement spectroscopy.

Perhaps it is useful to begin by discussing what might be the most important aspects of sites to be characterized. Of course, we would like to know as much as we can about both the nature of the sites and their concentration. From the point of view of understanding the chemistry, the nature or structure would appear to be more important. However, most of the time we put a premium on site density since that will allow us to compare catalysts between two laboratories. It is understood that almost always we have to be content with a measurement of surface atom density which does allow a quantitative comparison between laboratories but almost certainly has little to do with the actual site density involved in the reaction. That is, we usually measure the adsorption sites by a chemisorption probe which is assumed to have a 1:1 stoichiometry with the sites, *e.g.*, H_2 dissociation on metals at room temperature. We are aware of the friction involved here since there is ample evidence that the stoichiometry assumed, *e.g.*, $H/M = 1$, is only rarely correct and even when it is, it would not be under the conditions of reaction (Kip *et al.*, 1987). Even qualitatively this chemisorptive titration can be misleading for very small particles. In the range of metal particles consisting of only a very few atoms, H_2 chemisorption has been found to decrease with increasing dispersion, if the latter quantity is derived from Extended X-ray Adsorption Fine Structure (EXAFS) data (Xu *et al.*, 1992).

There are one or two exceptional cases where the adsorption site density used to normalize rates between laboratories may be close to the active site density. The most obvious is the use of N_2 chemisorption on Fe at the reaction temperature to measure the active site density for the NH_3 synthesis reaction (Topsøe *et al.*, 1981). Here it is known that the adsorption of N_2 is the rate limiting step in the reaction, so that if one uses the adsorption isotherm at reaction temperature, one assumes that the observed adsorption site density must be a reasonable approximation to the correct one (although it will still be an overestimate, because under reaction conditions the steady-state coverage will be lower). Another case where the measured site density must be about right is that observed by ^{27}Al NMR for n-hexane over a ZSM-5 zeolite (Haag *et al.*, 1984), since the n-hexane cracking activity correlates with Al in the framework over several orders of magnitude, and the acid sites are known to be associated with Al. Still, this kind of site density cannot be simply extended to other zeolites, *e.g.*, to Y-zeolite, since it is known that in this case the activity for cracking passes through a maximum when the Al site density is varied (Carvajal *et al.*, 1990). From the point of view of characterization, we might conclude that site density is not inherently very revealing except in so far as the order of magnitude will limit some possibilities, for example, if it is as large as 10^{15} sites/cm^2 on a metal surface, the site cannot plausibly involve more than a few atoms.

In these examples only one type of site is of relevance in each catalyst. For instance, in the NH_3 synthesis catalyst the active sites are certain ensembles of Fe atoms, whereas, in the cracking catalyst protons of high Brønsted acidity are crucial. In many catalysts the situation is, however, more complex because two or more types of sites are involved in the catalytic reaction. Some catalytic systems can be described as "bifunctional"; in these catalysts different steps of a catalytic reaction make use of different sites, for instance, in petroleum reforming (de-) hydrogenation steps are catalyzed by Pt sites and carbenium ion reactions by acid sites. In some catalysts the sites are essentially independent of one another; reaction intermediates are supposed to "shuttle" between metal sites and acid sites (Mills *et al.*, 1953). This may be an oversimplification for catalysts such as Pt supported in acid zeolites, as there are indications that Brønsted acid protons and metal clusters form metal-proton adducts (Homeyer *et al.*, 1990). In these complexes the metal atoms are electron-deficient (DallaBetta and Boudart, 1973), because the positive charge of the proton will be shared with the adjacent metal atoms.

When a catalyst ingredient modifies another site by some chemical interaction it is called a "catalyst promoter" or, if the catalytic activity is lowered, a "poison". Promotion of the iron in the ammonia synthesis catalyst by alkali ions is a classical example. Although the primary function of inert oxides such as Al_2O_3 or SiO_2 is to increase the dispersion of the active material supported by them, these supports can also have a promoting function, that is, change the turnover frequency or the selectivity of the catalytic process. For structure-sensitive reactions it suffices that the support affects the geometry of the supported particles of the catalytically active material. Chemical bonding between metal particles and ions of the support, often called chemical anchoring (Jiang *et al.*, 1988), will stabilize a high dispersion of the active material; for extremely small particles electronic changes at the metal/gas interface, caused by the Volta potential at the metal/support interface, have also been visualized. Expressions such as a "strong metal-support interaction" have been proposed for these phenomena (Tauster *et al.*, 1978). The chemical interaction can imply a rather drastic rearrangement of atoms; for instance, for Pt (Mériaudeau *et al.*, 1982) or Ni (von Engels *et al.*, 1981) supported on TiO_2 it has been shown that under reduction conditions the metal becomes partially covered with a Ti suboxide, while Ti^{3+} ions are concentrated near the metal particles (Bonneviot and Haller, 1988).

These examples illustrate the importance of chemical interactions between an active site and its environment. Most catalyst modifiers have been found empirically; in some cases the nature of this interaction was later clarified by using physical characterization methods, but reliable predictions are not possible with the present state of this science. An important objective of catalyst characterization is, therefore, to identify not only the active sites but also their interactions with the environment in and below the catalyst surface. A long-term goal is to use this knowledge in a predictive manner in order to prepare superior catalysts "by design".

