MODELLING OF FISCHER–TROPSCH CATALYTIC SYNTHESIS BY PATTERN RECOGNITION METHOD. CHEMISORPTION OF HYDROGEN ON METALS

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 2 and
[b] *Institute of Inorganic Chemistry,*
Czechoslovak Academy of Sciences, 250 68 Řež

Forty nine metals characterized by a set of fifteen fundamental physical variables were classified with respect to chemisorption of hydrogen. Dimensionality reduction of this physical model led to the determination of nine linearly almost independent variables. This reduced set discriminated the chemisorbing metals from the inactive ones to a satisfactory extent. The physico–chemical significance of these variables for the chemisorption of hydrogen as one of the elementary steps of Fischer–Tropsch catalytic process is discussed.

The recent revival of interest in suitable ways of chemical processing of coal leads to efforts to develop novel processes in catalytic Fischer–Tropsch synthesis. So far, selection and prediction of new catalysts cannot be accomplished by theory alone. Tedious empirical approaches have to be used that call for more effective methods of the measured data analysis.

Recently, the applicability of pattern recognition methods to problems of heterogeneous catalysis has been demonstrated. The methods are suitable both for the prediction of industrial catalysts[1] and for the selection of basic properties of active elements (metals) relied to the given activity in an explicitly unknown way[2].

A necessary but not sufficient property of a Fischer–Tropsch catalyst is its ability to interact with both reactants — hydrogen and carbon monoxide. In the present work the classification of transition as well as nontransition metals is carried out with respect to their behaviour towards hydrogen. A two-class symmetric pattern recognition[3] was used for this classification. The metals were characterized by fifteen fundamental physical data available for all forty nine metals taken for study. The variables exhibiting a high linear dependence on other variables were determined by the procedure described previously[4]. The deletion of them caused only a small relative loss of information. While this dimensionality reduction did not impair either correctness or reliability of recognition[3] only the remaining variables were used for the classification.

Furthermore the linear correlations of each remaining variable with each of the deleted ones were calculated. With some couples high correlation coefficients were found enabling the substitution of some of the remaining variables by the variables highly correlated. Thus alternative sets of variables may be obtained making possible a broader physico–chemical interpretation.

EXPERIMENTAL

Values of fifteen variables for individual metals were taken from the Sargent-Welch table[5] and completed from additional sources: Values of 2nd and 3rd ionization energies were taken from ref.[6]. The 3rd ionization energy of Cs, Sr, Ba and the heat of vaporization of Ga come from ref.[7]. Debye temperatures of transition metals are given in ref.[8], those of other metals and Sc in ref.[9]. The value of the heat of vaporization of Nb is taken from ref.[10]. All data were autoscaled. Data on chemisorption activity of metals towards hydrogen are given in refs[11-13]. Pattern recognition calculations were carried out on the GIER type computer.

RESULTS AND DISCUSSION

Dimensionality Reduction of the Model

Previous papers[2,4] have shown that deletion of linearly highly dependent variables enables a substantial reduction of dimensionality of both symmetric[4] and asymmetric[2] pattern recognition approaches. The degree of linear dependence is estimated using eigenvalues resulting from Karhunen–Loève transformation. The loss of information is given in relative eigenvalues, λ_{rel}, scale. In each step of the reduction process the variable is discarded that corresponds to the largest component of the eigenvector related to the lowest eigenvalue. At a certain dimensionality D a) relative
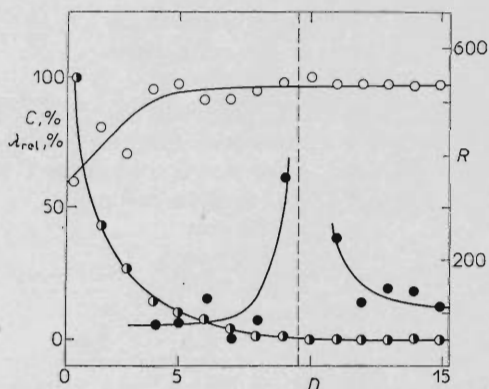

Fig. 1

Dimensionality reduction in modelling of chemisorption of hydrogen on metals. ◑ λ_{rel} relative loss of information (%); ● R reliability of recognition; ○ C correctness of recognition (%)

loss of information increases b) reliability of the recognition R decreases and c) correctness of recognition decreases or at least does not change perceptibly. In this work these three conditions are fulfilled for the dimensionality $D = 9$ (Table I, Fig. 1). At this dimensionality there is a decrease in $\lambda_{rel} = 0.76\%$ and simultaneously R goes down while the correctness keeps its original value of 97·3%.

