TOPICS IN HETEROGENEOUS CATALYSIS VIEWED BY MÖSSBAUER SPECTROSCOPY

J. Dumesic

HAL Id: jpa-00216758
https://hal.science/jpa-00216758

TOPICS IN HETEROGENEOUS CATALYSIS
VIEWED BY MÖSSBAUER SPECTROSCOPY

J. A. DUMESIC

Department of Chemical Engineering, University of Wisconsin
Madison, Wisconsin 53706, U. S. A.

Résumé. — Quelques sujets dans la catalyse hétérogène étant particulièrement aptes pour être étudiés par application de spectroscopie Mössbauer, sont d'abord introduits et ensuite discutés avec référence aux exemples de la littérature. Ces sujets se trouvent en régions telles que la préparation et caractérisation de catalyseurs, les propriétés de surface de catalyseurs, et les procédés d'adsorption chimique et réaction qui ont lieu au-dessus de catalyseurs. Aussi, des considérations expérimentales pertinentes à l'application de spectroscopie Mössbauer aux problèmes de ce type, sont brièvement discutées.

Abstract. — Topics in heterogeneous catalysis that are particularly well suited for study using Mössbauer spectroscopy are first introduced and then discussed with reference to examples from the literature. These topics are in the areas of catalyst preparation and characterization, surface properties of catalysts, and chemisorption and reaction processes occurring over catalysts. Experimental considerations pertinent to the application of Mössbauer spectroscopy to problems of this type are also briefly discussed.

1. **Introduction.** — One may consider topics in solid surface phenomena ranging from (i) the preparation, characterization and study of real (i. e. industrially usable) and model catalytic materials at pressures greater than or approximately equal to atmospheric, to (ii) the study of « well-defined » solid surfaces and simple catalytic reactions at pressures less than or perhaps approaching atmospheric. These topics may then be divided somewhat arbitrarily into *heterogeneous catalysis* and *surface science*, respectively. In both of these areas a primary research objective is to determine the surface electronic, geometric, dynamic and chemisorptive properties under reaction conditions ; however, while this research objective is the same for both areas, its implementation is significantly different. This arises mainly from the different pressure ranges and samples typically studied.

At low pressures (less than ca. 10^{-4} torr) over well-defined surfaces a number of spectroscopic techniques serve to supply the desired surface information. For example, Auger electron spectroscopy (AES) may be used to provide the surface elemental composition, x-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) give information about the electronic structure of the surface, low energy electron diffraction (LEED) may be used to determine the geometric surface structure, and molecular beam rare gas scattering gives surface dynamics information. At higher pressures (atmospheric pressure) over real catalysts these surface techniques cannot be used, and it is indicative of the experimental difficulties under these conditions that two of the most sensitive « surface techniques » are simple gas chemisorption measurements and catalyst activity and selectivity determinations.

Mössbauer spectroscopy, however, is a technique that is applicable to the study of *both* well-defined surfaces at low pressures and real catalysts at higher pressures. At low pressures, Mössbauer spectroscopy is a tool that complements those listed above, while at higher pressures, this technique may provide information unobtainable from other physical methods. For this reason, the applications of Mössbauer spectroscopy to problems in heterogeneous catalysis will be emphasized in the following discussions.

A number of reviews have been written dealing with the applications of Mössbauer spectroscopy to solid surface phenomena [1-17] ; in the most recent of these, Dumesic and Topsøe [17] discussed specifically those applications to heterogeneous catalysis. Thus, an exhaustive review of the literature need not be given here. Instead, various topics in heterogeneous catalysis will be introduced and discussed, as viewed by Mössbauer spectroscopy.

2. **Experimental considerations.** — Typically, three different types of experiments are carried out in the application of Mössbauer spectroscopy to heteroge-

neous catalysis : spectra are collected (1) either before or after the sample is used as a catalyst in a given chemical process, (2) with the sample exposed to a given adsorbing gas (*in situ* experiments), or (3) while the sample is actually functioning as a catalyst under reaction conditions. The main feature of these experiments that distinguishes them from other Mössbauer spectroscopy applications deals with the sample cells.

The problem statement for the design of Mössbauer spectroscopy cells for the study of solid surface phenomena is the following : to design an *in situ* cell that has *windows* transparent to the γ radiation, and that can operate at temperatures of interest for surface studies (this may mean high temperatures, e. g. 700 K) and of interest for observation of the various hyperfine interactions (this may mean low temperatures, e. g. 77 K). Cells of this type have recently been discussed elsewhere [17]. In addition, for the study of catalytic phenomena *during* catalysis, the constraint is imposed that the *working state* of the catalyst be well defined. In general, this state is determined by (1) the reactant and product gas (or liquid) phase concentrations at the inlet and outlet of the catalytic reactor, (2) the mode of operation of the reactor (e. g. integral or differential), and (3) the flow rate of the reactant gas mixture through the reactor.

As an example, a simple system for the study of catalytic processes at temperatures higher than 300 K is shown in figure 1. The sample cell is cylindrically
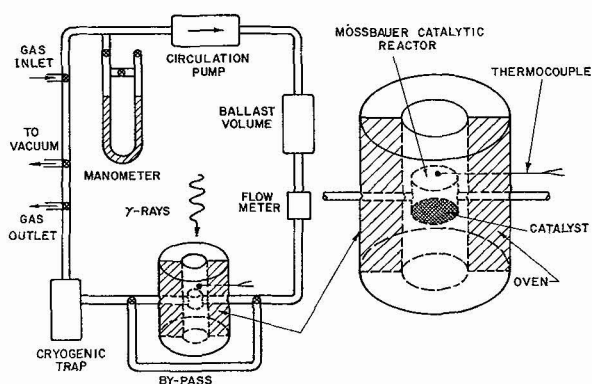

FIG. 1. — *Mössbauer Catalytic Reactor* and Circulation System. Figure according to Dumesic *et al.* [18].

shaped, and the two ends of the cylinder serve as the γ-ray windows. During operation the catalyst, in powder form, lies in the cell as a thin layer over the cylinder base with the cell placed in a vertical γ-ray beam, and the reactant gas mixture flows horizontally over the thin catalyst layer. The connecting gas handling system allows the catalytic reactor (i. e. the sample cell) to be operated in the simple flow mode or the recirculation mode. In the former, the reactant gas mixture passes through the reactor only once, after

which the gas mixture is analyzed to obtain the product concentrations ; in the latter mode, the reactant gas mixture is brought into contact with the catalyst many times using a circulation pump. After each pass, during which the extent of conversion of reactants to products is small, the products formed are frozen out of the gas phase using appropriate cryogenic traps. Thus, this simple cell and gas handling system meet the requirements of an *in situ* Mössbauer spectroscopy cell and a catalytic reactor with a well-defined mode of operation. A more detailed discussion of these concepts can be found elsewhere [18].

Finally, it should be noted that the sample selection also plays a role in the effective application of Mössbauer spectroscopy to problems in heterogeneous catalysis [17, 18]. Specifically, the catalyst (preferably highly dispersed) should contain a Mössbauer isotope that either directly participates in or is a « witness » of the catalytic process.

3. Catalyst preparation and characterization.

— It was mentioned above that real catalysts are often multicomponent, *highly dispersed* systems. The dispersion of a particular phase (e. g. species A) is defined as the percentage of the total number of atoms (of species A) in the phase that are on the surface of the catalyst ; and, when speaking of a *higly dispersed* phase, a dispersion greater than ca. 10 % is usually implied. It seems reasonable to assume (as a first approximation that will be discussed later) that an effective way to use a given amount of a catalytic material is to put that material in a highly dispersed state. In this manner a large fraction of the material can be made accessible to the reactant gas or liquid phase. Thus, one is brought to the question of the catalyst preparation and characterization.

