

## MODELLING OF THE CATALYTIC FISCHER-TROPSCH SYNTHESIS BY PATTERN RECOGNITION. CHEMISORPTION AND DISSOCIATION OF CARBON MONOXIDE ON METALS

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A set of forty nine metals was classified with respect to chemisorption of carbon monoxide and a set of nineteen transition metals was similarly treated with respect to dissociation of the chemisorbed molecule. In both cases the metals were characterized by a set of fifteen variables of basic physical importance. Dimensionality reduction yielded eight linearly weakly dependent variables related to chemisorption of CO whereas the reduced set for dissociation had four parameters only. The physico-chemical significance of the characterizing linearly weakly dependent variables is discussed.

Carbon monoxide is one of the two reactants in Fischer-Tropsch synthesis. On metal surfaces it chemisorbs in molecular form (bonded to one or two adsorption sites) capable of subsequent splitting into carbon and oxygen atoms. The extent of this dissociation depends on the type of the metal and on the crystal face index; it generally increases with temperature. Rabo and coworkers<sup>1</sup> correlated the two forms of chemisorption with the general characteristics of products formed after reaction with hydrogen. Metals tending to split the CO molecule preferentially catalyze the formation of hydrocarbons whereas on metals with little or no dissociation of CO at not too high temperatures the synthesis leads to oxygenated products, *e.g.* methanol. This division, though coarse and not reflecting the distribution of products, is nevertheless useful as a clue to the general direction of the synthesis.

In the present work the classification of a set of metals is carried out according to the two above mentioned initial interactions of carbon monoxide with the catalyst surface, *i.e.* chemisorption and dissociation of the adsorbed molecule. For classification the following criteria were used: The training set for elements active towards CO was set up from metals on which chemisorption at 273 K or room temperature had been established experimentally. For the training of dissociation the metals were divided into groups according to Brodén and coworkers<sup>2</sup>: the active class comprises metals where dissociation occurs on a polycrystalline surface or at least on one low-index crystal face at room temperature. For chemisorption forty nine

metals (transition and nontransition) were treated; for dissociation only transition metals were classified as data for other metals had not been published. In both cases the same set of fifteen parameters as in the preceding papers<sup>3,4</sup> was used for the characterization of metals.

The dimensionality reduction  $D$  was accomplished by a procedure described earlier<sup>5</sup> consisting in stepwise deletion of linearly dependent variables. The deletion is carried out until the reliability of recognition begins to drop perceptibly with the given degree of correctness.

The classification algorithm is based on the measurement of distance between the object and each of the classes of the system. The classes are defined in a transformed and normalized space on the basis of the respective training sets. The object is then identified with the class the representation of which lies "nearest"<sup>6</sup>. This classification approach was used in symmetric and asymmetric forms for diverse types of chemical objects characterized by various parameters<sup>3,4,6</sup>. In this work, this classification algorithm is used for the first time in a hierarchical manner: In the first step all forty nine studied metals were categorized with respect to their ability to chemisorb CO and in the second step nineteen chemisorbing transition metals were classified according to their ability to dissociate the chemisorbed molecule.

## EXPERIMENTAL

Values of the fifteen variables for the metals were taken from the same sources as in the preceding work<sup>4</sup>. All data were autoscaled. Data on chemisorption of carbon monoxide are from refs.<sup>7-10</sup> while dissociation data are from refs<sup>11-13</sup>. Where no data on dissociation of the chemisorbate were available only those transition metals were classified where chemisorption itself had been found experimentally. Pattern recognition computation was carried out using the GIER-ALGOL-III program.

## RESULTS

### *Dimensionality reduction*

The procedure employed for modelling chemisorption is shown in Table I and Fig. 1. It is seen that the three criteria for the determination of dimensionality<sup>4,5</sup> are fulfilled for  $D = 8$ ; further deletion decreases the relative information  $\lambda_{re1}$  by about 2%, the reliability drops to a half and even the correctness starts to go under its initially constant value of 96.8%. It is seen qualitatively in Fig.1 that whereas the correctness of classification does not waver in the region of low relative loss of information the reliability, on the other hand, proves to be markedly unstable (the right part of the curve before the break). The sensitivity of the latter measure increases even more in the region behind the break (left part of the curve) where both the loss of information and the decrease of correctness are high. Large variation of reliability with the change of the

percentage correctness is caused by the definition proper of the reliability measure<sup>6</sup>. The latter includes not only the dependence on the degree of dissimilarity but above all the influence of the number of incorrectly classified prototypes. Therefore, in the