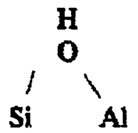
3.2 SOME WAYS TO CHARACTERIZE SITES

We are going to focus on physical methods of characterizing sites, but before we move into this, we need to remind ourselves of the catalytic chemical adage about site characterization, *i.e.*, that a catalytic reaction is more sensitive and specific than any physical technique. One cannot dispute this, but it is worth adding that it is not always easy to deduce structural information from chemisorption or the reaction itself. Carefully chosen probe catalytic reactions can rank activity and selectivity of a group of catalysts and, when the probe molecules are appropriately complex and combined with isotopic labeling, can also determine the mechanism and the structure of adsorbed species. (See R. L. Burwell (1990) and references therein for progress on what he has labeled the organometallic zoo described by such experiments). In most cases, probe reactions cannot indicate why a catalyst is good or bad, so complimentary spectroscopic analysis is always needed.

For purposes of illustration, we will only consider very simple molecules in the examples given below. Here we can point to a case study which started with a simple combination of chemisorption (hydrogen) and reaction (ethane hydrogenolysis) and evolved to include several complimentary spectroscopies (infrared, Mössbauer, X-ray absorption, *etc.*) and produced a commercial catalyst, the Exxon Pt-Ir/Al_2O_3 reforming catalyst (Sinfelt, 1983). It is interesting to note that the catalytic test reaction which was used most in this development is an undesirable side reaction, but this does not suggest itself as a general strategy to be used.

3.2.1 Classical Site and Kinetic/Reaction Probes

Perhaps the most widely used chemisorptive site probe is some generalized base to determine the strength/density of acid sites. The use of infrared spectroscopy with appropriate probe molecules to quantify acidity has been recently reviewed by Knözinger (1993) and will not be further discussed here. For this approach to be useful, one must have some chemical model for the site and, of course, the concepts of Brønsted and Lewis acidity are such essential parts of fundamental chemistry that there is no need to describe them. However, a specific structure for any site is still helpful, and perhaps the most widely known and accepted site picture that we have is that of the bridging hydroxyl for Brønsted acid sites in silica-alumina (Hansford, 1947).



$$\mathrm{Si}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{O}}-\mathrm{Al}$$

(1)

Experimental evidence on the chemistry of acidic sites has been only recently emerging. New concepts have been also proposed recently to explain the fundamental cause of the great difference in acid activity between crystalline zeolite and amorphous silica-alumina gel (Rabó and Gajda, 1989-90).

A somewhat more powerful approach (than simple chemisorption) is to use a catalytic reaction to probe the sites. Traditionally, cumene cracking and toluene disproportionation have been used as probes "counting" Brønsted acid sites. Often this means building some particular structure into the reactant molecule which will then reflect some aspect of the site structure by virtue of how reactive the molecule is. Here organic chemistry offers an almost unlimited variety from simple things like primary, secondary, and tertiary hydrogen (or carbon) to the complexity of optical activity. (See Rooney, 1993, for some excellent examples of the use of molecular structure to probe sites). As a recent example of this approach using what might be called a classical reaction, the deuterium exchange pattern of methyl cyclopentane was used to analyze the electronic effects of support on supported Pt (Baird *et al.*, 1992). The H/D exchange of cyclopentane has been used to distinguish mono-atomic Pt sites from multiatomic Pt_n sites. On the former sites the exchange occurs *stepwise*, whereas larger metal ensembles preferentially catalyze the *multiple* mode of isotope exchange (Lei and Sachtler, 1993).

3.2.1.1 Reaction Selectivity as a Probe for Acidity

Several catalytic reactions have been developed which provide a relative, but quantitative measure of solid acidity. Among the latter is the recently reported reaction of 2-methyl-2-pentene, advanced by Kramer and McVicker (1985). The isomerization of 2-methyl-2-pentene combines a double bond shift (which requires relatively low acid strength, *i.e.*, it occurs on essentially all acid sites) and a methyl shift (which requires relatively high acid strength). The fact that double bond isomerization occurs on essentially all acid sites allows this reaction to effectively act as a normalization of the site density when the selectivity of the methyl shift relative to double bond shift is considered. Thus, this reaction may be considered a measure of site strength while other reaction rate probes will be some convolution of site density and site strength. This reaction has several advantages as a probe for acidity. It involves a single reactant, the acidity correlates with selectivity (between the methyl and double bond isomerization) rather than rate, it spans a wide range of solid acidity, and it correlates with the commercially important measure of cracking activity, the MAT number (Kramer and McVicker, 1986).