The preparation is usually initiated by forming a catalyst precursor (e. g. using methods of precipitation, impregnation or ion exchange [19]), after which this composite material is treated (e. g. calcined, or reduced) to put the catalytic component in its active state. An important consideration in this procedure is the surface and bulk mobility of the catalytic component. For example, a high mobility often results in the formation of a poorly dispersed sample ; on the other hand, there are cases for which a relatively high mobility is desirable, such as in the *redispersion* of an initially poorly dispersed active phase.

Mössbauer spectroscopy reflects this important information mainly in the recoil-free fraction and the resonance line width. These effects are illustrated nicely in the work done at the Institute of Chemical Physics [20-25], in which the mobility of different states of tin on high surface area silica gel was studied. The result of the spectral area analysis is the plot shown in figure 2 of the tin mean square vibrational amplitude, $< X^2 >$, as a function of temperature ; clearly, a large value of $< X^2 >$ is then associated

with a high tin mobility. Furthermore, the temperature dependence of the spectral line width, due to diffusional line broadening, provided information complementary to that obtained from this spectral area analysis.
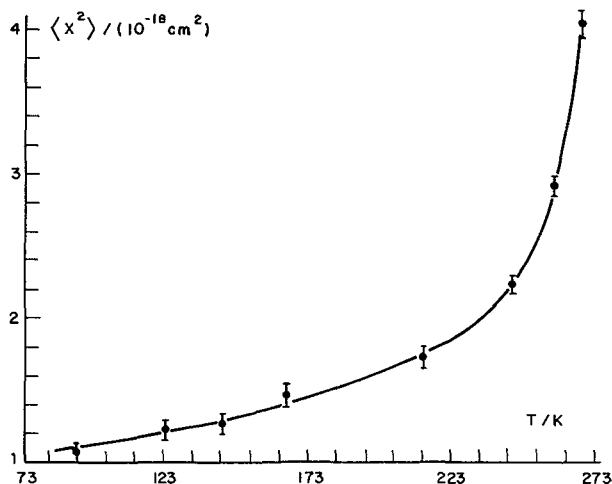

FIG. 2. — Mean Square Vibrational Amplitude of $SnO_2.nH_2O$ on Silica. Figure according to Suzdalev et al. [20].

For effective catalyst preparation, one must also consider the choice of catalytic materials. As a simplification, one may often speak of (1) the active component (i. e. the material that gives rise to the catalytic activity) and (2) the support (i. e. the material over or within which the highly dispersed active phase is found). (It should be noted that in bifunctional catalysis, both of the above phases are active for various parts of the overall catalytic process.) The choice of the active component is dictated by the catalytic reaction, and as such will not be discussed here ; however, the choice of the support rests to a large extent upon the nature of the interaction between it and the active phase, and this is amenable to study using Mössbauer spectroscopy.

For example, if the interaction between the two phases (the support interaction) is too weak, then the active phase may well sinter under catalytic reaction conditions leading eventually to a poorly dispersed catalyst. In contrast, if the support interaction is too strong, then an undesired oxidation state of the active component may be stabilized. These ideas are illustrated in the preparation of highly dispersed metallic iron. The support interaction for carbon is too weak resulting in large iron particles [26]. Silica provides too strong an interaction resulting in the formation of a highly dispersed Fe^{2+} phase upon catalyst reduction as shown by Mössbauer spectroscopy [27] ; when large amounts of iron are added to

the silica metallic iron is finally produced after reduction, but Mössbauer spectroscopy showed that the resulting phase is poorly dispersed [28, 29]. Finally, magnesium oxide has been found to be a convenient support for the preparation of highly dispersed metallic iron [30].

Virtually all of the Mössbauer parameters are sensitive in various cases to the support interaction. The isomer shift provides information about the oxidation state of the active phase and its modification or stabilization by the support interaction, as shown in the work of Ross and Delgass [31, 32]. After H_2 and CO treatment of Eu^{3+} supported on η-Al_2O_3 and Cab-O-Sil, the fraction of the europium converted to Eu^{2+} was found to be a function of the amount (weight %) of europium on the support. This point was illustrated analogously for iron in the previously referenced work of Hobson and Campbell [27]. For supported gold catalysts, Delgass et al. [33] observed that an electron deficient gold species (compared to metallic gold) was produced by a support interaction with η-Al_2O_3, and this was found from its isomer shift in the Mössbauer spectrum.

The quadrupole splitting gives information about the symmetry of the atoms in the active phase, and when this information is taken together with that obtained from the isomer shift, Mössbauer spectroscopy becomes sensitive to the location on and interaction with the support of the active metal atoms. The work performed on iron exchanged zeolites is a good example of problems of this type [34-44]. The combined consideration of these two parameters (isomer shift and quadrupole splitting), for example, were instrumental in leading Delgass et al. [38] to the assignment of Fe^{2+} ions in both the hexagonal prisms and near the hexagonal windows in dehydrated Y-zeolites.

The recoil-free fraction provides a measure of the strength of binding between the active component and the support. In this manner, Garten et al. [40] found that the adsorption of methylamine, dimethylamine and piperidine on Fe^{2+} exchanged in mordenite led to a spectral area decrease, thereby indicating a decrease in the support interaction upon adsorption. This is a fairly general result ; for example, analogous results were found by Dickson and Rees [41-43] for ethanol adsorption on and hydration of Fe^{2+} ions exchanged in A-zeolites. It should also be noted that by changing the size of the adsorbing gas and noting its effect on the Mössbauer parameters, additional information can be obtained about the location of active atoms within the support [38, 40].

Finally, support interactions were studied using the magnetic hyperfine interaction by Suzdalev et al. [45, 46] and Goldanskii et al. [47]. For Fe^{3+} exchanged in a sulforesin, the effect of water adsorption on the iron was to convert an asymmetric spectral doublet into a magnetically hyperfine split pattern as seen in figure 3. Thus, the adsorption of water weakened the

iron — support interaction resulting in an increase in the spin-lattice relaxation time for the Fe^{3+} ions.
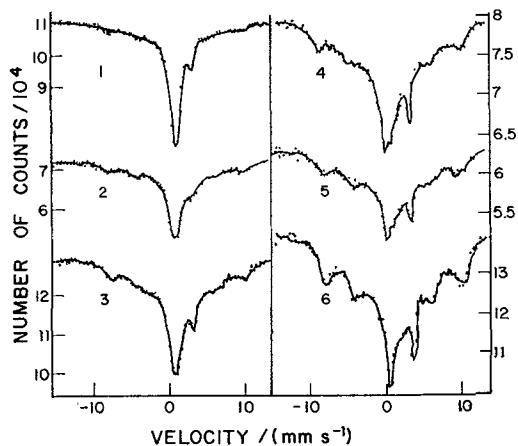

Fig. 3. — Effect of Degree of Hydration on the Mössbauer Spectrum of an Ion-Exchange Resin Containing Iron. Water concentration : (1) 0 ; (2) 0.32 ; (3) 1.24 ; (4) 2.93 ; (5) 4.5 ; (6) 6.0 H_2O molecules per sulfonic acid group. Zero velocity is with respect to a ^{57}Co in chromium source. Figure according to Goldanskii et al. [47].

To some extent the isomer shift [54] and the recoil-free fraction [55-62] may also be particle size dependent and therefore applicable to particle size measurement. It should be noted, however, that the relation between these parameters and the particle size may be rather complex, and experimental calibration of the spectral changes with particle size is usually required.