TABLE I  
Dimensionality reduction of the model of chemisorption of carbon monoxide on metals

$D^a$	Variable	$\lambda_{rel}^b$	$R^c$	$C^d$
1	molar heat capacity	100	(65.9)	54.8
2	2nd ionization energy	43.6	(117.8)	54.8
3	electric conductivity	27.0	(6.2)	67.7
4	heat of fusion	14.0	(70.2)	93.5
5	Debye temperature	10.1	24.7	90.3
6	1st ionization energy	8.2	23.8	83.9
7	atomic volume	3.9	23.8	83.9
8	electronegativity	1.9	46.8	96.8
9	heat of vaporization	1.2	62.0	96.8
10	molar electric conductivity	0.76	57.4	96.8
11	3rd ionization energy	0.54	48.1	96.8
12	specific heat	0.31	64.1	96.8
13	melting point	0.24	75.8	96.8
14	atomic radius	0.07	68.9	96.8
15	covalent radius	0.04	43.4	96.8

<sup>a</sup> Dimensionality of the model<sup>5</sup>, <sup>b</sup> relative loss of information (%)<sup>5</sup>, <sup>c</sup> reliability of recognition<sup>6</sup>, <sup>d</sup> correctness of recognition (%)<sup>6</sup>.

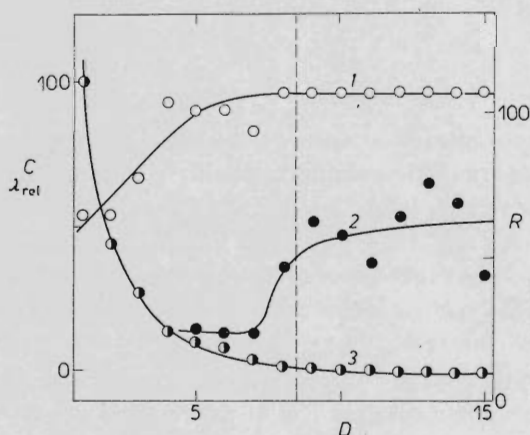


FIG. 1  
Reduction of dimensionality in the modelling of chemisorption of carbon monoxide on metals. ○  $\lambda_{rel}$  relative loss of information (%), ●  $R$  reliability of recognition, ○  $C$  correctness of recognition (%)

low dimensionality region with large loss of correctness one cannot ascribe equal importance to reliabilities as in the region of higher dimensionalities with correctness constant or nearly constant. For this reason the corresponding values in Table I are given in brackets and are not shown in Fig. 1.

TABLE II

Dimensionality reduction of the model of the type of chemisorption of carbon monoxide on transition metals

$D^a$	Variable	$\lambda_{rel}^b$	$R^c$	$C^d$
1	heat of fusion	100	3.6	66.7
2	molar heat capacity	46.8	17.9	73.3
3	molar electric conductivity	21.2	72.3	93.3
4	electronegativity	13.4	218.3	86.7
5	Debye temperature	5.5	230.0	93.3
6	2nd ionization energy	3.1	214.0	86.7
7	1st ionization energy	2.1	59.8	80.0
8	3rd ionization energy	1.6	73.0	86.7
9	specific heat	0.49	150.6	80.0
10	atomic radius	0.28	116.5	86.7
11	heat of vaporization	0.17	632.5	93.3
12	atomic volume	0.07	—	100.0
13	electric conductivity	0.03	—	100.0
14	melting point	0.01	—	100.0
15	covalent radius	0.005	—	100.0

$a$  Dimensionality of the model<sup>5</sup>,  $b$  relative loss of information (%)<sup>5</sup>,  $c$  reliability of recognition<sup>6</sup>,  $d$  correctness of recognition (%)<sup>6</sup>.