3.2.1 2 n-Hexane Cracking as a Probe Reaction

Even a relatively simple reaction can be diagnostic in the right hands. Haag *et al.* have developed the cracking of n-hexane on HZSM-5 such that it can now be used as a probe reaction to characterize other acid catalysts (Haag *et al.*, 1991). The general mechanism for acid catalyzed reactions envisions the addition of a proton to the molecule, the rearrangement of the protonated species, and the removal of the proton. For example, we can write for the isomerization of cyclopropane ($c\text{-}C_3H_6$) to propene ($n\text{-}C_3H_6$) on solid acid HA:

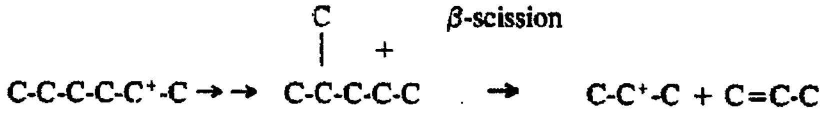
$$\text{c-C}_3\text{H}_6 + \text{HA} \rightarrow \text{c-C}_3\text{H}_7^+ + \text{A}^- \qquad (2)$$

$$\text{c-C}_3\text{H}_7^+ + \text{A}^- \rightarrow \text{n-C}_3\text{H}_7^+ + \text{A}^-$$

$$\text{n-C}_3\text{H}_7^+ + \text{A}^- \rightarrow \text{n-C}_3\text{H}_6 + \text{HA}$$

This is a quite general mechanism and can be applied to many molecules. When applied to a paraffin, one arrives at a non-classical penta-coordinated carbonium ion. This leads to what is called the monomolecular cracking mechanism (Haag *et al.*, 1991). As noted by Haag *et al.* (1991), one kind of evidence for this mechanism is that $\text{C}_6\text{H}_{15}^+$ formed from n-hexane on zeolite catalysts, *e.g.*, HZSM-5, produces the same distribution of products as when this same ion is produced in the gas phase via chemical ionization by CH_5^+ in an ion cyclotron resonance mass spectrometer. The conditions which favor this mechanism are high temperature and low paraffin partial pressure and/or low conversion. The latter assures low olefin concentrations (as products). When significant olefin concentrations exist in the feed or are formed by the monomolecular cracking mechanism, these are more easily protonated than the paraffin and lead to the classical (bimolecular) mechanism involving a carbonium ion chain reaction, which for n-hexane may be written:

$$\text{C-C-C-C-C-C} + \text{C-C}^+\text{-C} \rightarrow \text{C-C-C-C-C}^+\text{-C} + \text{C-C-C} \qquad (3)$$



$$\text{C-C-C-C-C}^+\text{-C} \rightarrow\rightarrow \text{C-}\overset{\overset{\text{C}}{|}}{\text{C}}{}^{+}\text{-C-C-C} \xrightarrow{\beta\text{-scission}} \text{C-C}^+\text{-C} + \text{C=C-C} \qquad (4)$$

This is referred to as a bimolecular mechanism, because the step (4) involving rearrangement of the carbonium ion and β-scission occurs very rapidly and the rate determining step is the hydrogen transfer reaction of step (3). The conditions at which the bimolecular reaction path predominates are low temperature and high olefin concentration. In practice, both mechanisms may contribute to varying extents, depending on the composition of the feed and the reaction conditions. As discussed by Haag *et al.* (1991), the overall rate (which is a sum of the two mechanisms) can be formulated such that in two limiting cases they produce apparent first order kinetics. However, the apparent first order rate constant represents the rate limiting formation of penta-coordinated carbonium ion (in the limit of high temperature and low olefin concentration) and formation of tri-coordinated carbonium ion (in the limit of low temperature and large olefin concentration).

3.2.1.3 n-Hexane Aromatization as a Probe

To this point, the probe reactions discussed have been ones where a particular property, for example, acidity was being sensed. Overall knowledge of the mechanistic details of a reaction can be used to identify a new catalyst with a different mechanism for the same reaction and this, too, can be a powerful characterization approach. This is nicely illustrated by the n-hexane to benzene reaction which is one reaction among many that occur on conventional reforming catalysts. The original proposal of Mills *et al.* (1953) for reforming of alkanes has been confirmed and elaborated on by many researchers and is now found in standard textbooks on catalysis (Gates, 1992), that is, it is well understood and widely accepted. Thus, if the attributes of a catalyst needed to convert n-hexane into benzene, *i.e.*, both dehydrogenation and acid sites, and the intermediates involved, *i.e.*, methyl-cyclopentane, are found not to exist for a new n-hexane to benzene catalyst, it may safely be concluded that a new mechanism is at work. This is the case for the Pt/L-zeolite aromatization catalysts.

Many of the important observations and characteristics of Pt/L-zeolite aromatization catalysts were presented in the original publication of Bernard (1980). It was noted (i) that benzene selectivity was a strong function of conversion, (ii) that at the same conversion, L-zeolite was superior to other zeolites tested, (iii) that the K^+ cation exchange of other zeolites did not render them competitive with L, (iv) that introduction of acidity into Pt/L-zeolite degraded the selectivity, (v) that n-hexane conversion to benzene was faster than methylcyclopentane conversion to benzene (which is not the case on a conventional bimetallic reforming catalyst) and (vi) that the Pt site density was rate controlling (while it is usually acid site density in conventional reforming catalysts). Observation (i) indicates that comparison of supports must be done at the same conversion (but that is standard good practice for any catalytic comparison) and (ii) and (iii) suggest there is something special about KL-zeolite. Observations (iv) and (v) argue against a conventional bifunctional mechanism and (vi) is direct evidence for monofunctionality involving Pt.