The most widely used method for particle size determination using Mössbauer spectroscopy involves superparamagnetic relaxation [17, 63]. Basically two approaches have been taken to the problem. In the first, theoretically generated spectra for various relaxation times (e. g. [64-66]) are compared (through computer analysis) with the observed spectrum for the highly dispersed sample to yield the average particle size and the particle size distribution [67]. If the particle size distribution is sufficiently broad, then a second approach may be taken in which particles with relaxation times, τ, longer than the nuclear Larmor precession time, τ_L, are assumed to be completely hyperfine split while particles with $\tau < \tau_L$ are assumed to be completely superparamagnetic [68]. As the temperature of the sample is varied, the relative spectral areas of hyperfine split and superparamagnetic components change, and the particle size distribution is thereby deduced [68]. The result of this procedure is demonstrated in figure 4 for α-Fe_2O_3 particles. It is

Throughout the above discussions, the factors important for the formation of highly dispersed samples were mentioned. In addition, it should now be shown that Mössbauer spectroscopy can also be used to obtain information about the actual value of the dispersion under catalytic reaction conditions. This is due to the sensitivity of the Mössbauer parameters to the size of the particles that make up the highly dispersed active phase.

The first parameter to consider is the quadrupole splitting. Due to the lower symmetry of surface atoms compared to the atoms « within » the particle, the quadrupole splitting for the former is expected to be different than that for the latter. This is the so-called shell model [48-50] for the quadrupole splitting, and from this model it follows that as the particle size decreases (the dispersion increases) (1) the average quadrupole splitting for the particle should change, and (2) separate spectral contributions from the surface and bulk atoms may possibly be resolved. Two complications may arise, however, in using this model for particle size determination. First, the quadrupole splitting for these highly dispersed systems may also be dependent on the gaseous environment over the sample [50] ; second, lattice distortions of the entire particle may affect the observed quadrupole splitting due to an internal pressure effect [51-53]. In general, however, through proper experimental calibration the quadrupole splitting provides a convenient particle size measurement.

Fig. 4. — Temperature and Particle Size Dependence of the Superparamagnetic Fraction for α-Fe_2O_3. The particle size histogram is obtained from the superparamagnetic fraction and the anisotropy constant. Figure according to Kündig et al. [68].

implied in both of the above methods that the magnitude of the magnetic anisotropy energy constant can be estimated from physical arguments or obtained experimentally on samples of known particle size.

A recent development pertinent to particle size determination has been made by Mørup and Topsøe [69]. The observed magnetic hyperfine field for highly dispersed samples is often found to be smaller than that for the corresponding massive samples. One explanation of this phenomenon is due to small collective thermal excitations of the magnetization within its magnetic anisotropy energy well. These excitations give rise to magnetic field fluctuations that produce a non-zero, but reduced, average magnetic field at the nucleus ; this is in contrast to *traditional* superparamagnetic fluctuations that give rise to a vanishing average magnetic field for the time scale of Mössbauer spectroscopy. Then, a measure of the decreased magnetic hyperfine field provides a probe of the anisotropy energy well, and the latter is related to the particle size. The combined use of traditional superparamagnetic relaxation methods and that technique based on collective thermal excitations of the magnetization may give important information about the particle size distribution and the nature of the dominant magnetic anisotropies [17, 70].

To close this discussion of catalyst preparation and characterization, *unsupported* catalysts must be mentioned. The above discussion has dealt with *supported* catalysts, and these are typically characterized by active component (1) dispersion between ca. 10 and 100 %, and (2) weight percent between ca. 1 and 10 %. On the other hand, unsupported catalysts are usually characterized by active component (1) dispersion between ca. 1 and 10 %, but (2) weight percent between ca. 90 and 100 %. That is, the dispersion is sacrificed for a greater active component surface area per *volume* of catalyst. (This may be important in catalytic reactor design considerations.)

The surface area of these unsupported catalysts must often be stabilized by the addition of small amounts (ca. several percent) of *textural promoters*. For example, Al_2O_3 is added to iron ammonia synthesis catalysts for this reason. An important question, however, is what is the mechanism of the Al_2O_3 promotion ? For this reason the location of the aluminum in the active catalyst must be determined. In this respect, Mössbauer spectroscopy has been shown to be instrumental [71]. For a reduced catalyst, the aluminum was concluded to be present both on the iron surface and within the iron particles as aluminum-rich clusters ; and, both of these *phases* may well contribute to surface area stabilization.

In addition to the textural promoters, small amounts of other compounds are added to unsupported catalysts, and this has the effect of increasing the catalytic activity per unit surface area ; these are the so-called *chemical promoters*. Again, knowledge of the location of these promoters in the catalyst is essential for understanding their effect. Along these lines it was found that the addition of lead to a magnetite based carbon monoxide shift catalyst increased the catalytic

activity ; and, Mössbauer spectroscopy showed that the lead entered the tetrahedral cation sites of the spinel structure [72]. In so doing the lead changed dramatically the bulk structure of the catalyst thereby resulting in the enhanced catalytic activity. For comparison, it should be mentioned that x-ray diffraction did not reveal these structural changes, illustrating the utility of Mössbauer spectroscopy in the study of catalytic systems of this type.

4. Surface properties of catalysts. — The understanding of catalytic processes on solid surfaces is linked to a knowledge of (1) the surface chemical state, and (2) the surface structure under reaction conditions. In this respect, Mössbauer spectroscopy is of value. When the average dimension of the catalyst particles is of the order of the escape depth for the internal conversion electrons, the surface sensitivities of the transmission and conversion electron backscattering geometries are comparable. A typical value of the electron escape depth (for 7 keV electrons) is ca. 100 nm corresponding to a dispersion of ca. 1 %. Thus, for samples with dispersions greater than ca. 1 % the transmission mode is favored, while for dispersions less than this value the backscattering geometry becomes more sensitive to surface phenomena. In addition, it should be noted that the backscattering mode also provides the possibility of depth profile analysis [73, 74].

The samples for surface study using Mössbauer spectroscopy are usually in the form of films or powders. In the former case, Meisel [15] used thick films and the backscattering geometry to study the oxidation of iron by water vapor ; and, Keune and Gonser [76] used thin films and the transmission mode to study the reaction of residual gases with vacuum deposited iron. When using powders for surface studies, highly dispersed samples are used almost exclusively since they allow *in situ* experiments to be conducted at high pressures.

Consider first the measurement of the surface chemical state. In general, the electronic properties of the surface atoms may be different than those of atoms within massive samples, and the surface composition (i. e. the relative surface concentrations of the different species of a multicomponent sample) may not be the same as the overall bulk composition. Both of these effects are expected to influence the catalytic activity and/or selectivity of the sample [77]. Two limiting cases may be imagined for the measurement of these effects using Mössbauer spectroscopy : (1) the *surface* and *bulk* contributions to the spectrum are sufficiently different so that they may be resolved (this is the shell model mentioned above with reference to the quadrupole splitting), or (2) the distinction between surface and bulk atoms is unclear and one must speak of a distribution of Mössbauer parameters.

