CATALYTIC ACTIVITY OF TRANSITION METALS IN HYDROGENOLYSIS OF ETHANE CALCULATED BY THE SIMPLEX METHOD

Karel KUCHYNKA[a], Jiří FUSEK[b] and Oldřich ŠTROUF[b]

[a] *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 121 38 Prague and
[b] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 250 68 Řež

Received December 28th, 1979

The catalytic activity of transition metals in hydrogenolysis of ethane was approximated by a polynomial of second order with variables of basic physical importance, *viz.*, molar heat capacity, covalent atomic radius of the metal, heat of melting, and first ionization potential of the metal atom. The physico-chemical significance of the correlation of these variables with the catalytic activity of transition metals is discussed.

Our preceding work[1] dealt with the classification of transition metals by the one-class (asymmetric) pattern recognition method into active and inactive ones with respect to the catalysis of ethane hydrogenolysis:

$$C_2H_6 + H_2 \rightarrow 2\,CH_4\,, \qquad (A)$$

and the structure of the class of catalytically active metals was described by a second-order polynomial. Since the activity has a continuous character, it has not only to be decided whether the metal is active or not, but also how large is its activity.

In the present work we approximate the catalytic activity level of transition metals with a polynomial whose terms involve linearly independent variables characterizing the metal. All these variables have a basic physical character. The degree of the polynomial was determined on the basis of optimum ensembles of coefficients derived by the recently described simplex method[2]. Correlations between the variables and the catalytic activity of the metal were evaluated from the physico-chemical point of view. We interpreted physically also the linear correlations between these variables and those left out after decreasing the dimensionality, which was described elsewhere[3].

RESULTS AND DISCUSSION

Calculation of the Catalytic Activity

The values of rate constants for hydrogenolysis of ethane catalysed by eleven transition metals were taken from the work of Sinfelt[4] and their catalytic activity was approximated by a polynomial function of seven practically linearly independent variables determined by the pattern recognition method[1] (Table I). Coefficients of this polynomial equation were determined by the Simplex method[2]; the calculations were carried out on a Hewlett–Packard 9825 type computer. First, we tested the first-order polynomial (Eq. (*1*), $N = 7$, $a_i \neq 0$, $b_i = 0$) for seven linearly independent variables and the activity was expressed as natural logarithm of the rate constant of the hydrogenolysis (A):

$$\ln k' = \sum_{i=1}^{N} a_i x_i + \sum_{i=1}^{N} b_i x_i^2 + c\,, \tag{1}$$

where k' is the calculated rate constant, N number of variables x_i, a_i and b_i coefficients, and c additive constant. The constant minimum sum of the squares of deviations between the logarithms of experimental and calculated rate constants k and k'

$$\sum_{j=1}^{11} (\ln k - \ln k')^2_{\min} = r^{B} \tag{2}$$

TABLE I

Linearly Independent Variables[1] and Coefficients in Eq. (*1*)[a] for Relevant Variables

i	Variable x_i	Coefficient a_i	Coefficient b_i
1	molar heat capacity	8·50	— 1·5
2	covalent radius	—46·64	—24·0
3	electric conductivity	—	—
4	heat of fusion	16·31	— 1·13
5	1st ion. potential	3·04	— 0·008
6	specific heat	—	—
7	3rd ion. potential	—	—

[a] $N = 4$; $a_i, b_i \neq 0$; $c = -230{\cdot}5$.

represents the "best" response, r^B, in the simplex procedure[2]. For the mentioned case, we found 48·7. Nevertheless, the agreement in the sequence of experimental and calculated constants was insufficient.