3.2.1.4 Competitive Hydrogenation as an Electronic Probe

Often there is a need to sense the local electronic perturbation of a metal particle and the effect of this restructuring on catalysis. The shift in the infrared frequency of the C-O stretch of chemisorbed CO has often been used for this purpose (Peri, 1984). However, CO vibrational frequencies are often affected by dipole coupling (as a function of coverage) to a greater extent than they are by electronic perturbations. A reaction probe which has been developed and demonstrated is the competitive hydrogenation of benzene and toluene (Tri *et al.*, 1982). Hydrogenations are generally considered structure insensitive (Boudart *et al.*, 1968), and this is advantageous if it is the electronic nature of the metal particle that we are trying to probe. The competitive hydrogenation of aromatics is governed by their relative adsorption coefficients, and these in turn reflect the local electronic charge on the metal particle. In the competitive hydrogenation of toluene and benzene, toluene is the better electron donor and therefore is expected to form stronger π-bonds with Pt. As pointed out by Tri *et al.* (1982), it is the ratio of adsorption equilibrium constants $K_{t/b} = (K_{toluene})/(K_{benzene})$ which one wishes to measure because the rate is a product of the adsorption constants and rate constants. Because both toluene and benzene are π-electron donors and their ionization potentials are known, it is possible to predict how $K_{t/b}$ would vary with charge on the Pt cluster, while the effect on the rate constant is not so obvious. This parameter can be determined kinetically by measuring competitive benzene hydrogenation as a function of partial pressures of toluene and benzene at a temperature where both reactions are zero order in aromatic reactant. This probe reaction has also been used in the analysis of the sites in the Pt/L-zeolite aromatization catalyst (Larsen and Haller, 1989).

3.2.1.5 Hydrogenolysis as a Probe in Bimetallic Catalysts

There are many industrial catalysts that are based on the use of two metals. These catalysts present a particularly difficult characterization task because often the two metals will have quite comparable physical and chemical properties. This is the case for Pt-Re/Al_2O_3 which is, after exposure to a sulfur-containing gas, a widely used commercial reforming catalyst. In the total absence of traces of sulfur, both metals catalyze hydrogenolysis, but Pt-Re alloys are much more active for this reaction than either Pt or Re. This high specific activity of the bimetal particles can be used as a probe for alloying. The hydrogenolysis of cyclopentane has been demonstrated to be a reliable probe for the existence of bimetal particles in catalysts which contain both Pt and Re (Augustine and Sachtler, 1989). Electron microscopy is not very helpful, because it does not distinguish atoms of similar mass, such as Re and Pt. Likewise, the fact that Re and Pt have about the same number of electrons gives them similar backscattering functions and makes EXAFS analysis highly problematic (see below). Here then is another example where catalysis is the most sensitive way to characterize an important structural parameter (the formation of alloys) of the catalyst.

A useful probe discriminating between metal catalyzed hydrogenolysis and bifunctional (*i.e.* metal + acid) catalysis is the conversion of methylcyclopentane. In the absence of acid sites, a transition metal such as Pt or Pd catalyzes hydrogenolytic fission of one C-C bond in the ring. With some catalysts, the three possible ring opening products, n-hexane, 2-methylpentane, and 3-methylpentane are formed in ratios strongly deviating from statistics, as has been shown by Gault (1981). Such distribution provides valuable information on the site geometry, possibly also on its electronic structure (Lerner *et al.*, 1992). In the presence of acid sites, the bifunctional reaction of ring enlargement is catalyzed, with cyclohexane and benzene as the products. If formed in ratios deviating from the thermodynamic equilibrium ratio, this information is possibly indicative for sites which combine metal particles and Brønsted acids into a common *metal-proton adduct* (Bai and Sachtler, 1991; Lerner *et al.*, 1993).

For bimetal/zeolite catalysts such as Pt + Cu in NaY prepared by ion exchange and reduction, the addition of Cu to the Pt particles lowers the hydrogenolytic catalysis as a consequence of the well-known *ensemble effect*. Simultaneously, the enhanced concentration of protons, which are generated during reduction of both metals, favors the bifunctional catalysis of ring enlargement (Moretti and Sachtler, 1989).

3.2.2 **Development of Surface Science for Catalytic Studies**

The study of single crystal surfaces cleaned and maintained in ultra-high vacuum and investigated either in the field electron or the field ion microscope or with a variety of novel spectroscopies (Auger Electron Spectroscopy, Photoelectron Spectroscopy or Electron Loss Spectroscopy) or with Low Energy Electron Diffraction forms a very important part of surface science (Koel and Somorjai, 1985). Important new concepts have been identified by means of these techniques, for example regarding the kinetics, dynamics of ad- and desorption, the effect of defect sites, the structure of adsorbed species, and the participation of subsurface atoms. In the past decade, much attention has been focused towards developing these new techniques to a state of high reliability and precision. For the future it is hoped that they will increasingly be applied to samples and conditions which simulate real catalysis. One strategy is to combine these techniques with high pressure reactors, so that a crystal can be shuttled between the ultra-high vacuum chamber and the reactor. This approach has already provided us with new inspiring models (Rodriguez and Goodman, 1991). Unfortunately, very little of this work has involved *in situ* analysis under reaction conditions because the probe particles require a good vacuum to operate. Infrared reflection absorption is an exception (Evans *et al.*, 1993) but is most frequently used in the before and after reaction mode of the other spectroscopies. What is suggested here is that there should be effort expended to develop photon based surface science that will allow true *in situ* analysis on well defined and characterized surfaces.