These two cases are illustrated nicely in the work on

Pt-Fe and Pd-Fe highly dispersed bimetallic clusters. For the Pt-Fe system, Bartholomew and Boudart [78] found that the *surface* and *bulk* contributions to the Mössbauer spectrum could be resolved (as seen in Figure 5) and used to determine the small particle sur-
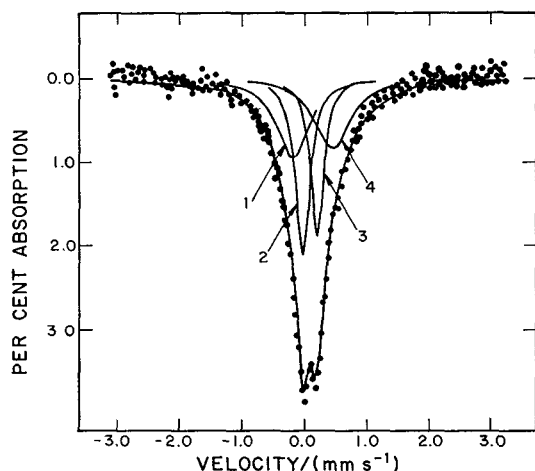

Fig. 5. — Computer-Fitted Mössbauer Spectrum for Small Particle Pt-Fe Alloy. Peaks (1) and (4) form the outer « surface » doublet. Peaks (2) and (3) form the inner *bulk* doublet. Zero velocity is with respect to a ^{57}Co in copper source. Figure according to Bartholomew and Boudart [78].

face composition. Furthermore, while the surface and bulk compositions need not be the same, the former may in addition be sensitive to the gaseous environment over the sample [79] ; these effects were in fact seen by Mössbauer spectroscopy. Small differences in the electron density at the nucleus of the surface and bulk atoms were also observed by these authors. On the other hand, Garten [80] found for the Pd-Fe system that the surface and bulk contributions could not be separated for reduced samples. However, after room temperature exposure of the samples to oxygen the *surface* atoms were found to oxidize to Fe^{3+}, while the *bulk* atoms remained as the initial Pd-Fe alloy. In this way the surface and bulk atoms could be separated in the Mössbauer spectrum using this treatment. This is shown in figures 6 and 7 for samples before and after the oxygen treatment, respectively ; it must be noted that the progressively higher reduction temperatures produce larger Pd-Fe alloy particles. The ambiguity of a surface analysis of this type (as pointed out by Garten) is that the (oxygen) treatment may affect a *pre-surface layer* rather than the surface atoms only ; the technique, however, still has qualitative value for surface composition analysis and, in general, for surface reactivity study.

At this point it seems appropriate to briefly discuss the catalytic properties of small particles (highly dispersed samples), since small particles are important

commercially and they are well suited for surface analysis using Mössbauer spectroscopy. It is often found that the catalytic activity and/or selectivity of a given active phase depends on the dispersion of that phase [81-85]. This variation may be the result of particle size dependent electronic properties or surface structure.

With respect to the former, particle size dependent electronic properties may be due to the finite number of atoms in the particle [86], an interaction with the support [87], and/or lattice modifications [54]. If present, these deviations should be evidenced in the Mössbauer parameters. For example, small isolated particles can be modeled by metal atoms at low concentration in a frozen rare gas matrix ; in this way Barrett and McNab [88] studied the electronic properties of Fe-Fe dimers. Alternatively, a highly dispersed catalytic system can be modeled by electrodeposition of the active metal on a suitable electrode surface or by vapor deposition of thin metal films. These techniques were used by Bowles and Cranshaw [89] in the investigation of electronic interactions between highly dispersed tin and a platinum electrode, and by Lauer *et al.* [90] to study thin films of iron on copper, respec-
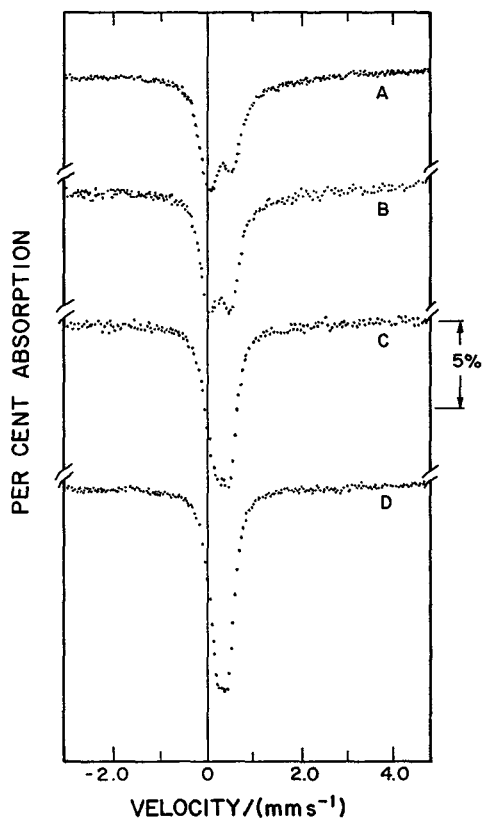

Fig. 6. — Mössbauer Spectra of FePd/η-Al$_2$O$_3$ Catalyst Reduced at Various Temperatures. Reduced in H$_2$(A) 1 h at 673 K ; (B) 1 h at 773 K ; (C) 1 h at 873 K ; (D) 2 h at 973 K. All spectra recorded at 298 K in 1 atm H$_2$. Zero velocity is with respect to a ^{57}Co in chromium source. Figure according to Garten [80].
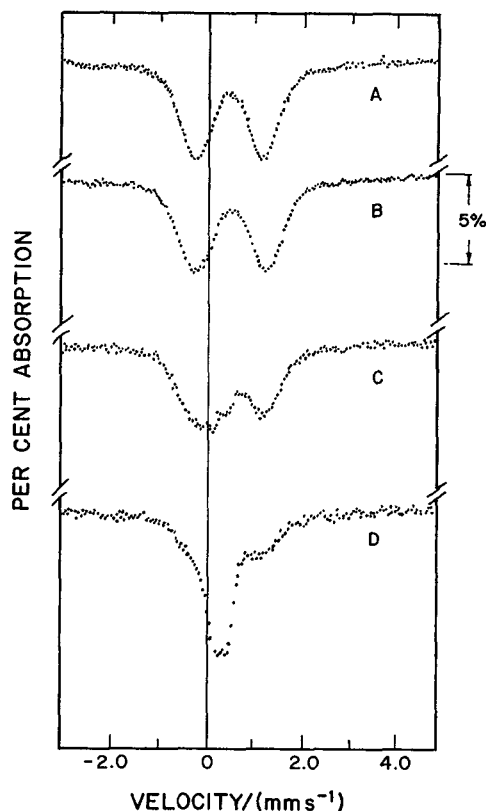
Fig. 7. — Mössbauer Spectra of FePd/η-Al₂O₃ Catalyst Reduced at Various Temperatures Followed by Evacuation and Exposure to 1 atm O₂ at 298 K. Exposed to oxygen after reduction (A) 1 h at 673 K ; (B) 1 h at 773 K ; (C) 1 h at 873 K ; (D) 2 h at 973 K. All spectra recorded at 298 K in 1 atm O₂. Zero velocity is with respect to a ⁵⁷Co in chromium source. Figure according to Garten [80].

tively. Finally, Boudart *et al.* [30] studied the electronic properties of highly dispersed iron ammonia synthesis catalysts, and they found no significant deviations from bulk properties for particles as small as 2 nm.

In addition to the electronic properties of the particle, it was mentioned above that one also speaks of the particle *surface structure* when interpreting the catalytic properties of highly dispersed systems. In this context, the catalyst surface structure is meant to describe the detailed geometric arrangement of the surface atoms. This definition is then consistent with the terminology of *structure sensitivity*, in which kinetic processes that depend on catalyst particle size are called structure sensitive [91]. Indeed, often the origin of an observed structure sensitivity is interpreted in terms of the relative numbers of face, edge and corner atoms on the particle surface (i. e. the surface structure), and their dependence on particle size. For purpose of analysis, relations are sought between the surface structure and physically obtainable quantities, in the present discussion the Mössbauer parameters.

One such parameter is the recoil-free fraction and its anisotropy. That is, the anisotropy of the recoil-free fraction can be determined for highly dispersed samples by taking advantage of the Goldanskii-Karyagin effect [92], remembering to take into consideration effects due to partial orientation of the sample [93, 94] ; then, this measured anisotropy can be related to the surface structure. While this relation is generally rather complex [92, 95, 97], a simplification may be in order for qualitative arguments [95]. Specifically, the mean square vibrational amplitude in a particular direction of a surface atom may be obtained by counting the number of bonds (and projections of bonds) in that direction between the central atom and its neighbors. In this way, the anisotropy of the recoil-free fraction for a surface atom is related to its « local structure » ; then, the surface structure is given by specifying the relative concentrations of surface atoms with specific numbers and orientations of nearest neighbors [98].

