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Analysis of factors controlling catalytic activity by neural network

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Abstract

An artificial neural network was applied to the analysis of factors controlling catalytic activity by taking, as examples, experimentally established correlations of catalytic activities with primary factors including both monotonous and volcano-type correlations. Three equations were proposed and applied to the estimation of relative importance of each given factor from the weightings of connecting links in the trained artificial neural network of an error back-propagation model. In all the examples, the primary factors that had been proposed in experimental studies were successfully identified by using an equation based on our previous proposal. Further, the possibility of identifying secondary factor was also discussed.

Keywords: Artificial neural network; Analysis of factors; Factors controlling catalytic activity; Oxidation of propene; Oxidation of butane; Oxidation of methane; Decomposition of formic acid

1. Introduction

An artificial neural network (ANN) is widely used in various fields of science and technology for the estimation of results from given possible factors. In catalysis, the present authors demonstrated that ANN can be applied to the estimations of the acid strength of mixed oxides [1] and of the catalytic activity and selectivity of oxide catalysts [2], and proposed that ANN can be a powerful tool for the design of catalysts [3]. Actually, Hou et al. [4] applied ANN to the optimization of catalyst composition for propane ammoxidation, and it was demonstrated that the optimum catalyst was obtained after three trial-and-error cycles aided by ANN. In these days, ANN is increasingly applied to the optimization of catalyst composition, sometimes, being used as a part of combinatorial chemistry approach [5]. Further, it is attempted to apply ANN to the selection of catalyst component [6] by estimating catalyst performance from the physico-chemical properties of catalyst components, though such an estimation had been revealed possible in our earlier works [2]. All of these applications of ANN in catalysis as well as those in the other fields are based on the function of ANN to estimate the results from the possible factors.

Recently, we proposed another type of application of ANN: i.e., the analysis of factors leading to the identification of primary factor controlling catalytic properties [7], though a similar but slightly different method had been applied to the identification of factors modifying the effect of ambient ozone on white clover [8]. In this study, three equations, based on these studies, were proposed to estimate relative importance of each given factor, and they were applied to four experimentally established correlations of the catalytic activities with the physico-chemical properties of catalyst components obtained in the oxidation of propene on oxides [9], the oxidation of butane on lanthanide oxides [10], the decomposition of formic acid on metals [11], and the oxidation of methane on lanthanide oxides by pulse method [12]. In the first and second examples, the catalytic activities decreased monotonously with respective primary factors, and in the third and fourth examples, volcano-type correlations were established. Further, discussion was made on the possibility of identifying the secondary factor.

2. Neural network

In this study, a conventional fully connected feedforward multi-layer neural network supervised by error back-propaga-

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tion learning is used as the experimental framework, since this kind of neural network is widely used in the applications to chemistry because of its strong learning capability. Fig. 1 schematically shows an overview of the structural organization of the neural network used in the first example. The neural network consists of artificial neurons or units (shown by the circles in the figure), which are interconnected with each other and arranged into three layers: an input layer, a hidden layer, and an output layer. The input layer contains four units representing the input data which are possible factors controlling catalyst activity, i.e., ΔHo, Xi, IP1, and A.N. in this case, and the output layer contains one unit representing the output data to be predicted, i.e., log V_{300} in this case.

If a set of known pairs of input data and output data is given to the neural network as a training signal, the network calculates a set of output data from the given set of input data. Then the difference between thus calculated output data and the given output data is propagated backward through the network to adjust the weights of connecting links (shown by the lines in the figure) between the neurons (circles). This procedure is iterated, until the calculated output data become close to the given output data. In the conventional application of ANN, the final set of weightings of connecting links is used to estimate the output data of a target from the corresponding input data. In the present study, the following three equations were proposed to calculate a 'contribution' of ith input data to kth output data (C_{ik}), which is expected to represent the relative importance of each input data, from the set of weightings:

$$C_{ik} = \left|\sum_{j} a_{ij} \times b_{jk}\right| \tag{1}$$

$$C_{ik} = \sum_{j} (|a_{ij}| + |b_{jk}|) \tag{2}$$

$$C_{ik} = \sum_{j} |a_{ij}| \tag{3}$$

where a_{ij} and b_{jk} are the weightings of connecting links between ith input unit and jth hidden unit and between jth hidden unit and kth output unit. Eq. (1) is essentially the same as that previously proposed by us [7] except that the absolute value is adopted in this study. On the other hand, Eqs. (2) and (3) are temporarily proposed here on the basis of a brief description in the literature [8] that the sum of the absolute weightings leading from each input was used to indicate the importance of each input data.