By way of an example of replacing of an electron surface science tool with an analogous photon tool, we cite the recent work on photon scanning tunneling microscopy (Ferrell *et al.*, 1992). The photon STM provides images of both insulators and conductors, but requires that the surface be either thin or not too strongly absorbing at the wavelength used. STM provides better spatial resolution but poorer spectroscopic resolution, that is, they are complementary tools. The photon STM has the potential to combine with vibrational spectroscopy, for example, resonance or surface-enhanced Raman. Other photon surface science tools under development include second-harmonic (and sum frequency) generation through nonlinear optical processes at a surface.

The need for photon (or some equivalent) surface science approach that will allow analysis under reaction conditions on well defined surfaces (probably characterized by current electron based surface science) is great. In addition to this general need, there are listed below some specific areas where new developments in surface science would be most welcome.

3.2.2.1 Oxide Surfaces

Surface science has made very significant contributions to our understanding of elementary steps on metals, but we need to see similar progress on oxides. Oxides are more difficult to study by surface science techniques for many reasons. Some oxides are difficult to grow as large single crystals. They are more prone to defects and can become non-stoichiometric at even modest temperatures in ultra-high vacuum. Of course, the fact that they are mostly insulators can compromise many of the electron spectroscopies by virtue of the static charge that results from electron emission, and the HREEL's spectra are compromised by the huge optical phonon losses in the oxide surfaces. Both the promise and problems are evident in a recent CO and CO_2 study on $Cr_2O_3(111)$ (Kuhlenbeck and Freund, 1992). While they add complications to the experiments, all of these problems can be overcome and many laboratories have projects underway, for example, Evans *et al.* (1993) have presented a study of Rh on single crystal $TiO_2(110)$ which combined many of the conventional surface science tools with reflection absorption infrared spectroscopy (Evans *et al.*, 1993).

3.2.2.2 High Coverages

While there have been many experiments performed under steady-state, high pressure conditions on single crystals, the vast majority of surface science experiments are performed in vacuum or at very low partial pressures. The resulting low coverages can completely alter the selectivity and dominant reactions. While this can still be interesting surface chemistry, it would be even more interesting to use surface science to learn about practical reactions (at relatively high pressures and surface coverages).

In some recent work it has been shown that methyl radicals on Ni(111) readily recombine with subsurface H atoms to form gas phase methane (Johnson *et al.*, 1992) while the dominant reaction is decomposition of the methyl radicals with surface H atoms rather than recombination. One suspects this is the result of the rather low H surface coverages that can be accomplished in these experiments and that the decomposition would be inhibited at high surface coverages of H. Of course, one approach is to get the high coverages the same way as they are obtained in real catalysis, that is, raise the pressure, but this means that *in situ* analysis has been given up.

Sometimes it may be possible to simulate high pressure by increasing the local coverage by other means. For example, Campbell *et al.* (1988) have found that high pressure conditions are simulated by postdosing Bi onto Pt(111). This forces species such as adsorbed H or hydrocarbon fragments into higher local coverages where they react as if at high pressures. Clearly, this is not a general solution and we need to find innovative ways around this problem.

3.2.2.3 Kinetic Characterization on Single Crystal/Model Catalysts

Of course, there are other reasons to go to high pressure other than just coverage considerations. This also makes possible kinetic characterization of the surfaces. While such studies might use kinetic probe reactions, the minimum we might expect to learn is whether the rate on the single crystal or model surface was comparable to that on high area conventional catalysts. This would then ensure that whatever surface science characterization was possible would be relevant to the steady-state catalysis. A recent example of such an investigation was reported by Coulter and Goodman (1992). They investigated oxidative dimerization of methane on thin-film MgO and Li/MgO (on which electron spectroscopies could also be performed) and showed that kinetics on the model catalysts gave about the same rates as the polycrystalline Li/MgO under similar conditions.

3.3 TIME RESOLVED SURFACE SPECTROSCOPY

While many stable adsorbed species have been identified by various spectroscopies, there is no guarantee that they play any role in the reaction, even if they originate from one of the reactants. One approach to determine if a given species is kinetically significant, that is, if it forms and reacts on a time scale sufficiently fast to sustain the steady-state reaction, is to perform a transient experiment. Tamaru (1964) first proposed this principle, and its summary was provided in 1978 and 1991 and more recently by Frennet (1993). The most effective approach is to have the transient occur effectively at steady-state by a switch in one or more of the reactants, isotopically labeled, and follow the evolution of the isotopically labeled intermediates on the surface, for example, by infrared spectroscopy, or in the gas phase by mass spectrometry. Of course, a better experiment is to follow both the surface concentration and the gas phase simultaneously, but few of these experiments have been performed. A recent example using mass spectrometry to follow an isotope transient to estimate the rate coefficients for chain initiation, propagation, and termination during Fischer-Tropsch synthesis over Ru/TiO_2 is given by Krishna and Bell (1993).