In a similar manner, the quadrupole splitting and the relaxation of the magnetic hyperfine field can be used to obtain surface structure information. For the former, the electric field gradient for a surface atom is determined by considering the local symmetry of that surface atom ; and for the latter, Néel's phenomenological theory of magneto-surface anisotropy may be used (when applicable) to provide the requisite relation between surface structure and magnetic relaxation time [99, 100]. For example, Boudart *et al.* [101] showed that the magnetic anisotropy energy barrier for small metallic iron particles is surface sensitive. In addition, the catalytic properties of these particles (for the ammonia synthesis reaction) were particle size dependent [102]. Then, using the surface sensitive magnetic anisotropy energy barrier, this structure sensitivity was interpreted in terms of the surface concentration (and its particle size dependence) of iron atoms with seven nearest neighbors [103], these atoms being particularly active for the synthesis of ammonia.

In cases where it is not possible to obtain or interpret detailed surface information using Mössbauer spectroscopy, it may still be possible to find a correlation between the catalytic properties of a sample and observables in the Mössbauer spectrum. Along these lines, Delgass *et al.* [33] found a correlation between the presence of an electron deficient gold species (compared to metallic gold) and catalytic activity for the oxidation of CO to CO_2. The quadrupole splitting of Fe^{3+} ions has been correlated with the selectivity to acrylonitrile in the ammoxidation of propylene over mixed iron oxides [104, 105] and zeolites [40]. Topsøe and Boudart. [72] found that the isomer shift of iron ions in magnetite based CO shift catalysts seemed to be related to the catalyst activity. The reducibility of Fe^{3+} to metallic iron and of Eu^{3+} to Eu^{2+} have been found to correlate with the catalytic

activities of these metals for butene hydrogenation [106] and the reverse CO shift [38] reaction, respectively. It should be noted here that when working with highly dispersed samples or when using the conversion electron backscattering mode, the Mössbauer spectrum will be surface sensitive and correlations of the above type may then be fairly straightforward ; however, for other types of samples Mössbauer spectroscopy is a « bulk » technique, and any correlation between the spectrum and catalytic activity will be necessarily indirect.

5. **Chemisorption and reaction.** — The first step in most catalytic processes is the chemisorption of reactant molecules on the catalyst surface, and it seems that a logical starting point for this section is the interaction of surface sites with gases. In such studies the Mössbauer isotope may be part of the catalyst surface and/or present in the chemisorbed species. Since the resulting Mössbauer spectrum is a sum of the contributions from the various different species present, in contrast to an average value only, information may be obtained about the nonuniformity of the surface for the studied chemisorption or catalytic process.

An investigation of this type (for which the Mössbauer isotope was part of the catalyst surface) was made by Hobson and Gager [107, 108]. These authors

FIG. 8. — Ammonia Adsorption Effect on the Mössbauer Spectrum of Silica Supported Iron. Ammonia added : *a*) 0.5 × 10⁻² millimoles NH₃ ; *b*) 1.64 × 10⁻² millimoles NH₃ ; *c*) 2.99 × 10⁻² millimoles NH₃ ; *d*) 4.31 × 10⁻² millimoles NH₃. Zero velocity is with respect to SNP. Figure according to Hobson and Gager [108].

studied the interaction of ammonia with iron supported on silica gel by collecting Mössbauer spectra for samples with different amounts of adsorbate (see Figure 8). A plot of the spectral area changes versus the amount of chemisorbed ammonia indicated definite surface non-uniformities, interpreted in terms of chemisorption on both the iron and the silica support. In addition, the multipeak Mössbauer spectrum (two overlapping doublets, peaks 1-2 and 1-3) was indicative of different types of iron adsorption sites. More recently, Gager et al. [109] have also studied the adsorption of H_2S and H_2O on silica gel supported iron.

As an example of an adsorption study for which the Mössbauer isotope is contained in the chemisorbed species, reference is made to the work of Karasev et al. [110, 111] and Maksimov et al. [112]. These authors studied the adsorption of SnR_4 (R = alkyl group) on γ-Al_2O_3 and Re_2O_7 supported on γ-Al_2O_3, respectively. The surface species present were found to be SnR_4, $SnR_{4-m}(OMe)_m$ ($m = 1, 2, 3$) and $Sn(OMe)_4$, where OMe represents a surface oxygen-metal ion group.

One should now consider the possibility of using Mössbauer spectroscopy to study the kinetics of reaction processes. If the time scale for the chemical changes is greater than the time required to collect the Mössbauer spectrum, then the application of Mössbauer spectroscopy is straightforward ; in addition, temperature *quenching* procedures can be employed to effectively reduce the data collection time at the reaction temperature to several seconds. A review of Mössbauer spectroscopy applied to the study of chemical reactions has recently been published by Vertes [113].

The oxidation of metallic iron films is an example of a process that has been studied by Mössbauer spectroscopy. Channing et al. [114, 115], using the transmission geometry, found that Fe_3O_4 is an intermediate in the ultimate formation of α-Fe_2O_3 upon exposure of iron to oxygen at 750 K. Simmons et al. [116] used the conversion electron backscattering mode to detect nonstoichiometric Fe_3O_4 after oxygen treatment of iron at 700 K. The kinetics of iron oxidation by water at ca. 500 K were studied by Pritchard and Dobson [117] ; again, Fe_3O_4 was the major reaction product, and the rate of reaction decreased as the magnetite layer thickness increased.

The oxidation of highly dispersed samples was studied by Topsøe et al. [118] and Suzdalev et al. [119]. The former authors worked with small particles of Fe_3O_4, and the latter investigated highly dispersed tin. In both cases, however, the behavior of these particles was not the same as that for the respective massive samples. This is reminiscent of the *particle size effects* discussed previously.

Another class of reactions that are well suited for study using Mössbauer spectroscopy are decomposition reactions [120-123]. The particularly interesting feature of experiments of this type is the combined
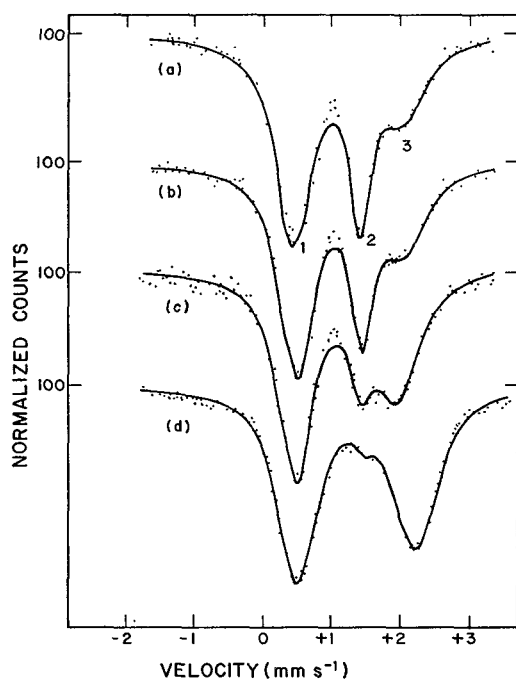
use of differential thermal analysis (DTA) and gravimetry (DTG) with Mössbauer spectroscopy. Peaks in the DTA and DTG curves at specific temperatures (indicating changes in enthalpy and weight of the sample, respectively) identify temperature intervals in which certain decomposition products are stable. A Mössbauer spectrum then recorded with the sample temperature between two such peaks (or after temperature quenching) serves to identify the corresponding solid decomposition products.