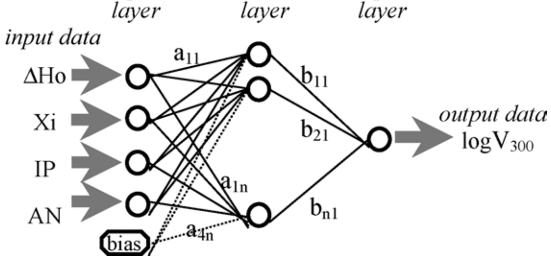

Fig. 1. Construction of neural network used in the first example. For nomenclatures, see text.

It is known that, especially when the number of training iteration is too large, error back-propagation neural network overfits the training data set, bringing sometimes rather serious error in predicted values. This problem was solved as follows: first, a 'leave-one-out' test was conducted, that is, ANN was trained by using a training set of the input and output data, of which both of the input and output data of one catalyst were left-out. And, the output data of the left-out catalyst were calculated by introducing the corresponding input data into thus trained network, and the calculated output data were compared with the given value to calculate the absolute error. This procedure was repeated for all the catalysts, and the sum of absolute errors was recorded as a function of training iterations to find the optimum iteration giving a minimum error. Then, ANN was trained again by using a whole training set of the input and output data, and the contribution mentioned above was calculated by using the weightings of connecting links at the optimum iteration determined by the leave-one-out test.

3. Results

3.1. Oxidation of propene over oxide catalysts

The first example is a well known correlation of catalytic activity of oxides in the oxidation of propene with the heat of formation of oxide per oxygen atom (ΔHo). It was reported that the reaction rate decreased monotonously with increasing ΔHo in both L- and H-series [9] as shown by open symbols in Fig. 2. In the present study, the data on Ag_2O was excluded from the training set, because Ag_2O was considered to lie on an ascending part of volcano-type correlation [13]. ANN of the structure shown in Fig. 1 was applied to this system: the input data included not only ΔHo but also dummy parameters such as electronegativity of cation (Xi), first ionization potential (IP1), and atomic number (A.N.); and the output data was the logarithm of reaction rate (log V_{300}). Twelve and eight runs were conducted for L- and H-series, respectively, by changing the number of hidden units from 2 to 30. In all the runs, the

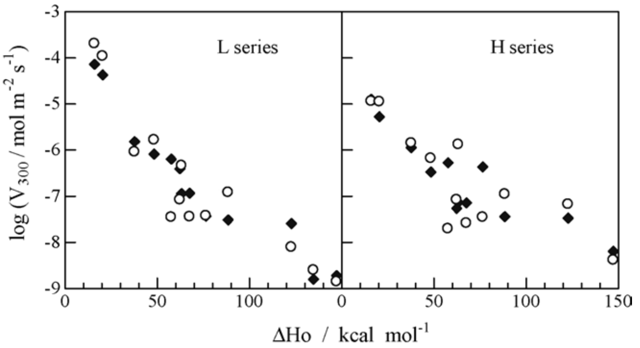

Fig. 2. Catalytic activities of oxides in propene oxidation: (○) experimentally observed [9]; (◆) estimated by ANN.

Table 1
Relative contributions of input data to catalytic activity of oxides in the oxidation of propene

	Eq. (1)		Eq. (2)		Eq. (3)	
	C_{av}	σ	C_{av}	σ	C_{av}	σ
L-series[a]						
ΔHo	65	4	33	3	46	10
Xi	17	3	24	1	22	3
IP1	13	4	22	1	17	3
A.N.	5	2	21	2	15	6
H-series[a]						
ΔHo	55	3	33	3	45	9
Xi	13	9	21	3	16	7
IP1	22	4	25	2	24	4
A.N.	10	3	21	1	15	5

[a] Reaction condition was different from series to series. For details, see ref. [9].

estimated reaction rates in the leave-one-out test agreed very well with the experimental values. Typical results are shown by closed symbols in Fig. 2.