Classification of Metals

Recognition of thirty seven prototypes on the basis of nine linearly almost independent variables (Table II) was performed by a classification method described recently[3]. This method is based on the definition of the class by means of the similarity of available prototypes. Here, the class of chemisorbing metals was defined by twenty five prototypes all being recognized correctly with the single exception of calcium only. The class of nonadsorbing metals was characterized by twelve prototypes; all these prototypes were recognized correctly. A relatively high total correctness of recognition (97.3%) at the dimensionality $D = 9$ justifies to some extent also the use of the above similarity for the classification of metals with unknown behaviour towards hydrogen.

TABLE I

Dimensionality reduction of the model of hydrogen chemisorption on metals

D^a	Variable x_i	λ^b	R^c	C^d
1	molar heat capacity	100·0	77·2	59·5
2	2nd ionization energy	43·6	77·2	81·1
3	electric conductivity	27·0	12·5	70·3
4	heat of fusion	14·0	78·7	94·6
5	Debye temperature	10·1	88·3	97·3
6	1st ionization energy	8·2	130·2	91·9
7	atomic volume	3·9	54·7	91·9
8	electronegativity	1·9	87·6	94·6
9	heat of vaporization	1·2	360·6	97·3
10	molar electric conductivity	0·76	—	100·0
11	3rd ionization energy	0·54	246·1	97·3
12	specific heat	0·31	112·1	97·3
13	melting point	0·24	149·0	97·3
14	atomic radius	0·06	142·4	97·3
15	covalent radius	0·04	112·2	97·3

[a] Dimensionality of the model; [b] relative loss of information (%); [c] reliability of recognition; [d] correctness of recognition (%).

It was found that from the ten classified nontransition metals seven are nonchemisorbing ones whereas three of them (Be, Ge, Sb) can chemisorb H_2. Only two transition metals were classified viz. cerium and manganese; both possibly possess a chemisorptive ability. From the Table II it is evident that the categorization of the metals is not trivial with respect to their transition or nontransition character as well as, in the case of nontransition metals in respect of their position in the Periodic table. Only the classification of transition metals is trivial in respect of this position: thus. all IB and IIB metals belong to the nonchemisorbing class, all other to the chemisorbing one. Cerium and manganese were classified in accordance with this found trend.

According of the above analysis the reactivity of metals towards hydrogen is found to depend on no more than nine atomic or elemental properties. Five of them are related to the energy of the interatomic bond in the metal: heat of vaporization, heat of fusion, molar heat capacity, Debye temperature and atomic volume. The effects of the heat of fusion and the heat of vaporization can be considered in combination which represents a good approximate measure of the sublimation heat of metals, this heat being directly proportional to metal–metal bond energy. The molar heat capacity and the Debye temperature are mutually dependent in a nonlinear manner this relation underlying the Debye interpretation of specific heat[14]. Debye temperature is directly proportional to maximum frequency of atomic oscillators in the crystal which is a function of bond energy between atoms of the metal. Furthermore, the maximum frequency is indirectly proportional to the atomic volume[15] depending nonlinearly on the propagation velocity of elastic waves, this quantity being also dependent on the energy of interatomic bond. The atomic volume is thus related to the metal–metal bond energy in a relatively complicated way. The fact that more than a half of the linearly almost independent variables can be related to the metal––metal bond energy indicates the importance of this quantity in hydrogen chemisorption. Furthermore the well-known Pauling's relation[16] expresses energy of hydrogen–metal chemisorption bond as a simple function of the bond energy of metal atoms and their electronegativity; the latter quantity was also selected by our algorithm. The remaining quantities in the Pauling's equation are related to hydrogen only and thus they are constant here. The above selection thus emphasizes the influence of the chemisorption bond energy. Naturally, the variables derived from the metal–metal bond energy are also related to the activation energy of chemisorption because they refer to the vibration energy of surface metal atoms that react with hydrogen. The interpretation of this effect is beyond the aim of this paper.

Remaining three variables have to be considered individually. The first ionization energy is a measure of polarization ability of univalent cation of metal towards, in our case, the molecule of hydrogen. The second ionization energy corresponds formally to the process of two outer electrons elimination which exposes *p*-electron orbitals (in alkaline earth metals) and partially or completely occupied *d*-orbitals

TABLE II
Classification of metals according to their ability to chemisorb hydrogen at a dimensionality $D = 9$