In contrast to the above reactions, the time scale of most catalytic processes is too short for practical observation of the associated kinetics using Mössbauer spectroscopy. Instead, the utility of Mössbauer spectroscopy lies in the determination of the steady state surface properties under reaction conditions. More quantitatively, catalytic reaction rates are often expressed as *turnover numbers*, defined as the number of product molecules formed (or the number of reactant molecules consumed) per surface atom per second. A typical value of the turnover number for catalytic reactions occurring at atmospheric pressure lies between 10^{-2} and 1 s^{-1} corresponding to reaction time scales of 10^2 and 1 s.

Studies of this type have been carried out by Maksimov et al. [124, 125], Dumesic et al. [103], and they have been discussed elsewhere [18]. The reactions studied were (1) the partial oxidation of propylene to acrolein over $CoMoO_4$ doped with ^{57}Fe [124], (2) the partial oxidation of methanol to formaldehyde over nonstoichiometric iron molybdate [125], and (3) the synthesis of ammonia from hydrogen and nitrogen over metallic iron [103]. For the first two reactions, the iron initially entered the catalysts mainly in the trivalent state. However, during reaction partially reduced forms of iron were observed ; indeed, these forms disappeared upon termination of the reactions. The interpretation of these results was in terms of oxygen vacancy formation (due to hydrogen transfer from the organic adsorbate to the oxide surface, followed by surface dehydroxylation) during reaction, and partial electron transfer from these vacancies to neighboring Fe^{3+} ions. In the third reaction mentioned above, the magnetic state of highly dispersed metallic iron catalysts was measured under reaction conditions. Catalysts with high activities were characterized by small magnetic anisotropy energy barriers. Using Néel's theory of magneto-surface anisotropy (as discussed previously) it was thereby concluded that

surface iron atoms with seven nearest neighbors were particularly active for the catalytic synthesis of ammonia. It was also shown that the surface concentration of these specific surface atoms was dependent on the gaseous environment over the sample, illustrating the necessity for *in situ* Mössbauer experiments in problems of this type.

In most of the examples given in this paper, the catalyst or chemisorbed species contained a Mössbauer isotope. For this reason it seems appropriate to close this section by noting that through the addition of small amounts (several percent) of a Mössbauer isotope to a given catalytic system, this isotope can serve as a probe of its structure. This concept becomes important for the general application of Mössbauer spectroscopy to heterogeneous catalysis. In this way, ^{57}Fe was used to probe highly dispersed platinum [78] and palladium [126] catalysts ; ^{119}Sn has been used to study molybdenum catalysts [127] ; and the structure of highly dispersed cobalt-molybdate catalysts for hydrodesulfurization was probed using ^{57}Fe [128] and ^{57}Co [129]. The ultimate choice of a particular Mössbauer isotope as the probe of a certain catalyst depends on (1) the compatibility of the isotope with the structure that it must probe, (2) the extent to which this isotope actually serves as a *witness* of the catalytically active surface sites, and (3) the sensitivity of the isotope nuclear energy levels to surrounding chemical changes. This latter consideration has recently been discussed for the various Mössbauer isotopes by Dumesic and Topsøe [17].

6. **Concluding remark.** — The understanding of catalytic phenomena on solid surfaces is closely related to a knowledge of the surface properties of the catalyst under reaction conditions. Two approaches can be taken to the problem depending on point of view. One may study the solid state properties of the catalyst and ultimately extend these to the surface ; and, one may choose to investigate the surface adsorbed species present on the catalyst. Indeed, both of these complementary approaches may be taken using Mössbauer spectroscopy, with the appropriate Mössbauer isotope in the catalyst structure or the adsorbed species, respectively. In addition, Mössbauer spectroscopy may be used to study problems in catalyst preparation and characterization. These features have led to the continued application of this technique to problems in heterogeneous catalysis.

References

[1] HERBER, R. H., *Prog. Inorg. Chem.* **8** (1967) 1.
[2] GREENWOOD, N. N., *Chem. Brit.* **3** (1967) 56.
[3] DELGASS, W. N. and BOUDART, M., *Catal. Rev.* **2** (1968) 129.
[4] SHIRLEY, D. A., *Ann. Rev. Phys. Chem.* **20** (1969) 25.
[5] GOLDANSKII, V. I. and SUZDALEV, I. P., *Proc. Conf. Appl. Mössbauer Effect* (I. Dezci, Ed.) Tihany (Hungary), p. 269 (1969).

[6] HOBERT, H. and ARNOLD, D., *Z. Chem.* **9** (1969) 410.
[7] GOLDANSKII, V. I. and SUZDALEV, I. P., *Russ. Chem. Rev.* **39** (1970) 609.
[8] GREENWOOD, N. N., *Angew. Chem. Internat. Edit.* **10** (1971) 716.
[9] MÖSSBAUER, R. L., *Angew. Chem. Internat. Edit.* **10** (1971) 462.

[10] BOUDART, M., GARTEN, R. L. and DELGASS, W. N., *Mem. Soc. Roy. Sci. Liege* **1** (1971) 135.

[11] HOBSON, M. C., Jr., *Adv. Coll. Inter. Sci.* **3** (1971) 1.

[12] HOBSON, M. C., Jr., *Surf. Membrane Sci.* **5** (1972) 1.

[13] HOBSON, M. C., Jr., in *Characterization of Solid Surfaces* (P. F. Kane and G. B. Lanabee, Eds.) (Plenum Press, N. Y.), p. 379, 1974.

[14] GAGER, H. M. and HOBSON, M. C., Jr., *Catal. Rev. Sci. Eng.* **11** (1975) 117.

[15] GOLDANSKII, V. I., MAKSIMOV, Yu. V. and SUZDALEV, I. P., in *Proc. Int. Conf. Mössbauer Spec.* (Cracow, Poland 1975) Akademia Górzniczo-Hutnicza Im. S. Staszica W. Krakowie, Vol. 2, p. 163, 1975.

[16] DELGASS, W. N., *Mössbauer Effect Methodology* **10** (1976).

[17] DUMESIC, J. A. and TOPSØE, H., *Adv. Catal.* **26** (1976) 121.

[18] DUMESIC, J. A., MAKSIMOV, Yu. V. and SUZDALEV, I. P., *Mössbauer Effect Methodology* **10** (1976).

[19] MORIKAWA, K., SHIRASAKI, T. and OKADA, M., *Adv. Catal.* **20** (1969) 97.

[20] SUZDALEV, I. P., GOLDANSKII, V. I., MAKAROV, E. F., PLACHINDA, A. S. and KORYTKO, L. A., *Sov. Phys. JETP* **22** (1966) 979.

[21] GOLDANSKII, V. I., SUZDALEV, I. P., PLACHINDA, A. S. and SHTYRKOV, L. G., *Dokl. Akad. Nauk SSSR* **169** (1966) 872.

[22] SUZDALEV, I. P., PLACHINDA, A. S., MAKAROV, E. F. and DOLGOPOLOV, V. A., *Russ. J. Phys. Chem.* **41** (1967) 1522.

[23] SUZDALEV, I. P., PLACHINDA, A. S. and MAKAROV, E. F., *Sov. Phys. JETP* **26** (1968) 897.

[24] KORDYNK, S. L., LISICHENKO, V. I. and SUZDALEV, I. P., *Kolloid. Zhurnal* **33** (1971) 374.

[25] PLACHINDA, A. S., SUZDALEV, I. P., GOLDANSKII, V. I. and NEIMARK, I. E., *Teor. Eksp. Khim.* **6** (1970) 347.

[26] KALVIUS, M., *Mössbauer Effect Methodology* **1** (1965) 163.

