APPROXIMATION OF ADSORPTION HEATS OF CARBON MONOXIDE ON TRANSITION METALS BY MEANS OF AN EMPIRICAL MODEL

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The class structure of transition metals chemisorbing carbon monoxide was determined by expressing the following fundamental parameters in the form of functions: The molar heat capacity, the 1st and 2nd ionization energy, the heat of fusion, Pauling electronegativity, the electric conductivity, Debye temperature, the atomic volume of metal. Adsorption heats have been predicted for twelve transition metals.

Energy data on the bonds between molecules of initial reactants and metal surfaces (based on adsorption heat value) are of importance for selection of the catalysts in the Fischer–Tropsch process. The set of accessible experimental data of this kind is not complete and also the reliability of the measured values is strongly limited by the data inaccuracy. The opposite approach, of calculating the adsorption heats using theoretical methods, has so far not been possible[1]. For the above reasons, one has to turn to some of the empirical approaches illustrated in the previous paper[2] on the case of approximation of the adsorption heats of hydrogen on transition metals. In the first step of the procedure, the linearly independent variables of atomic or elemental nature, which are to characterize the chemisorption activity of individual metals towards the given molecule, are selected by means of the Kaarhunen–Loewe transformation. Dependence of the activity on the selected variables is then described by suitable simple functions.

In the present paper, the above procedure is applied for the other participant in the Fischer–Tropsch synthesis – carbon monoxide. Polynomials of the first and second order have been tested in order to approximate the adsorption heats.

DATA AND CALCULATIONS

Values of the experimental adsorption heats of carbon monoxide on Ti, Zr, Nb, Ta, Mo, W, Mn, Re, Fe, Co, Rh, Pd, Pt, Cu and Ag were taken from the compilation of Toyoshima and Somorjai[3]. The values for physico-chemical parameters were given in our previous paper[4]. Eight

linearly independent variables appearing in the polynomials were selected with the method of pattern recognition[4]. Coefficients in the corresponding equations were found by means of the Simplex procedure[5] and least squares technique. Computations were carried out on a Hewlett-Packard 9825 computer.

RESULTS AND DISCUSSION

In the first step, a first order polynomial was applied for the approximation, using all eight linearly independent variables (Table I) determined recently by the method of pattern recognition:

$$Q'_{(CO)} = \sum_{i=1}^{N} a_i x_i + b \,, \qquad (1)$$

where $Q'_{(CO)}$ denotes the calculated value of the adsorption heat (Table II), N gives the number of variables ($N = 8$), a and b are coefficients and x_i are individual variables.

The accordance between $Q'_{(CO)}$ and the experimental values of the adsorption heats $Q_{(CO)}$ was expressed as a sum of squared deflections $\sum_{j=1}^{M} (Q'_{(CO)} - Q_{(CO)})^2 = 3{\cdot}140 \,.\, 10^4$ ($M = 15$), giving the mean deflection value approximately 46 kJ/mol. For the approximation with a second-order polynomial, dimensionality was reduced

TABLE I

The linearly independent variables and coefficients of the polynomials (*1*) and (*2*)

i	Variables x_i	Coefficients of equations (*1*)[a]	Coefficients of equation (*2*)[b]	
		a_i	a_i	b_i
1	molar heat capacity	$-9{\cdot}848 \,.\, 10^1$	—	—
2	2nd ionization energy	$-4{\cdot}060 \,.\, 10^{-1}$	—	—
3	electric conductivity[c]	$-4{\cdot}561 \,.\, 10^2$	$1{\cdot}405 \,.\, 10^2$	$-8{\cdot}443 \,.\, 10^2$
4	heat of fusion	$1{\cdot}170 \,.\, 10^1$	—	—
5	Debye temperature	$-1{\cdot}569 \,.\, 10^{-1}$	—	—
6	1st ionization energy[c]	$-2{\cdot}170$	$3{\cdot}772 \,.\, 10^{-1}$	$-3{\cdot}727 \,.\, 10^{-3}$
7	atomic volume[c]	$2{\cdot}819 \,.\, 10^1$	$1{\cdot}569 \,.\, 10^2$	$-6{\cdot}176$
8	electronegativity[c]	$-2{\cdot}143 \,.\, 10^2$	$-1{\cdot}623 \,.\, 10^3$	$3{\cdot}378 \,.\, 10^2$

[a] Coefficient $b = 1{\cdot}649 \,.\, 10^3$; [b] coefficient $c = 1{\cdot}291 \,.\, 10^3$; [c] variable with the highest contribution to $Q'_{(CO)}$ (see the text).

to one half by omitting the variables which had shown the lowest average contribution to the final value of the adsorption heat $Q'_{(CO)}$. This contribution was evaluated by the approximation according to equation (*1*), using normalized values of the variables, x_i^x, instead of the original x_i ones. The values were normalized to a mean average of zero and standard deviation of one (autoscaling). The obtained coefficients a_i^x were arranged according to their descending values and four variables with the largest a_i^x values (Table I) were used in the next approximation. The values $Q'_{(CO)}$ calculated from equation (*2*) are listed in Table II

$$Q'_{(CO)} = \sum_{i=1}^{N} a_i x_i + \sum_{i=1}^{N} b_i x_i^2 + c\,, \qquad (2)$$

where $N = 4$.

