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SELECTIVITY IN CATALYSIS BY METALS AND ALLOYS

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Although we are mainly using catalysts because of the higher selectivity of catalytic processes in comparison with the noncatalytic ones, the subject of selectivity has had relatively little attention in the literature. Books on catalysis can be found in which the term selectivity does not even appear in the index. It is quite generally believed that selectivity will finally be explained as "a different activity in different reactions by different catalysts," more or less automatically when data on activity of various catalysts are available and well understood. However, as experience teaches (we shall see below) the opposite is true:

the activity of catalysts even in apparently simple reactions is
determined by the selectivity properties of the catalysts. There-
fore, it seems appropriate to concentrate attention directly on
selectivity problems.

We shall proceed in the following way. First, we shall summ-
arize the leading ideas in the theory of the catalytic activity
in Section I, in order to see which factors might be responsible
for the selectivity of catalysts. This will be briefly discussed
at the end of Section II. Second, we shall review the attempts
at a formal description of the selectivity of catalysts with the
same purpose as above. Since much of what we know about factors
determining the selectivity of metals has been found in studies
on alloys, some information on the electronic structure of metals
and alloys will be presented as well as some remarks on the sur-
face composition of alloys in Section III. Finally, several ex-
amples of reactions will be discussed where the factors determin-
ing the selectivity are already identified, at least to some
extent.

I. CATALYTIC ACTIVITY OF METALS; CORRELATIONS AND PREDICTIONS

We can discern two streams of thoughts in the theory of cata-
lytic activity of metals: (a) Dowden's (1948, 1950, 1952) theory,
or (b) the semiempirical rules related to the so-called Sabatier
principle (Sabatier, 1911; Tanaka and Tamaru, 1966; Schuit *et al.*,
1961; Makishima *et al.*, 1961; Golodetz and Roiter, 1963).

Dowden's theory was formulated around 1950 and consisted of the
following ideas:

(1) Reacting molecules are activated by a charge transfer on
the catalyst surface in the state of adsorption. Schematically,

$$
\begin{array}{ccc}
A & + \quad B & = \quad C \\
e\uparrow\downarrow e & e\uparrow\downarrow e & e\uparrow\downarrow e \\
\hline
\multicolumn{3}{c}{\text{metal}} \\
\multicolumn{3}{c}{\leftarrow \ e \ \rightarrow}
\end{array}
\tag{1}
$$

A good catalyst mediates this transfer fast.

(2)   A fast activation of the reaction components is possible if the metal possesses a certain number of d-holes (unoccupied energy levels of high d-character) and a high value of the density of state $N(E_F)$ at the Fermi level E_F as well as a high gradient of $N(E)$ at E_F.

It soon appeared that it was extremely difficult to find a relation between any single parameter characterizing the electronic structure (number of d-holes, electric conductivity, work function, d-character according to Pauling, etc; see Hayward and Trapnell, 1964; Trapnell, 1957; Ponec, 1974; Ponec et al., 1974) and the chemisorption and catalytic properties. On the other hand, it also became clear that the interaction of the reacting components with the surface of the catalyst is much more complicated than a simple electron transfer from and to an intact molecule (Fahrenfort et al., 1960). Since the interaction of the reacting components with the surface reminds us of formation of "normal" chemical compounds, in around 1960 the old ideas of Sabatier became popular again.

According to Sabatier (1911) the essence of catalysis is the formation of intermediate compounds between the catalysts and reacting components (Sabatier formulated his idea first for alcoholates) and these intermediates must be neither too stable nor unstable, i.e., an *optimum stability* is needed (Sabatier principle) for an optimum catalytic effect. Schematically, the reactions proceed like

$$A + B \quad C \atop | \quad | \rightarrow | \atop K \quad K \quad K \qquad (2)$$

In most cases the stability is probably related to the chemisorption bond strength (dissociative energy of A-K, etc.). These data are usually not known in advance, and therefore Tanaka and Tamaru (1963, 1966) suggested correlating the catalytic data with the heat of formation of the highest oxide per metal atom ΔH_f^0. Parameter ΔH_f^0 in its turn is related to the chemisorption bond strength.

The Sabatier principle and correlation as just mentioned helped to systemize and classify quite successfully the catalytic activity of various metals in the recent past. An example is given in Fig. 1.

It is, of course, another question why such correlation exists. Let me mention here that in 1940 Beeck (1945, 1948, 1950; Beeck et al., 1940) said that the right part of correlation, i.e., the antipathetic relation "high heat-low activity," is due to side reactions leading to deactivation of the catalysts. In fact, in this way we have to deal with a "heat-selectivity" correlation.