[27] HOBSON, M. C., Jr. and CAMPBELL, A. D., *J. Catal.* **8** (1967) 294.

[28] YOSHIOKA, T., KOEZUKA, J. and IKOMA, H., *J. Catal.* **16** (1970) 264.

[29] HOBERT, H. and ARNOLD, D., in *Proc. Conf. Appl. Mössbauer Effect* (Tihany, Hungary, 1969) Akademiai Kiado, Budapest, p. 325, 1969.

[30] BOUDART, M., DELBOUILLE, A., DUMESIC, J. A., KHAMMOUMA, S. and TOPSØE, H., *J. Catal.* **37** (1975) 486.

[31] ROSS, P. N., Jr. and DELGASS, W. N., *Catalysis*, Vol. I (J. W. Hightower, Ed.), p. 597 (North Holland, Amsterdam), 1973.

[32] ROSS, P. N., Jr. and DELGASS, W. N., *J. Catal.* **33** (1974) 219.

[33] DELGASS, W. N., BOUDART, M. and PARRAVANO, G., *J. Phys. Chem.* **72** (1968) 3563.

[34] DELGASS, W. N., GARTEN, R. L. and BOUDART, M., *J. Chem. Phys.* **50** (1969) 4603.

[35] GOLDANSKII, V. I., SUZDALEV, I. P., PLACHINDA, A. S. and SHTYRKOV, L. G., *Dolk. Akad. Nauk SSSR* **169** (1966) 872.

[36] MORICE, J. A. and REES, L. V. C., *Trans. Faraday Soc.* **64** (1968) 1388.

[37] WEDD, R. W. J., LIENGME, B. V., SCOTT, J. C. and SAMS, J. R., *Solid State Commun.* **7** (1969) 1091.

[38] DELGASS, W. N., GARTEN, R. L. and BOUDART, M., *J. Phys. Chem.* **73** (1969) 2970.

[39] GARTEN, R. L., DELGASS, W. N. and BOUDART, M., *J. Catal.* **18** (1970) 90.

[40] GARTEN, R. L., GALLARD-NECHTSCHEIN, J. and BOUDART, M., *Ind. Eng. Chem. Fundam.* **12** (1973) 299.

[41] DICKSON, B. L. and REES, L. V. C., *J. C. S. Faraday I* **70** (1974) 2038.

[42] DICKSON, B. L. and REES, L. V. C., *ibid.* **70** (1974) 2051.

[43] DICKSON, B. L. and REES, L. V. C., *ibid.* **70** (1974) 2060.

[44] MEISEL, W., PLACHINDA, A. S. and SUZDALEV, I. P., *Z. Anorg. Allg. Chem.* **382** (1971) 188.

[45] SUZDALEV, I. P., AFANASEV, A. M., PLACHINDA, A. S., GOLDANSKII, V. I. and MAKAROV, E. F., *Sov. Phys. JETP* **28** (1969) 923.

[46] SUZDALEV, I. P., KORNEEV, V. P. and KRUPIANSKY, Yu. F., *Proc. Conf. Appl. Mössbauer Effect* (Tihany, Hungary, 1969) Akademiai Kiado, Budapest, p. 147, 1969.

[47] GOLDANSKII, V. I., SUZDALEV, I. P., PLACHINDA, A. S. and KORNEEV, V. P., *Dolk. Akad. Nauk SSSR* **185** (1969) 629.

[48] KÜNDIG, W., ANDO, K. J., LINDQUIST, R. H. and CONSTABARIS, G., *Czech. J. Phys.* **B 17** (1967) 467.

[49] HOBSON, M., Jr., *J. Electrochem. Soc.* **115** (1968) 175C.

[50] GAGER, H. M., HOBSON, M. C., Jr. and LEFELHOCZ, J. F., *Chem. Phys. Lett.* **15** (1972) 124.

[51] SCHROEER, D., in *Mössbauer Effect Methodology* **5** (1969) 141.

[52] SCHROEER, D. and NININGER, R. C., Jr., *Phys. Rev. Lett.* **19** (1967) 632.

[53] SCHROEER, D., *Phys. Lett.* **27A** (1968) 507.

[54] SCHROEER, D., MARZKE, R. F., ERICKSON, D. J., MARSHALL, S. W. and WILENZICK, R. M., *Phys. Rev.* **B 2** (1970) 4414.

[55] GOLDANSKII, V. I. and SUZDALEV, I. P., *Russ. Chem. Rev.* **39** (1970) 609.

[56] MARSHALL, S. W. and WILENZIK, R. M., *Phys. Rev. Lett.* **16** (1966) 219.

[57] SUZDALEV, I. P., GEN, M. Ya., GOLDANSKII, V. I. and MAKAROV, E. F., *Soviet Phys. JETP* **51** (1966) 118.

[58] AKSELROD, S., PASTERNAK, M. and BUKSHPAN, S., *Phys. Rev.* **B 11** (1975) 1040.

[59] ROTH, S. and HÖRL, E. M., *Phys. Lett.* **25A** (1967) 299.

[60] VIEGERS, M. P. A., VAN EIJKEREN, J. C. H., VAN DEVENTER, M. M. and TROOSTER, J. M., in *Proc. Int. Conf. Mössbauer Spec.* (Cracow, Poland, 1975) Akademia Górniczo-Hutnicza Im. S. Staszica W Krakowie, Vol. 1, p. 201, 1975.

[61] VAN WIERINGER, J. S., *Phys. Lett.* **26A** (1968) 370.

[62] RUPPIN, R., *Phys. Rev.* **B 2** (1970) 1229.

[63] COLLINS, D. W., DEHN, J. T. and MULAY, L. N., *Mössbauer Effect Methodology* **3** (1967) 103.

[64] WICKMAN, H. H., KLEIN, M. P. and SHIRLEY, D. A., *Phys. Rev.* **152** (1966) 345.

[65] BLUME, M., *Phys. Rev. Lett.* **18** (1967) 305.

[66] BLUME, M. and TJON, J. A., *Phys. Rev.* **165** (1968) 446.

[67] MCNAB, T. K., Ph. D. Dissertation, University of Western Australia, 1968.

[68] KÜNDIG, W., BÖMMEL, H., CONSTABARIS, G. and LINDQUIST, R. H., *Phys. Rev.* **142** (1966) 327.

[69] MØRUP, S. and TOPSØE, H., *Appl. Phys.* in press.

[70] MØRUP, S., TOPSØE, H. and LIPKA, J., this conference.

[71] TOPSOE, H., DUMESIC, J. A. and BOUDART, M., *J. Catal.* **28** (1973) 477.

[72] TOPSØE, H. and BOUDART, M., *J. Catal.* **31** (1973) 346.

[73] BONCHEV, Z. W., JORDANOV, A. and MINKOVA, A., Proc. *Conf. Appl. Mössbauer Effect* (Tihany, Hungary, 1969) Akademiai Kiado, Budapest, p. 333, 1969.

[74] BONCHEV, Z. W., JORDANOV, A. and MINKOVA, A., *Nucl. Instrum. Meth.* **70** (1969) 36.

[75] MEISEL, W., *Z. Chem.* **11** (1971) 238.

[76] KEUNE, W. and GONSER, U., *Thin Solid Films* **7** (1971) R 7.

[77] SINFELT, J. H., *Adv. Catal.* **23** (1973) 91.

[78] BARTHOLOMEW, C. H. and BOUDART, M., *J. Catal.* **29** (1973) 278.

[79] WILLIAMS, F. L. and NASON, D., *Surf. Sci.* **45** (1974) 377.

[80] GARTEN, R. L., *J. Catal.*, in press.

[81] O'CINNEIDE, A. D. and CLARKE, J. K. A., *Catal. Rev.* **7** (1973) 213.