Reutt-Robey *et al.* (1988) have reported a particularly elegant example of time-resolved infrared spectroscopy applied to what is expected to be a true elementary step. The law of mass action only applies to surface reactions involving two (or more) surface species only if one or more of these species diffuse on the surface rapidly on the time scale of reaction. In the case of CO oxidation on Pt, the rate at high temperature can be shown to be proportional to the product of coverages, $\Theta_{CO}\Theta_O$. Because oxygen atoms are known to diffuse slowly at reaction temperature, it is presumed that CO must diffuse rapidly. Just how rapidly this diffusion is on a microscopic dimension (20 atom length) has been shown by following the diffusion of CO initially on a Pt(111) terrace to a step. This can be followed by reflection infrared spectroscopy because the absorption frequency of CO on the terraces is different from CO on step sites. This migration was followed with a temporal resolution as fast as 5 msec and, by varying temperatures, a diffusion barrier of only 4.4 kcal/mol was determined. While there are several examples of diffusion over macroscopic dimensions, it is microscopic experiments, such as this, which are probably the most important for catalytic kinetics. The macroscopic diffusion will necessarily average over defects where the diffusion rate is very low because the fast diffusing species are likely to desorb before they can diffuse over a macroscopic distance (and therefore contribute little to reaction). This has recently been demonstrated for CO diffusion on supported Pd using ^{13}C NMR (Becerra *et al.*, 1993). On the smallest clusters the diffusion activation energy was 6 ± 2 kcal/mol but decreased to 4 ± 1 kcal/mol for the large particles (12% exposed by CO chemisorption) which presumably have a lower defect density.

In the example of CO surface diffusion on Pt given above, the elementary step has been slowed down by lowering the temperature to the point where it could be followed. This is probably a reasonable thing to do for migration, but for a chemical reaction the mechanism might change; so we are in need of time resolved surface spectroscopies with much better time resolution. If it is possible to repeat the transient very rapidly, then it is possible to work out algorithms where data are collected at the same time into the transient and then to construct a spectrum at that "time". This approach has been used by looking at the infrared emission of vibrationally excited desorbed CO_2 from a Pd surface (Mantell *et al.*, 1985). The transient was a pulse of reactant directed at a surface. The pulse was about 200 μs and spectra could be obtained at spacings of about 30 μs through the transient using an efficient data collection algorithm that collects data continuously and then shuffles it into a matrix in which all the data at a given time into the transient could be transformed into a spectrum. In principle, this approach could be applied to other spectroscopies. Time-resolved measurement on a picosecond time scale has been demonstrated using infrared lasers to saturate and monitor the recovery of infrared absorptions on surfaces (Casassa *et al.*, 1986). While this approach has not yet been applied to reactions on surfaces, this appears to be technically possible.

3.4 NEEDED SPECTROSCOPIC ATTRIBUTES

Most practical catalysts are either comprised of amorphous materials or small crystalline particles and, consequently, do not possess long-range order. Moreover, the existence of long-range order does not in itself assist in the characterization of the relevant properties of the catalysts. For example, many industrially important oxidation catalysts contain particles of metal oxide that are large enough to exhibit diffraction patterns, but the bulk structure does not necessarily enlighten us about the surface structures which are relevant to catalysis. Thus, techniques which are element specific and provide local structural information without the requirement of long-range order are very desirable. The element specificity is important so that we might tune to different components and interrogate them with respect to the surrounding order. Techniques which have these properties are NMR, X-ray absorption, EXAFS, X-ray absorption near-edge structure (XANES), and Mössbauer spectroscopies. As it happens, the wavelengths of the electromagnetic spectrum used by these spectroscopies are either very short (hard X-ray or γ-ray) or long (radio frequency) so that these spectroscopies do not require a vacuum and can be used at reaction pressures, and under some circumstances, at reaction temperatures. Unfortunately, this same property makes them bulk techniques so that special precautions must be taken to make them surface sensitive, for example, have the element of interest entirely exposed to the reactants (as in zeolites) or in very small particles so that essentially all atoms may be exposed to the reactants in the fluid phase.

We have already referred to the recent NMR investigation of CO on Pd with regard to the information provided on the activation energy for surface diffusion (Becerra *et al.*, 1993). But even for a site about which we know a great deal, the a-top and bridged-bonded sites of CO, this study provides several kinds of new information. The Knight shift informs us that the bridged-bonded site results in more interaction between the conduction electrons and those on the C than does the a-top site, that the bridged-bonding site is somewhat weaker and, at least at full coverage, is the dominant site on which migration occurs (although not simply because of the lower enthalpy of adsorption). While this is clearly not direct information on the active site, it is necessary structural information about the chemisorbed reactant and the site that bonds it.

While NMR is providing a wealth of new structural information on zeolites, oxide catalysts, adsorbed species on metals, *etc.*, the challenge is to make this spectroscopy truly applicable under reaction conditions. That is, the trend in solid state NMR is toward improved resolution by ever more complex motion of the sample, for example, magic angle spinning, dynamic angle spinning, double-rotation (Wu *et al.*, 1990), and this motion of the sample does not make it easy to imagine the sample as a steady-state reactor. An alternative to discrete Fourier transformation of NMR data that has been proposed is the maximum entropy method (Jones and Hore, 1991). While the maximum entropy method would normally be used with magic angle spinning to improve resolution, perhaps this or other new line shape analyses can be developed that will permit NMR of the catalyst during reaction.