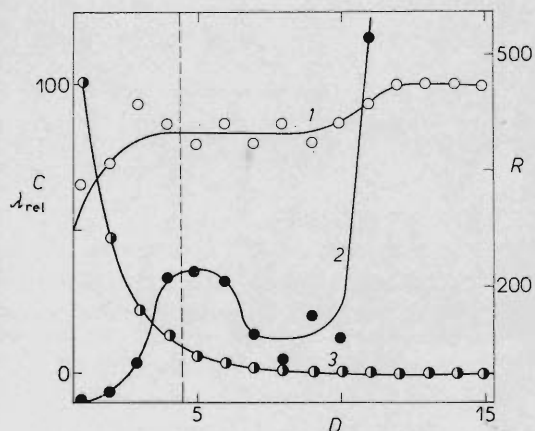


FIG. 2  
Reduction of dimensionality in the modelling of the type of chemisorption of carbon monoxide on transition metals.  $\circ$   $\lambda_{rel}$  relative loss of information (%),  $\bullet$   $R$  reliability of recognition,  $\circ$   $C$  correctness of recognition (%)

TABLE III

Classification of metals with respect to the chemisorption of carbon monoxide at dimensionality  $D^m = 8$

Group	Metal	$S_{q_1}/S_{q_2}^a$	Prototypes <sup>b</sup>	Classification <sup>b</sup>
IA	Li	8.0	<i>b</i>	<i>b</i>
	Na	6.8	—	<i>b</i>
	K	2.6	<i>b</i>	<i>b</i>
	Rb	3.1	—	<i>b</i>
	Cs	3.6	—	<i>b</i>
IIA	Be	1.8	—	<i>b</i>
	Mg	2.9	<i>b</i>	<i>b</i>
	Ca	2.9	—	<i>b</i>
	Sr	3.2	<i>a</i>	<i>a</i>
	Ba	1.2	<i>a</i>	<i>a</i>
IIIA	Al	1.6	<i>b</i>	<i>b</i>
	Ga	1.5	—	<i>b</i>
	In	4.8	<i>b</i>	<i>b</i>
	Tl	4.6	—	<i>b</i>
IVA	Ge	2.2	—	<i>a</i>
	Sn	3.4	<i>b</i>	<i>b</i>
	Pb	3.9	<i>b</i>	<i>b</i>
VA	Sb	1.7	—	<i>b</i>
	Bi	2.2	—	<i>b</i>
IB	Cu	2.0	<i>a</i>	<i>b</i>
	Ag	1.8	<i>b</i>	<i>b</i>
	Au	1.1	—	<i>b</i>
IIB	Zn	5.9	<i>b</i>	<i>b</i>
	Cd	5.4	<i>b</i>	<i>b</i>
	Hg	2.9	—	<i>b</i>
IIIB	Sc	4.3	—	<i>a</i>
	Y	1.5	—	<i>a</i>
	La	1.0	<i>a</i>	<i>a</i>
	Ce	2.4	—	<i>b</i>
IVB	Ti	6.9	<i>a</i>	<i>a</i>
	Zr	4.1	<i>a</i>	<i>a</i>
	Hf	2.1	—	<i>a</i>
VB	V	5.4	—	<i>a</i>
	Nb	3.1	<i>a</i>	<i>v</i>
	Ta	1.6	<i>a</i>	<i>a</i>
VIB	Cr	3.5	<i>a</i>	<i>a</i>
	Mo	5.7	<i>a</i>	<i>a</i>
	W	2.0	<i>a</i>	<i>a</i>
VIIB	Mn	2.5	<i>a</i>	<i>a</i>
	Re	5.5	<i>a</i>	<i>a</i>

TABLE III  
(Continued)

Group	Metal	$S_{q_1}/S_{q_2}^a$	Prototypes <sup>a</sup>	Classification <sup>b</sup>
VIII B	Fe	4.2	<i>a</i>	<i>a</i>
	Ru	2.6	<i>a</i>	<i>a</i>
	Os	3.4	—	<i>a</i>
	Co	4.1	<i>a</i>	<i>a</i>
	Rh	2.3	<i>a</i>	<i>a</i>
	Ir	1.8	<i>a</i>	<i>a</i>
	Ni	6.9	<i>a</i>	<i>a</i>
	Pd	1.1	<i>a</i>	<i>a</i>
	Pt	1.1	<i>a</i>	<i>a</i>

<sup>a</sup>  $S_{q_1}/S_{q_2}$  is a ratio of similarities to the less similar  $q_1$  and more similar  $q_2$  classes, <sup>b</sup> *a* means membership in the class of chemisorbing elements and *b* in the class of nonchemisorbing ones.