The agreement between $Q'_{(CO)}$ and $Q_{(CO)}$ was expressed as the sum $\sum_{i=1}^{M} (Q'_{(CO)} - Q_{(CO)})^2 = 2{\cdot}822 \,.\, 10^4$ ($M = 15$), with the mean deflection approximately 43 kJ/mol. The degree of fitting to the experimental values $Q_{(CO)}$ is thus comparable with the fit of the values which were calculated according to (*1*). This occurs in spite

TABLE II

The experimental $Q_{(CO)}$ and calculated $Q'_{(CO)}$ values of adsorption heats of carbon monoxide on transition metals (kJ/mol)

Group	Metal	$Q_{(CO)}$	$Q'_{(CO)lin}$ [a]	$Q'_{(CO)q}$ [b]	Group	Metal	$Q_{(CO)}$	$Q'_{(CO)lin}$ [a]	$Q'_{(CO)q}$ [b]
I	Cu	39	0	−35	VI	Cr	—	364	343
	Ag	36	71	105		Mo	310	360	352
	Au	—	−17	121		W	419	356	385
II	Zn	—	234	389	VII	Mn	327	343	398
	Cd	—	360	423		Re	289	335	281
	Hg	—	297	272					
III	Sc	—	749	691	VIII	Fe	193	234	218
	Y	—	850	410		Ru	—	243	193
	La	—	1 034	306		Os	—	184	172
	Ce	—	955	452		Co	198	226	184
IV	Ti	641	528	557		Rh	193	163	172
	Zr	628	674	632		Ir	—	138	155
	Hf	—	729	737		Ni	—	201	184
V	V	—	440	410		Pd	180	184	205
	Nb	523	544	507		Pt	201	172	197
	Ta	561	548	582					

[a] Values of adsorption heats calculated according to equation (*1*). [b] Values of adsorption heats calculated according to equation (*2*).

of the fact that only four variables which mostly affected the final value, were used in the approximation. Justification for such a selection of variables x_i^x was verified by better agreement of the results obtained with the selected variables – compared to the remaining ones. The reliability of the results cannot be checked by usual statistical tests because of lack of accessible data. The results were therefore verified in terms of their interpolation robustness by the "leave n-out" method, for $n = 1$; In fifteen approximations, always one of the metals had been left out, in turn, and the predicted value $Q'_{(CO)}$ for the deleted metal was calculated. The sum of deflections in both cases of verification $Q^{ver}_{(CO)}$ was higher than the sum of deflections obtained in the case when all fifteen metals were applied in the approximation; if a linear polynomial was used, the above sum $\sum_{i=1}^{M} Q_{(CO)} - Q^{ver}_{(CO)})^2$ equalled $2{\cdot}555 \cdot 10^4$ while for the second order polynomial, the sum amounted to as much as $8{\cdot}282 \cdot 10^4$ ($M = 15$). Consequently, the linear expression with eight variables approximates less well the known values, on the other hand, it is more robust in prediction of values by interpolation than the approximation with a second-order polynomial using four variables with the highest contribution. Nonetheless, the mean deflection for the predicted values is almost 108 kJ/mol.

The above described observation is in agreement with the well known fact that values approximated for objects which have been used for the adjustment of parameters in the approximation process give better fit than values which were approximated for objects not used in the training. This means that the efficiency of prediction is equal (or less) to the efficiency of recognition. It is also evident that better results in recognition do not necesarily mean improved prediction power for the obtained expression. This is proved by the lower level of prediction by interpolation, in the approximation using a second order polynomial (Eq. (2)), which in fact provides somewhat better agreement for recognition. The calculated adsorption heat values follow, in the periodic table of elements, the trend of the experimental values – a characteristic decrease from left to right. The adsorption heats calculated with either the linear or quadratic expressions are not very different for most of the metals. Only with rare earth elements, for which no experimental data are known, this difference becomes quite pronounced (Table II). This fact illustrates that the class structure need not be represented by one function only, even in the case when very similar objects are concerned. Characteristic advantage of majority of methods of pattern recognition is namely their independence on homogeneity and complexity of the structure. Our method of classification[6] applied on chemical systems[4,7,8], equally, does not require any *a priori* knowledge concerning the structure. The methods of pattern recognition lead to mere selection of parameters determining the target variable. In order to know the level of this property, one has to know the functional expression[2,9] of the parameters, *i.e.* the structure or substructure of the corresponding class.

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