We therefore considered a second-order polynomial. At first, we chose from the original set of seven variables only those which exerted the largest influence on the resulting activity in the above-mentioned analysis. The influence of the variables was evaluated simply according to their contribution to the activity and to the variability of this contribution. We then studied the approximation by a second-order polynomial (Eq. (*1*), $N \doteq 4$, a_i, $b_i \neq 0$) for the four remaining "relevant" variables (Table I). The coefficients a_i, b_i, and c for the "best" minimum sum of squares of differences $r^B = 15{\cdot}6$ are given in Table I. The sequences of the experimental and calculated activities are in agreement to 82%, as shown in Table II. It is seen that cobalt and rhodium show large differences between experimental and calculated rate constants: k' for Co is six times higher than k, and k' for Rh lower by a factor of 0·1. The latter case represents the maximum deviation found.

Some calculated rate constants k' for metals with an unknown efficiency are of the same order as the experimentally found ones[4]. The largest value of k' (of the

TABLE II

Experimental[4] (k) and by the Simplex Method Calculated (k') Catalytic Activity of Metals

Group	Metal	k	k'	Order	Group	Metal	k	k'	Order
I	Cu	5	9	10^{4}	VI	Cr	—	1	10^{1}
	Ag	—	2	10^{-7}		Mo	—	4	10^{4}
	Au	—	1	10^{-8}		W	—	2	10^{6}
II	Zn	—	6	10^{-9}	VII	Mn	—	5	10^{2}
	Cd	—	2	10^{-21}		Re	1	1	10^{6}
	Hg	—	3	10^{-37}	VIII	Fe	2	2	10^{5}
III	Sc	—	7	10^{-12}		Ru	2	7	10^{7}
	Y	—	3	10^{-27}		Os	2	0·7	10^{8}
	La	—	7	10^{-45}		Co	8	51	10^{5}
	Ce	—	4	10^{-33}		Rh	5	0·5	10^{6}
IV	Ti	—	2	10^{-5}		Ir	1	1	10^{6}
	Zr	—	3	10^{-10}		Ni	1	2	10^{7}
	Hf	—	2	10^{-18}		Pf	1	2	10^{1}
V	V	—	7	10^{0}		Pt	8	14	10^{0}
	Nb	—	5	10^{-1}					
	Ta	—	3	10^{-8}					

sixth order) was found for tungsten, of the fourth order for molybdenum, of the second order for manganese, of the first order for chromium, and of the zeroth order for vanadium (Table II). The latter activity is comparable with the lowest experimental activity for platinum ($k = 8$). The activities of W, Mo, and Mn were expected on the basis of the results of the preceding study of pattern recognition[1]. In contrast, Cr and V show unexpectedly high values of calculated activities in comparison with their measures of similarity[1]. Therefore, the cases of metals whose measures of similarity are close to the class limit have to be interpreted very critically.

The set of four variables (Table I) on which according to our analysis the catalytic activity in ethane hydrogenolysis has to depend, brings some new correlation features. For example, the accentuation of the influence of the heat of melting is surprising, since the catalytic activity is usually in a one-parameter correlation with the heat of sublimation, which enables to estimate the bonding energy between the metal and adsorbate. Unfortunately, it is not known whether the melts of the metals under study are mono- or polyatomic; in the latter case, the concepts about the role of atomic clusters in chemisorption would be supported.

The correlation between the activity and molar heat capacity, which is not known from the literature, is also interesting. In chemisorption of the reaction components, the electronic component of the heat capacity of the metal can be important; it can be considered as a measure of the potential energy of the system ionic lattice–free electrons. This energy comes into play in the repulsion of free electrons from the metal surface during approaching of a reactant molecule. Except for Ni, the metals denoted here as active have indeed a rather low value of the constant of electronic heat capacity[5], so that the process of exposing the orbitals of the surface lattice atoms, described recently by Knor[6], apparently does not hinder the interaction of the mentioned metals with the reactants.

Further we found a correlation between the activity and the covalent radius of the metal atom. This is conceivable since the covalent radius influences the distance between the neighbouring metal atoms on the surface, which is known to play a role in the geometry of chemisorption[7].

Finally, we found a correlation with the first ionization potential, which gives the affinity of the univalent metal cation to an electron. It plays a role in relation to chemisorption and catalysis both as a measure of the polarizing capability and in the mentioned repulsion of free electrons from the surface. With increasing ionization potential of the metal atom, the polarization of molecules of the reaction components increases and the repulsion of free electrons in the lattice is weakened.

