JOURNAL OF CATALYSIS 10, 69–72 (1968)

# Activation Entropy and Electronic Properties of Metal Catalysts*

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Received October 3, 1967; revised November 6, 1967

The catalytic properties of metals and alloys are explored on the basis of electron promotion to a localized band as a factor in heterogeneous catalysis. The availability of electronic energy levels in the solid is related to the activation entropy associated with the surface reaction. The analysis, in conjunction with existing molecular orbital calculations, suggests that filling of *d*-band holes distributed between the $e_g$ and $t_{2g}$ orbitals of transition metals is reflected in measurements of the catalytic properties of some Group VIII-IB alloys.

Recent studies in heterogeneous catalysis have dealt with the quantum mechanical treatment of solid surfaces in terms of metallic orbitals and their relationship to the bonding of absorbates. Because of the fundamental complexity of this problem when applied to a continuum solid surface, an attempt has been made to interpret surface reactivity in terms of the isolated surface atom–ligand bonding (similar to that encountered in organometallic compounds) and to extend the molecular orbital model of the solid state to the solid–gas interface (*1–3*). However, it is apparent that the energy levels and the electron occupancy of the valence-shell atomic orbitals of the surface atom will be influenced by the neighboring atoms in the lattice of the solid. Consequently, an understanding of the collective electronic properties of the solid is essential in exploring the concept of electron transfer and exchange in heterogeneous catalysis (*4*). In the case of metals, a measure of this effect can be deduced from a correlation of the catalytic properties of completely miscible alloys with changes in electronic properties of the solid.

## THEORETICAL ANALYSIS

Using the hypothesis that catalytic action is related to the promotion of an electron to a localized band (covalent or ionic), we can estimate the energetics associated with bonding of the surface intermediate (or with population of a surface energy state) from the entropy change per electron associated with this process. In the simple band model for metals (*5*) the entropy change per electron is governed by the gradient of the density-of-state curve at the Fermi level

$$\Delta S = \frac{1}{3}\frac{\pi^2\kappa^2 T}{N(\epsilon)}\left[\frac{\partial N(\epsilon)}{\partial \epsilon}\right]_{\epsilon_F} \qquad (1)$$

where $\kappa$ is the Boltzmann constant, $T$ is the temperature, $\epsilon$ is energy, and $N(\epsilon)$ is the density-of-states term which denotes the number of stationary states per unit volume of metal that are available to an electron in the energy range of $\epsilon$ to $\epsilon + d\epsilon$. At absolute zero temperature, all stationary states with energy below the Fermi level, $\epsilon_F$, are doubly occupied as demanded by the Pauli exclusion principle, so that the total number density of electrons is given by

$$2\int_0^{\epsilon_F} N(\epsilon)\, d\epsilon$$

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* This work was carried out under the sponsorship of a group of industrial companies whose support is gratefully acknowledged.

According to Eq. (1), changes in the electron-level density at the Fermi surface would be expected to contribute to the entropy term. Both positive and negative changes may occur, depending on the sign of the gradient $[d \ln N(\epsilon)/d\epsilon]$ at the Fermi level. For transition metals, the density-of-states curves of the *d* band exhibit nonmonotonic fluctuations as a function of energy. Therefore, the derivative would be expected to vary both in magnitude and sign as the *d* band is gradually filled by alloying with nontransition metals that tranfer *s* electrons into the *d* band.

A measure of the variation of the gradient $[d \log N(\epsilon)/d\epsilon]_{\epsilon_F}$ can be obtained from the electronic transport properties of metals. To a first approximation the thermoelectric power $Q$ is made up of two terms (*6*)

$$Q = \frac{\pi^2}{3}\kappa^2 T \frac{\partial}{\partial\epsilon}[\ln \Lambda + \ln \sigma]_{\epsilon_F} \qquad (2)$$

where $\Lambda$ represents the electron mean free path, and $\sigma$ is the area of the Fermi surface. Since $\Lambda$ is inversely proportional to $N(\epsilon)$, especially for transition metals that scatter *s* electrons into the high-density *d* band states, we can write Eq. (2) in the following form:

$$-Q = \frac{\pi^2\kappa^2 T}{3}\left[\frac{\partial \ln N(\epsilon)}{\partial\epsilon}\right]_{\epsilon_F} - \frac{\pi^2\kappa^2 T}{3}\left[\frac{\partial \ln \sigma}{\partial\epsilon}\right] \qquad (3)$$

The term in Eq. (3) associated with the Fermi surface area $\sigma$ and its variation with electron energy is difficult to assess, since it will depend on the detailed geometry of the Brillouin zone. However, if we assume the model of a free electron metal, $\sigma$ is found to be proportional to $\epsilon_F$. Since $\epsilon_F$ does not vary greatly as a result of alloying, we can approximate this contribution to Q by

$$\pi^2\kappa^2 T/3\epsilon_F = \text{constant}$$

The first term on the right-hand side of Eq. (3) is the entropy change of interest in this analysis. It can be expected, therefore, that experimental data on the variation of thermoelectric power with alloy composition offer valuable information on the entropy changes associated with electron promotion.

In Table 1, some published experimental results (*7*) on the thermoelectric power of the Pd-Ag systems are summarized. The data indicate that the thermoelectric power diminishes to a minimum value at 60 atom % Pd, a composition far removed from a filled *d* band. In terms of our model, the entropy change would be expected to follow a similar trend, except for a reversal of sign. In the presence of hydrogen, the thermoelectric power of the Pd-Ag system is further decreased (*8*) in magnitude but still attains a minimum at 60 atom % Pd (*8*). By comparison with available solubility data (*9*), it appears that the decrease is directly related to the amount of hydrogen absorbed.