More direct information on active sites on CoMo/Al_2O_3 HDS catalysts has been obtained by Mössbauer spectroscopy (Candia *et al.*, 1982). Mössbauer spectroscopy of the cobalt, an experiment that involves the preparation of radioactive samples, shows that hydrodesulfurization activity parallels the formation of a particular cobalt species that does not resemble any of the known bulk cobalt sulfides (Candia *et al.*, 1982). The same result appears in spectra of supported and unsupported mixtures of sulfided molybdenum and cobalt and has led the Topsøe group to propose a species they call "CoMoS" as the site of the hydrodesulfurization activity.

The attributes of synchrotron radiation, particularly as applied to EXAFS and XANES of catalysts, has been briefly reviewed by Joyner (1993). He has emphasized the need for *in situ* measurements in parallel with catalyst activity and selectivity measurements. Recently, both EXAFS and XANES have been used to follow formation of bimetallic particles using *in situ* temperature programmed reduction (TPR). Bazin *et al.* (1990) have followed the formation of Pt-Rh and Pt-Re on γ-Al_2O_3 using EXAFS and Jentys *et al.* (1992) combined XANES with TPR. The EXAFS measurements have the advantage that they provide directly structural parameters (coordination numbers, internuclear distances), but the resolution is greatly degraded by Debye-Waller effects, even at modest temperatures. XANES has the advantage that the spectra do not suffer from Debye-Waller degradation, but we do not have a good theory to interpret the electronic information that is, in principle, contained in the spectra. An approach which has much in common with XANES, but may have advantages when the whiteline intensity is not a linear function of oxidation state, is the measurement of the shift in the X-ray absorption edge, from which the binding energy can be monitored *in situ* in a TPR experiment (Hilbrig *et al.*, 1992).

A simple EXAFS analysis of a single first coordination shell with one kind of atom can result in both accurate internuclear distances and good approximations of the coordination numbers. However, there is a great deal of skepticism about the results for more complicated analyses which are common for real catalysts. The task is particularly difficult when one attempts multiple shell fits with more than two atoms of similar mass, for example, Pt-Re/Al_2O_3 catalysts and, indeed, different laboratories have come to quite different conclusions. There is a clear need for laboratories to exchange data, to share analysis programs, to set standards for the data to be used and to otherwise organize the application of the use of X-ray absorption analysis if it is to deliver on its potential for catalyst characterization.

3.5 THEORY

The continuing reduction in cost and increase in speed of computing has brought "theory" into the laboratories of the novice as well as the expert. The word theory is placed in quotes here to imply that we take the catholic definition that includes everything from reaction modeling to molecular modeling/molecular graphics to quantum chemistry. However, this does not imply that all aspects of theory are at the same stage of development. Chemical reaction engineering, where the focus is on the analysis of the reactor and pellet design, is widely applied in industry and is a mature science. Kinetic modeling is at a similar stage with regard to the necessary mathematics, but this is not the case with regard to parameter estimation that relies on sources other than experimental measurement. Dumesic *et al.* (1993) have introduced a systematic synthesis of experimental data, theoretical principles, and appropriate correlations to quantitatively formulate elementary reaction steps in what they have designated "microkinetics of heterogeneous catalysis". In the extreme, this faces the same problems that confront other theoretical efforts at the atomic scale.

The real frontier for theories of catalysis occur where the focus is on the atomic scale and where the simulation of catalyst properties and the dynamics of elementary processes is the goal. Lombardo and Bell (1991) provide a recent review of theoretical models of adsorption, desorption, diffusion, and reaction of metal surfaces, and van Santen (1991) has published a comprehensive monograph which covers both metal and oxide (including zeolite) catalysts. However, in all of this work the theoretical calculations make an implicit assumption of some knowledge about the structure of the adsorption or reaction site that is to be theoretically simulated. It may not take into account the relaxation or changes in structure that accompany adsorption and reaction at the site; and thus, there is no guarantee that the lowest energy configuration of a given possibility is achieved. Thus, if this is the criterion by which the presumed site is selected among several possibilities considered, the conclusion will be flawed, and of course the original set of possibilities may be conditioned by constraints of feasibility so that it does not include the real site. Some constraints can now be eliminated when simulating the structure of active sites in zeolites or other sites composed of low atomic number atoms. For most metals, this is still a difficult task because the large number of electrons in transition metals requires algorithms that are too computationally intensive to permit the inclusion of relaxation effects. (For a recent survey of theoretical models in common use today for electronic structure of transition metal systems, see Zerner, 1991). Even though one is forced to assume the structure of the active site at the outset, these theoretical simulations can yield insights into what might happen at the molecular scale that are not accessible by other means. Such theoretical simulations, particularly when coupled with experimental attempts to verify the results, are to be encouraged.

3.6 RECOMMENDATIONS

Our recommendations for catalyst characterization are placed into two groups. The first group of six are general in nature. The second group applies to characterization techniques and is more specific, although the particular techniques are mostly illustrative.

3.6.1 Recommendations for Catalyst Characterization

Catalysis is by definition a kinetic phenomenon. Thus, it is the sites on which the elementary reactions are occurring that will be most fundamental to our understanding of catalysis. We should always attempt to study the catalyst in the act of turning over, that is, while reaction is occurring at steady-state.