Dimensionality reduction in modelling the type of chemisorption of carbon monoxide on transition metals (Table II, Fig. 2) has an atypic complicated form. At dimensionalities  $D = 15-12$  the correctness of recognition is 100%. When next variable (atomic volume) is deleted the correctness decreases by 6.7%, yet further successive deletion of eight following variables reveals no visible trend. However, a maximum of reliability appears at  $D = 4$ . Although the loss of information rises to 5.5% the correctness is still 86.7% (Table II, Fig. 2). In this complicated case  $D^m = 4$  was chosen as the dimensionality of the model.

#### *Classification of Metals According to the Chemisorption Ability*

The result of classification is given in Table III. Similarly to the chemisorption of hydrogen it is seen that the separation of the set of metals into classes "chemisorbing" and "inert" is not trivial. Most metals behave identically in both chemisorption processes; those adsorbing  $H_2$  as well as CO represent a set of metals with possible catalytic activity in the Fischer-Tropsch process. Only for Be, Sb and Ce the classifications are not identical for both reactants so that these metals are expected to be inactive on account of their inability to bind one of the reaction partners.

#### *Classification of Transition Metals according to the Type of Chemisorption*

Only those transition metals were classified where chemisorptive ability had been proved experimentally (see the training set in Table III). Table IV shows that most metals were recognized correctly with one exception to each class: manganese placed

among the active and iron among the inactive metals. Apparent triviality of classification (IB, III–VIIB metals split CO whereas VIIIB metals do not) is broken by cobalt which according to both experiment and computation is an exception to the uniform behaviour of VIIIB metals.

### DISCUSSION

In the chemisorption model the same set of parameters and objects (metals) serves as a basis as in the case of hydrogen chemisorption<sup>4</sup>. However, the respective training sets differ: Both reference sets of active metals (for H<sub>2</sub> and CO) have seventeen elements in common and differ in ten others while the less populated training sets of inactive metals agree in nine elements and differ in four. The reduction of dimen-

TABLE IV

Classification of transition metals according to the type of chemisorption of carbon monoxide at dimensionality  $D^m = 4$

Group	Metal	$S_{q_1}/S_{q_2}^a$	Prototypes <sup>b</sup>	Classification <sup>b</sup>
IB	Cu	5.1	—	<i>b</i>
IIIB	La	3.0	—	<i>b</i>
IVB	Ti	4.0	<i>b</i>	<i>b</i>
	Zr	2.9	<i>b</i>	<i>b</i>
VB	Nb	19.8	<i>b</i>	<i>b</i>
	Ta	12.3	<i>b</i>	<i>b</i>
VIB	Cr	9.2	—	<i>b</i>
	Mo	4.2	<i>b</i>	<i>b</i>
	W	7.5	<i>b</i>	<i>b</i>
VIIIB	Mn	1.1	<i>a</i>	<i>b</i>
	Re	12.9	—	<i>b</i>
VIIIB	Fe	1.2	<i>b</i>	<i>a</i>
	Ru	1.7	<i>a</i>	<i>a</i>
	Co	10.6	<i>b</i>	<i>b</i>
	Rh	5.7	<i>a</i>	<i>a</i>
	Ir	3.6	<i>a</i>	<i>a</i>
	Ni	3.2	<i>a</i>	<i>a</i>
	Pd	6.9	<i>a</i>	<i>a</i>
	Pt	5.8	<i>a</i>	<i>a</i>

<sup>a</sup>  $S_{q_1}/S_{q_2}$  is a ratio of similarities to the less similar  $q_1$  and more similar  $q_2$  classes, <sup>b</sup> *a* means membership in the class of metals chemisorbing CO molecularly, and *b* in the class of metals chemisorbing dissociatively.

sionality leads to the selection of identical weakly linearly dependent variables appearing in the same succession as in the hydrogen chemisorption model. The heat of vaporization of metals is a border quantity in dimensionality reduction and both chemisorption models differ only in the rate of decrease of reliability accompanying the same loss of information caused by deletion of this property. Agreement in the remaining quantities is due to the fact that the set of fifteen variables available for all metals is the same for both models. The choice of these variables is influenced by the inherent randomness of the accessibility of the data. Their fundamental physical character permits, however, to expect that the set of variables selected should also involve those relevant to the classification. This assumption was substantiated by the achieved degree of correctness of classification remaining sufficiently high even after deletion of variables redundant in the sense of linear dependence. In these circumstances the finding of identical characterizing quantities for both chemisorption processes apparently reflects a physical reality. It may *e.g.* be concluded that the adsorption of hydrogen and carbon monoxide on identical sites found for tungsten<sup>14</sup> could be a more general phenomenon among metals.