II. FORMAL DESCRIPTION OF THE SELECTIVE BEHAVIOR

Wheeler (1951) suggested discriminating between three basic types of selectivities: (1) S_I, the selectivity in two (or more) parallel reactions of two (or more) starting compounds; (2) S_{II}, the selectivity in two (or more) parallel reactions of the same starting compound; (3) S_{III}, the selectivity in two simultaneous, consecutive reactions. Reaction examples can be (1) the competitive hydrogenation in a mixture of various unsaturates or aromatics, (2) the oxidation of olefines, reforming reactions of hydrocarbons, etc., and (3) the hydrogenation of acetylene, dienes, etc.

Only the simplest, not very realistic schemes for these reactions can be treated quantitatively. In order to characterize the selectivity we introduce first the differential selectivity S, eventually normalized to unity. S is given by differential quotients of the product pressure, e.g., $S_I = \dfrac{dp_x}{dp_y}$ or S_I (normalized) $= S_I/(S_I + 1)$. In a general case, this is a very complicated function of pressure and temperature and we shall confine our considerations to the first-order (monomolecular, or pseudomonomolecular, in a large surplus of one of the components) irrevers-
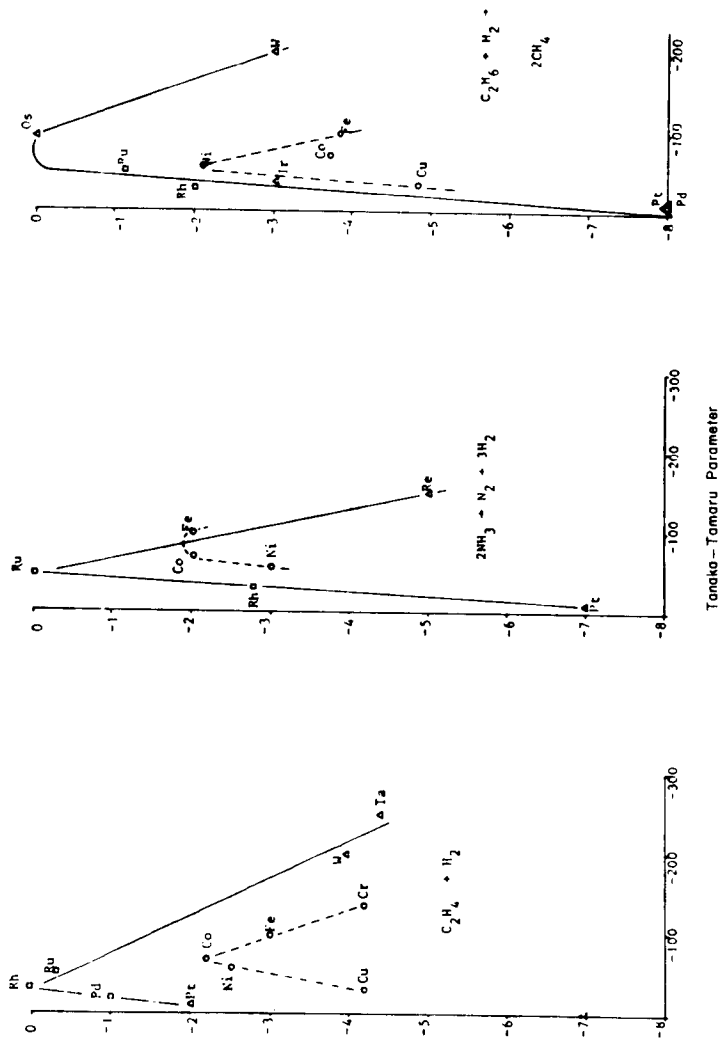
Fig. 1. Activity of various metals in the reactions indicated in arbitrary units:
$log\left[(r(me)/r(Rh)\right]$, *ethane hydrogenation;* $log\left[r(Me)/r(Ru)\right]$, *decomposition of* NH_3; $log\left[r(Me)/r(Os)\right]$, *ethane hydrogenolysis.* r, *reaction rate at standard temperature and standard conditions (various literature data are used in this correlation); Me, metal (Ponec and Schuit, 1974).*

ible reactions (i.e., far from equilibria). It should be noted that we can speak of a selectivity-determining step as with regard to the overall reaction we often speak of a rate-determining step. Those two steps need not always be identical.