[82] GWATHMEY, A. T. and CUNNINGHAM, R. E., *Adv. Catal.* **10** (1958) 57.

[83] BOND, G. C., *Disc. Faraday Soc.* **41** (1966) 200.

[84] SINFELT, J. H., *Catal. Rev.* **3** (1970) 175.

[85] ANDERSON, J. R. and BAKER, B. G., in *Chemisorption and Reactions on Metallic Films*, Vol. 2 (J. R. Anderson, Ed.) (Academic Press, N. Y.) p. 64, 1971.

[86] BAETZOLD, R. C., *J. Catal.* **29** (1973) 129.

[87] DALLA BETTA, R. A. and BOUDART, M., *Fifth Intl. Congress Catal.* (J. Hightower, Ed.) (Amer. Elsevier Co., N. Y.), p. 1329, 1973.

[88] BARRETT, P. H. and MCNAB, T. K., *Phys. Rev. Lett.* **25** (1970) 1601.

[89] BOWLES, B. J. and CRANSHAW, T. E., *Phys. Lett.* **17** (1965) 258.

[90] LAUER, J., KEUNE, W. and SHINJO, T., *Proc. Intl. Conf. Mössbauer Spectroscopy* (Crakow, Poland 1975) (Akademia Górniczo-Hutnicza Im. S. Staszica W Krakowie), Vol. 1, p. 41, 1975.

[91] BOUDART, M., ROBERT, A., *Welch Foundation Conferences on Chemical Research, XIV. Solid State Chemistry* (W. O. Milligan, Ed.) Houston, Texas, p. 299, 1971.

[92] SUZDALEV, I. P. and MAKAROV, E. F., *Proc. Conf. Appl. Mössbauer Effect* (Tihany, Hungary, 1969) (Akademiai Kiado, Budapest) p. 201, 1969.

[93] PFANNES, H. D. and GONSER, U., *Appl. Phys.* **1** (1973) 93.

[94] KREBER, E. and GONSER, U., *Nucl. Inst. Methods* **121** (1974) 17.

[95] BURTON, J. W. and GODWIN, R. P., *Phys. Rev.* **158** (1967) 218.

[96] CORCIOVEI, A. and RADESCU, E., *Phys. Lett.* **23** (1966) 32.

[97] VAIL, J., *Can. J. Phys.* **45** (1967) 2661.

[98] VAN HARDEVELD, R. and HARTOG, F., *Surf. Sci.* **15** (1969) 189.

[99] NÉEL, L., *C. R. Hebd. Sean. Acad. Sci.* **237** (1953) 1468.

[100] NÉEL, L., *J. Physique Radium* **15** (1954) 225.

[101] BOUDART, M., DUMESIC, J. A. and TOPSØE, H., Physical Basis of Catalysis (E. Drauglis and R. I. Jaffee, Eds.) (Plenum Press), p. 337, 1975.

[102] DUMESIC, J. A., TOPSØE, H., KHAMMOUMA, S. and BOUDART, M., *J. Catal.* **37** (1975) 503.

[103] DUMESIC, J. A., TOPSØE, H. and BOUDART, M., *J. Catal.* **37** (1975) 513.

[104] SKALKINA, L. V., SUZDALEV, I. P., KOLCHIN, I. K. and MARGOLIS, L. Ya., *Kinet. Katal.* **10** (1969) 378.

[105] KRIEGSMANN, H., ÖHLMANN, G., SCHEVE, J. and ULRICH, F. J., Sixth Intl. Cong. Catal., Preprint **B 23** 1976.

[106] HOBSON, M. C., Jr. and GAGER, H. M., *Fourth Inter. Congr. Catalysis* (G. K. Boreskov, Ed.), Vol. 2, p. 28, Akademiai Kiado, Budapest, 1971.

[107] HOBSON, M. C., Jr., *Nature* **214** (1967) 79.

[108] HOBSON, M. C., Jr. and GAGER, H. M., *J. Colloid and Inter. Science* **34** (1970) 357.

[109] GAGER, H. M., LEFELHOCZ, J. F. and HOBSON, M. C., Jr., *Chem. Phys. Lett.* **23** (1973) 386.

[110] KARASEV, A. N., POLAK, L. S., SHLIKHTER, E. B. and SHPINEL, V. S., *Zh. Fiz. Khimii* **39** (1965) 3117.

[111] KARASEV, A. N., KOLBANOVSKII, Yu. A., POLAK, L. A. and SHLIKHTER, E. B., *Kinet. Katal.* **8** (1967) 232.

[112] MAKSIMOV, Yu. V., DUMESIC, J. A., KUSHNEREV, M. Ya., NECHITAILO, A. E. and FRIDMAN, R. A., *J. Catal.* **45** (1976) 114.

[113] VERTES, A., in *Proc. Fifth Int. Conf. Mössbauer Spec.* (Bratislava, Czechoslovakia, 1973) Czechoslovak Atomic Energy Commission, Praha, p. 179, 1975.

[114] CHANNING, D. A. and GRAHAM, M. J., *J. Electrochem. Soc. Solid State Science* **117** (1970) 389.

[115] CHANNING, D. A., DICKERSON, S. M. and GRAHAM, M. J., *Corros. Sci.* **13** (1973) 933.

[116] SIMMONS, G. W., KELLERMAN, E. and LEIDHEISER, H., Jr., *Corrosion* **29** (1973) 227.

[117] PRITCHARD, A. M. and DOBSON, C. M., *Nature* **224** (1969) 1295.

[118] TOPSØE, H., DUMESIC, J. A. and BOUDART, M., *J. Physique Colloque* **35** (1974) C 6-411.

[119] SUZDALEV, I. P., MAKAROV, E. F., GARZANOV, I. Ya. and KORYTKO, L. A., *Kinet. Katal.* **6** (1965) 1108.

[120] HALSEY, M. J. and PRITCHARD, A. M., *J. Chem. Soc.* (A) (1968) 2878.

[121] SUZDALEV, I. P., SHKARIN, A. V., ZHABROVA, G. M., GOLDANSKII, V. I., KORYTKO, L. A. and KADENATSI, B. M., *Kinet. Katal.* **7** (1966) 919.

[122] ZHABROVA, G. M., SUZDALEV, I. P., GOLDANSKII, V. I., SHKARIN, A. V. and MAKAROV, E. F., *Teor. Eksp. Khim.* **3** (1967) 483.

[123] SUZDALEV, I. P. and KRUPYANSKII, Yu. F., *Kinet. Katal.* **10** (1969) 1254.

[124] MAKSIMOV, Yu. V., SUZDALEV, I. P., GOLDANSKII, V. I., KRYLOV, O. V., MARGOLIS, L. Ya. and NECHITAILO, A. E., *Chem. Phys. Lett.* **34** (1975) 172.

[125] MAKSIMOV, Yu. V., SUZDALEV, I. P., GOLDANSKII, V. I., MATVEEV, A. I., MAKAROV, E. F. and MARGOLIS, L. Ya., *Dokl. Akad. Nauk SSSR*, in press.

[126] GARTEN, R. L. and OLLIS, D. F., *J. Catal.* **35** (1974) 232.

[127] FIRSOVA, A. A., KHOVANSKAGA, N. N., TSYGANOV, A. D., SUZDALEV, I. P. and MARGOLIS, L. Ya., *Kinet. Katal.* **12** (1971) 792.

[128] TOPSØE, H. and MØRUP, S., in *Proc. Int. Conf. Mössbauer Spec.* (Cracow, Poland, 1975) Akademia Górniczo-Hutnicza Im. S. Staszica W Krakowie, Vol. 1, p. 305, 1975.

[129] CLAUSEN, B. S., TOPSØE, H., MØRUP, S. and CANDIA, R., this conference.