In classification of transition metals according to the extent of dissociation of CO the reduction of dimensionality leaves only four parameters. These represent a fairly incoherent set from the viewpoint of contemporary catalytic science — heat of fusion, molar heat capacity, molar electric conductivity and electronegativity. The molar heat capacity is a function of interatomic bond energy and together with electronegativity should determine the energy of the chemisorption bond if analogy to hydrogen could be expected<sup>4</sup>. Surface dissociation of CO molecule results, however, in formation of two nonidentical adsorption bonds with individual carbon and oxygen atoms so that the interpretation is not unequivocal.

Neither heat of fusion nor molar electric conductivity are usually being put in correlation with catalytic reactivity. The heat of fusion appeared as characterizing property in the classification of metals with respect to ethane hydrogenolysis<sup>3</sup> although the training set differed substantially from the present one. The fact that in both cases the process is known only for transition metals may be of some significance.

According to the performed classification the chemisorption of carbon monoxide might be expected to occur on scandium, yttrium, hafnium, vanadium, osmium and germanium. Furthermore four transition metals (rhenium, copper, lanthan and chromium) for which there are experimental data about chemisorption as such but not about the form of the adsorbate should split the chemisorbed molecule already at room temperature. Finally the unexpected classification of copper among metals dissociating CO ought to be viewed with reserve as this metal was already wrongly classified in the general chemisorption model.

We so far applied pattern recognition to four catalytic systems two of which concerned an extensive set of metals (chemisorption of H<sub>2</sub>, ref.<sup>4</sup> and CO in this work) while the remaining two involved sets narrowed to transition metals only (dissociation



of CO and hydrogenolysis of ethane<sup>3</sup>). In spite of their simplicity in mechanism the first two processes are characterized by almost twice as many parameters as the latter two that are more complicated. One of these — hydrogenolysis of ethane — is a process considerably more complex than chemisorption of simple molecules like H<sub>2</sub> or CO. On the other hand, the dissociation of carbon monoxide has a mechanism similar to that of chemisorption of hydrogen which, too, is dissociative. The considerable difference in the number of characterizing parameters may thus be caused by the unequal size of the sets of objects.

## REFERENCES

1. Rabo J. A., Risch A. P., Poutsma M. L.: *J. Catal.* **53**, 295 (1978).
2. Brodén G., Rhodin T. N., Bruckner C. F., Benbow R., Hurych Z.: *Surface Sci.* **59**, 593 (1976).
3. Štrouf O., Fusek J., Kuchynka K.: *This Journal* **46**, 65 (1981).
4. Kuchynka K., Fusek J., Štrouf O.: *This Journal*, in press.
5. Štrouf O., Fusek J.: *This Journal* **44**, 1370 (1979).
6. Fusek J., Štrouf O.: *This Journal* **44**, 1362 (1979).
7. Toyoshima I., Somorjai G. A.: *Catal. Rev. Sci. Eng.* **19**, 105 (1979).
8. Wagener S.: *J. Phys. Chem.* **60**, 567 (1956).
9. Wagener S.: *J. Phys. Chem.* **61**, 267 (1957).
10. Hayward D. O., Trapnell M. W.: *Chemisorption*, p. 75. Butterworths, London 1964.
11. Jones A., McNicol B. D.: *J. Catal.* **47**, 384 (1977).
12. Hooker M. P., Grant J. T.: *Surface Sci.* **62**, 21 (1977).
13. Foord H. F., Goddard P. J., Lambert R. M.: *Surface Sci.* **94**, 339 (1980).
14. Vorburger T. V., Sandstrom D. R., Waclawski B. J.: *Surface Sci.* **60**, 211 (1976).

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