A. *Selectivity of the First Type, S_I*

The reaction concerned is most simply

$$A \rightarrow P_1 \tag{3}$$

$$B \rightarrow P_2 \tag{4}$$

or in a more complicated case,

$$A + \nu_A'A' + \nu_A''A'' + \cdots = P_1 + \mu_1'P_1' + \mu_1''P_1'' + \cdots \tag{3'}$$

$$B + \nu_B'B' + \nu_B''B'' + \cdots = P_2 + \mu_2'P_2' + \mu_2''P_2'' + \cdots \tag{4'}$$
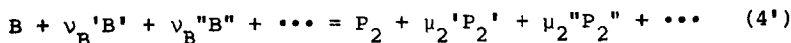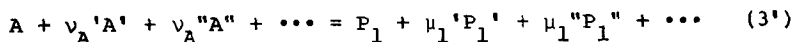
If the rate of adsorption is rate and selectivity determining in (3) and (4), then the selectivity is approximately given by the ratio of adsorption rate constants, because in the case of a slow adsorption the surface coverage is low:

$$S_I \sim \frac{k_{A,ads}p_A}{k_{B,ads}p_B} = \frac{p_A k_{A,ads}^0}{p_B k_{B,ads}^0} \exp\left(\frac{E_{B,ads} - E_{A,ads}}{RT}\right) \tag{5}$$

If the surface reaction determines the rate and selectivity, then

$$S_I = \frac{k_A \cdot f(\Theta_A)}{k_B \cdot f(\Theta_B)} \tag{6}$$

or simply

$$S_I = \frac{k_A \Theta_A}{k_B \Theta_B} \tag{6'}$$

for first order (with regard to Θ) reactions. Langmuir-type equilibrium adsorption will lead to an expression

$$S_I = \frac{(-dp_A)}{(-dp_B)} = \frac{dp_{P_1}}{dp_{P_2}} = \frac{k_A}{k_B}\frac{K_A}{K_B}\frac{p_A}{p_B} \tag{7}$$

where K_i stands for the adsorption coefficient and k_i for the re-
action rate constant.

Integration of (5) or (7) leads to a linear relation between
the logarithms of pressures:

$$\log p_A \approx \log p_B \tag{8}$$

The slope of this linear relationship depends either on the ratio
of the adsorption rate constants or on the product of the ratio
of adsorption equilibrium constants and reaction rate constants.

At low temperatures the desorption rate of compounds A and B
might be much lower than the rate of their surface reaction. Then
the steady-state value of θ_A and θ_B is maintained by the respective
rates of adsorption and reaction and the selectivity maily depends
on the ratio of the adsorption rate constants.

Arriving at this point of discussion, we should realize for the
first time in this chapter which factors in general might influ-
ence the selectivity of metals and alloys. Later we shall see that
these factors will be repeatedly found to be responsible for the
selectivity.

When an equation like Eq. (5) is valid, it is the difference in
activation energy of adsorption that is important and the number
of sites included in k_A on the surface that are available for a
certain mode of adsorption, necessary for the catalytic reaction.
With regard to the latter, if, for example, reaction (3) needs no
more than, say, one active site to occur and reaction (4) needs a
whole ensemble of several sites, then a dilution of the active
component of the alloy catalyst in a virtually inactive matrix
must lead to a considerable increase in selectivity
$S_I \ (= \frac{dp_a}{dp_B})$.

When an equation like Eq. (7) is valid, it is the difference in
adsorption heats and activation energies that is important and,
again, the number of sites forming an ensemble required by the

reaction. It is in some way surprising that the first factor, the energetic one, has been discussed in the literature many times, while the second, the influence on the selectivity of the ensemble size or ensemble geometry, has had much less attention. This is certainly not justified and we shall see that in almost all cases discussed below, this second "geometrical" factor will play some role.

B. *Selectivity in Parallel Reactions, S_{II}*

The simplest model scheme is

$$A \overset{\nearrow B}{\underset{\searrow C}{}} \quad \text{(products)} \tag{8}$$
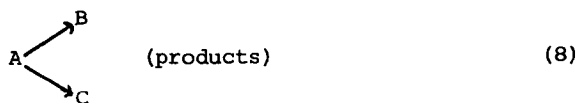
If the reaction is that simple in its microscopic mechanism, then the surface reaction must be responsible for the selectivity patterns, in any case. The selectivity is $S_I = k_B \cdot f(\Theta_A)/k_C \cdot g(\Theta_A)$.

In the simplest case of the first-order reaction, $f(\Theta_A) = g(\Theta_A) = \Theta_A$ and

$$S_{II} = \frac{k_B}{k_C} \tag{9}$$

An example of a normalized S_{II} selectivity as a function of temperature is shown in Fig. 2, for three parallel reactions.

However, in a more general case, the starting compound A is adsorbed on a given surface in various intermediate forms (I_1, I_2), each reacting further toward different products (B, C):

$$A(gas) \overset{\nearrow I_1 \to B}{\underset{\searrow I_2 \to C}{}} \quad \text{(schematically)} \tag{10}$$