Group	Metal	$S_{q_1}/S_{q_2}{}^a$	Prototypes[b]	Classification[b]
IA	Li	2·0	—	b
	Na	2·5	—	b
	K	2·0	b	b
	Rb	2·0	—	b
	Cs	1·8	—	b
IIA	Be	1·2	—	a
	Mg	3·5	b	b
	Ca	1·8	a	b
	Sr	2·7	a	a
	Ba	1·7	a	a
IIIA	Al	9·0	b	b
	Ga	1·6	—	b
	In	2·8	b	b
	Tl	2·6	—	b
IVA	Ge	3·8	—	a
	Sn	1·3	b	b
	Pb	4·5	b	b
VA	Sb	1·7	—	a
	Bi	1·4	—	b
IB	Cu	23·5	b	b
	Ag	14·8	b	b
	Au	5·3	b	b
IIB	Zn	8·9	b	b
	Cd	11·1	b	b
	Hg	7·2	b	b
IIIB	Sc	8·8	a	a
	Y	10·3	a	a
	La	2·6	a	a
	Ce	1·6	—	a
IVB	Ti	21·1	a	a
	Zr	28·4	a	a
	Hf	17·0	a	a
VB	V	27·1	a	a
	Nb	40·0	a	a
	Ta	20·3	a	a
VIB	Cr	4·7	a	a
	Mo	29·8	a	a
	W	26·5	a	a
VIIB	Mn	2·0	—	a
	Re	26·8	a	a

TABLE II
(Continued)

Group	Metal	S_{q_1}/S_{q_2}[a]	Prototypes[b]	Classification[b]
VIIIB	Fe	11·0	a	a
	Ru	15·2	a	a
	Os	47·4	a	a
	Co	7·4	a	a
	Rh	9·5	a	a
	Ir	32·6	a	a
	Ni	11·5	a	a
	Pd	5·1	a	a
	Pt	8·1	a	a

[a] Ratio of the similarity to the "farther" class q_1 (higher value of S_{q_1}) and the similarity to the "nearer" class q_2 (lower value of S_{q_2}). [b] a denotes chemisorbing elements and b nonchemisorbing ones.

TABLE III
Linear correlation of variables

Variable		r_{max}[a]	Coefficients[b]	
Remaining (y)	Deleted (x)		a	b
Molar heat capacity	covalent radius	0·51	2·720	2·501
2nd ioniz. energy	specific heat	0·75	1 382·0	287·5
Electric conductivity	molar el. cond.	0·69	0·05228	0·03903
Heat of fusion	melting point	0·90	0·002054	0·8241
Debye temperature	covalent radius	0·67	−533·9	1 066
1st ioniz. energy	atomic radius	0·71	− 71·93	278·4
Atomic volume	atomic radius	0·97	37·68	−43·50
	covalent radius	0·95	44·03	−46·10
Electronegativity	atomic radius	0·75	− 0·9663	3·121
Heat of vaporization	melting point	0·93	0·04706	23·13

[a] Maximum correlation coefficient. [b] In the equation $y = ax + b$.

(in transition metals) of the resulting bivalent cation; generally, low value of the 2nd ionization energy corresponds to an easy availability of the mentioned orbitals.

In difference to the above variables, the relation of electrical conductance to the chemisorption of hydrogen is rather unclear. It was found experimentally that the conductivity of thin metallic layers changes during this chemisorption. This change can be visualized e.g. as an electron exchange between adsorbate and metal, but this is not the only possibility and a consistent interpretation is still missing[17].

It is worth of mention that variables related directly to the geometry of the chemisorption, i.e. to the radii of particles in lattice, are absent from the set of selected variables. In this connection atomic volume is only a derived function rather belonging to the set of quantities related to the bond energy. The absence of geometric factor is in accordance with the experimentally established fact that hydrogen chemisorbs on a number of metals of markedly different atomic sizes (e.g. atomic radius of Ba is 0·222 nm whereas that of Fe only 0·126 nm).

CHEMICAL CONSEQUENCES

The application of pattern recognition to the classification of metals according to their reactivity towards hydrogen leads in the first place to the prediction of the behaviour of metals not yet studied under comparable experimental conditions: alkali metals, gallium, thallium and bismuth are probably inactive, whereas on beryllium and on antimony chemisorption may occur. Manganese for which contradicting data appear in literature is classified here as an active metal. The robustness of the classification method used is illustrated by the fact that germanium, not included in the training set for its atypical metallic character, was nevertheless correctly classified as a chemisorbing element in accordance with experiment[11]. The set of variables describing the classification demonstrates the influence of three aspects in the chemisorption: the polarization of hydrogen molecule at the surface of metal, the capture of this molecule by suitable orbitals of metal atoms and, above all, the influence of the energy of resulting chemisorption bond. The nine characterizing variables were selected from a larger set of fifteen parameters. The formation of this set had been limited above all by the requirements of both completeness and fundamental physical significance of the parameters. Naturally, the condition of completeness of the data introduce an element of randomness into the set formation that limits the number of correlations, distorts the significance of the found correlations and, furthermore, it may negatively affect the classification itself. In spite of this a priori limitation it appears in the studied case that the algorithm used (based only on the general assumption of similarity and otherwise unrelated to the specific problem under study) is able to yield conclusions that do not contradict physico-chemical reality.

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