TABLE 1

THERMOELECTRIC POWER OF Pd-Ag ALLOYS[a]

| Composition (atom % Pd) | Thermoelectric power (volts/deg) × $10^8$ |
|---|---|
| 100 | −1.5 |
| 90 | −10 |
| 80 | −17 |
| 70 | −23 |
| 60 | −36 |
| 50 | −22 |
| 40 | −10 |
| 30 | −5 |
| 20 | 0 |
| 10 | +4 |
| 0 | +6 |

[a] Reference (*7*).

The absolute magnitude of the entropy change cannot be estimated because of our lack of knowledge of the contribution of the changes in Fermi surface area with alloy composition. However, the qualitative information on the sign of the entropy change and the location of the minimum value offer an interesting solid-state parameter for correlation with catalytic parameters.

## CATALYTIC CONSEQUENCES

Since the entropy changes under discussion are related to the availability of electronic energy levels of importance in bond formation, it is of interest to examine the information to be gained from recent application of molecular orbital theory to surface phenomena. In accordance with crystal field theory, the five *d* orbitals associated with face-centered cubic (fcc) metals of the transition group (VIII$_3$) are split into two groups. The $e_g$ orbitals ($d_{x^2-y^2}$, $d_{z^2}$) represent the two orbitals of higher energy along the Cartesian axes, while the three $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$, $d_{xz}$) fall between the Cartesian axes and are of lower energy. Certain aspects of the band structure for fcc transition metals have been examined by Goodenough (*10*). This model concludes that the collective $t_{2g}$ electrons occupy a metallic band, while the $e_g$ electrons occupy localized states. The emergence of the various orbitals from the low index planes of an fcc crystal has been depicted by Bond (*2*) in an examination of the participation of the various orbitals in covalent bond formation with surface-adsorbed species. Qualitatively, such analysis offers an interpretation for the existence of weakly bound and strongly bound adsorbates in terms of the various orbitals involved in bond formation.

In addition, the molecular orbital approach yields for the fcc crystal a semiempirical density-of-states curve (*10, 11*) from which the extent of occupation of the various bands can be estimated. For a Group VIII metal such as nickel, Goodenough (*10*) assigns a ratio of 3:1 for the distribution of the 0.55 *d*-band holes between the $t_{2g}$ and $e_g$ bands, while for iron (0.95 *d*-band holes) a completely vacant $e_g$ band is postulated. Some very recent experimental studies (*12*) of the De Haas–Van Alphen effect in Pd suggest the existence of two *d*-band Fermi surfaces, one containing 0.36 *d*-band holes, and the other 0.19.

For the study of the catalytic properties of alloys, it is relevant to recognize that the narrow $e_g$ band with its high density of states will be more readily filled than the relatively broad $t_{2g}$ band by the introduction of *s* electrons from the nontransition metal of the alloy. The complete filling of one of these subbands at a specified alloy composition together with a pronounced change in the available electronic energy states may indeed be responsible for the maximum catalytic activity observed at a specified alloy composition. According to this interpretation, such variations in solid-state properties merely reflect the existence of a bound state for the absorbed intermediate that energetically is most favorable for catalytic reaction.

The distribution of *d*-band holes between metallic ($t_{2g}$) and localized ($e_g$) bands may be related to the observed surface properties in gas–solid interactions. As shown by Kowaka (*13*) for Pd-Ag alloys, both the rate of hydrogen adsorption and the rate of ethylene hydrogenation have maxima near 60 atom % Pd. As a hypothesis, one may relate these changes in surface activity to filling of the $e_g$ band, because of its narrow width relative to the $t_{2g}$ band. Such considerations are in line with (a) the geometric arguments arising from the molecular orbital description of chemisorbed states (*2*), and (b) the correlation between the experimental rate constants for hydrogenation of ethylene (*13*) and the thermoelectric power. These data show that the correlation curve for alloys containing more than 0.36 *d*-band holes (i.e., more than 60 atom % Pd) is different from that for alloys with more completely filled *d*-bands. Such observations strikingly demonstrate the influence of the distribution of *d*-band holes between the various *d*-band orbitals on catalytic properties.

Similar behavior has been exhibited for other catalytic hydrogenation reactions (*14*). Of special interest are the results obtained for ortho–para hydrogen conversion on Pd-Au (*15*) and on Pd-Ag alloys (*16*), as well as hydrogenation of butadiene (*17*) on Pd-Au alloys. Again a maximum in reaction rate is observed at 60 atom % Pd. In addition the results for ortho–para hydrogen conversion demonstrate little variation in activation energy in the range from 100 to 40 atom % Pd. Thus the observed changes in reaction rate must be associated with the pre-exponential term of the Arrhenius expression. This term is represented by the entropy change of the activation step of the chemical reaction in the thermodynamic formulation of the rate constant. In line with the analysis presented, the entropy change would be influenced by changes in the gradient of the density-of-states curve at the Fermi level of the solid. Indeed the change in reaction rate closely follows the entropy variations, as evidenced by the thermoelectric power measurements for this alloy system (*8*).

As Sachtler and Jongepier (*18*) pointed out, the interpretation of catalytic results for metal alloys must take into account the possibility of phase separation. For Pd-Ag alloys the available thermodynamic data (*19*) suggest the existence of a complete range of stable solid solutions.

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