- *There is a need to identify sites more precisely, both in the catalyst as prepared and in the steady-state of the catalytic reaction, that is, in the presence of reactants and products under the conditions of temperature and pressure of the catalytic reaction of interest.*

- *As active sites often comprise more than one atom, the design of an optimum catalyst requires a detailed knowledge of the ensemble size and of the chemical interaction of these atoms with their environment, including support, promoters, chemical anchors, and catalyst poisons.*

While our interest is in the characterization of catalytic sites in action, often insight into the nature of these sites can be provided by the study of the precursors to the active catalyst. This is true for all kinds of catalysts, including zeolites, mixed oxides, and supported metals, although the nature of precursor chemistry is very different. For example, the precursor chemistry of supported metals is particularly important not only to understand the nature of the final metal particles but also to make the catalyst preparation reproducible. We are almost wholly ignorant of the inorganic chemistry that transpires between a metal ion in solution and the resulting metal particle supported on an oxide (or other) surface. A statement that a given weight loading of metal on a particular support was prepared by "incipient wetness impregnation" can disguise many known and unknown effects. There may be dissolution of the support, retention of the anion by the support, migration of the precursors (into or out of the pores) which will be affected by the drying temperature, initial reduction temperature, rate of reduction, *etc.*

- *Complete characterization of catalyst sites (and description of catalyst preparation) should include the complete inorganic chemistry of catalyst preparation.*

We need new surface spectroscopic techniques which are element specific, provide local structure where no long-range order exists, and can be applied under reaction conditions. These would be more nearly ideal if they were also surface specific.

- *Whatever techniques we contemplate, making these techniques applicable under reaction conditions and developing time resolution will be important and will pose essential challenges which should be given our continued attention.*

We have already noted that chemical catalytic probes are by definition the most sensitive probes of catalytic sites, but this sensitivity does not necessarily provide the detailed site structural information that is sought. Every physical technique for catalysts characterization will have some particular strengths and weaknesses. A given technique may be more or less surface sensitive, for instance, ion scattering spectroscopy is more surface sensitive than X-ray photoelectron spectroscopy. The parameter measured may be a nonlinear function of coverage, for example, infrared intensity of CO on metals, or provide better information on surface symmetry or morphology than composition, *e.g.*, LEED and STM.

- *Characterization of catalyst sites should always involve complementary physical (spectroscopic) and chemical (chemisorption and/or catalytic kinetic) techniques* *of characterization and use as wide a combination of physical characterization techniques on the same catalyst as may be practical.*

We need to have the two approaches used in a complementary way. For example, the competitive hydrogenation of benzene and toluene was described as a reaction that qualitatively probed for the charge on small metal particles. It should be possible to design model systems on which both this reaction and a direct measure of the charge on the particles could be measured, for instance, by the XPS binding energy shift, so that the catalytic reaction could be calibrated against the physical method. It could then be used on catalysts where the changes were too small to measure directly by the physical technique, but by the calibration, the property could be reported on a quantitative basis. While the use of model reactions is among the oldest techniques we have for characterizing catalysts, it would be useful to have a modern review and critique of the many reactions that have been tried. This could serve as a reference for future developments.

The extension of the present level of theoretical analysis to treat very large systems is essential for low symmetry problems represented by surfaces.

- *New theoretical approaches which are atomically based and can treat site dynamics that accompany adsorption and catalytic turnover need to be developed.*

3.6.2 Recommendations for Surface Analysis

Certain physical techniques, such as X-ray absorption, have become widely used and have admitted potential for characterizing catalysts. However, the analysis is complex and not well understood by many users, and much of the work to date has not been cross-checked for reproducibility. There is also widespread skepticism about conclusions drawn from this work.

- *The community needs to agree on standard analysis programs, methods of assessing uncertainty, and minimum standards for experimental data that are analyzed and published, e.g., for X-ray absorption spectroscopy.*

- *We need new photon based surface science spectroscopies which can be applied to surfaces at high coverage and under reaction conditions. We seek surface science improvements that will make application to nonmetals routine.*

- *We need new and improved element specific spectroscopies that can determine local surface structure in high area catalytic materials. As a specific example, we need improved lineshape and data analysis for solid state NMR, along with continued improvements in field strength and dynamic probes.*

Until STM is routinely used in such a way that compositions as well as images are obtained *via* either experimental improvements or coupled theory, it will be analogous to the early contributions of LEED where symmetry was easy and obvious, but true structure required the development of a firm theoretical underpinning. There is a recent and promising STM report in this regard where it was demonstrated that polyanion arrays (on a graphite surface) with different compositions could be distinguished by a kind of density of states analysis (Watson *et al.*, 1992).

- *New surface analysis techniques should provide both symmetry/morphological and chemical composition.*

Some work has been done to devolop a method of elemental analysis to accompany STM involving inelastic tunneling to obtain vibrational frequency analysis as a function of position. The development of such a method of compositional analysis should be given a high priority, since the transient isotope switch approach may be applied in the steady-state of the reaction to identify the true active sites on catalyst surfaces on an atomic scale (Tamar, 1993).

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