Linear Correlation of Variables

When the dimensionality is decreased to a set of variables near the optimum[3], the least loss of information is assumed. In other words, all linearly dependent variables left out should be to a large extent reflected by one or more linearly independent variables.

We calculated a simple linear pair correlation between the relevant linearly independent variables (Table I) and each of the eight omitted linearly dependent variables mentioned in ref.[1]. Our aim was to decide whether some relevant linearly independent variable can be in a physico-chemical interpretation replaced by another variable from the omitted set, and whether some data can be replaced by data of another type. (Multiple linear correlations between variables exist naturally too, they are, however, not discussed here.) The maximum coefficients, r_{max}, for couples of variables with a most fitting linear correlation of all the eight possible ones are given in Table III. The correlations show for the individual couples very different deviations from linearity. The accurate linear dependence between the heat of melting and the melting point with a coefficient $r = 0{\cdot}96$ is the known Trouton's rule; and this is an evidence for the correctness of the algorithm used. In other cases with a relatively high correlation coefficients of the order of 0·1, we do not have to deal with a strict linearity. These correlations can hence be considered as a mere approximation of physical dependences and can be interpreted only qualitatively. For example, the mutual dependence of the covalent atomic radius and atomic volume follows from their definition or from elementary considerations. The relation of the first ionization potential to electronegativity is the result of the electron affinity of particles of the same element differing by only one electron. Finally, the relation between the heat capacity and the Debye's temperature is known in the region of low temperatures in the analytical form and forms the basis for obtaining data about Debye's temperatures[5].

TABLE III

Linear Correlation of Variables

Variable		Maximum correl. coeff. r_{max}
Relevant	omitted	
Coval. radius	atomic volume	$0{\cdot}98^b$
—	atomic radius	$0{\cdot}98^b$
Heat of fusion	melting point	$0{\cdot}96^b$
Mol. heat cap.	Debye's temp.	$0{\cdot}57^c$
1st ion. pot.	electronegat.	$0{\cdot}69^{a,c}$

[a] Similar r_{max} (0·66) was found also for the couple 1st ionization energy — 2nd ionization energy. [b] 1% significance level. [c] 10% significance level.

CONCLUSIONS

The results obtained by the methods of dimensionality reduction, linear correlation, and simplex are two-fold: First, the testing of tungsten, molybdenum, manganese, and eventually chromium and vanadium with respect to the possible catalytic activity in hydrogenolysis of ethane is recommended. This indication of potentially active elements is the main goal of our work. Other results, having the character of correlations, are an example for the application of the method of pattern recognition to finding out dependences, in our case physico-chemical ones. The algorithm finds out these relations without any knowledge about the character of the problem and is based only on the general assumption of similarity. However, because of a limited computer time, only such problems can be solved in which a partial preliminary selection can be done on the basis of experience. The procedure is complicated by the nonexistence of certain data leading to the necessity to omit a whole series of data for a certain quantity. The number of found dependences is thus potentially limited. For a quantitative method, such as simplex, the reliability of the available data is naturally also decisive. Therefore, at least the data for the sought quantity (catalytic activity) were taken from a single work; data for other physico-chemical quantities could not be always taken from a single source.

REFERENCES

1. Štrouf O., Fusek J., Kuchynka K.: This Journal, in press.
2. Štrouf O., Fusek J.: This Journal, in press.
3. Štrouf O., Fusek J.: This Journal *44*, 1370 (1979).
4. Sinfelt J. H., Catal. Rev. *3*, 175 (1969).
5. Gschneider K. A., jr: Solid State Phys. *16*, 275 (1964).
6. Knor Z.: Kinet. Katal. *21*, 17 (1980).
7. Fejes P. in the book: *Contact Catalysis* (Z. G. Szabó, D. Kalló, Eds), Vol. 1, p. 211. Akadémiai Kiadó, Budapest 1976.

Translated by K. Micka.