Table 1 summarizes the averaged values (C_{av}) and the standard deviations (σ) of the relative contributions of four input data calculated by Eqs. (1)–(3). For both L- and H-series, Eq. (1) gave enough large relative contribution of ΔHo in comparison with those of the dummy parameters so that one can identify ΔHo as a primary factor controlling catalytic activity in agreement with the conclusion of experimental study [9]. On the other hand, in the case of Eq. (2), the relative contribution of ΔHo was only slightly larger than those of the dummy parameters. In the case of Eq. (3), the relative contribution of ΔHo significantly varied from run to run, as indicated by relatively large standard deviation: it depended on the number of hidden units. In the runs with two hidden units, the relative contribution was as large as that calculated by Eq. (1). However, it decreased with an increase in the number of hidden units, and, in the runs with more than 20 hidden units, it became close to that calculated by Eq. (2).

3.2. Oxidation of butane over lanthanide oxides

It was reported that the catalytic activities of lanthanide oxides in butane oxidation also decreased monotonously with an increase in fourth ionization potential (IP4) of cation [10] as shown by open symbols in Fig. 3. In our previous paper reporting a preliminary result of analysis of controlling factor by taking this case as an example [7], six parameters including IP4 were used as input data. In this study, ANN of the same structure as that shown in Fig. 1, i.e., with the same number of input data, was used for comparison. The input data included IP4, typical valence of cation in oxide (Z), ionic radius of trivalent cation (r), and electronegativity of cation (Xi). Closed symbols in Fig. 3, which represent a typical result of leave-one-out test, indicate that the catalytic activity can be well estimated by using these four input data.

Table 2 summarizes the averaged relative contributions and their standard deviations obtained in 10 runs in both Series 1 and 2. In Series 1, the relative contributions of IP4 calculated by Eqs. (2) and (3) were so close to those of Z and r that the primary factor could not be identified. In case of Eq. (1), the relative contribution of IP4 was larger than the others, though the difference was not so large as that in the oxidation of propene mentioned above. The difference between Eq. (1) and the others became clearer in Series 2, where Xi exhibiting a minimum contribution in Series 1 was excluded from the input data. Eq. (1) gave significantly large contribution of IP4 in comparison with those of Z and r, while the contributions of IP4 calculated by Eqs. (2) and (3) were less than those of r. Thus, only Eq. (1) could identify IP4 that had been revealed as the primary factor in experimental study [10].

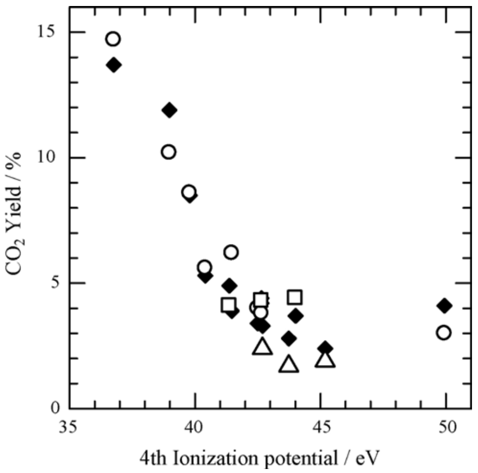

Fig. 3. Catalytic activities of lanthanide oxides in butane oxidation: (○, □, △) experimentally observed [10] ((□) Sm, Eu, and Gd; (△) Tm, Yb, and Lu); (◆) estimated by ANN.

3.3. Decomposition of formic acid on metals

It is well known that the decomposition of formic acid on metal catalysts offers a typical example of another type of correlation: a volcano-type correlation was established between the catalytic activity and the heat of formation of metal formate (ΔH_f) [12]. Closed symbols in Fig. 4 show a typical result of leave-one-out test, indicating that ANN successfully reproduced the volcano-type correlation by using ΔH_f, nearest neighbor distance (NND), density (d), and melting point (mp)

Table 2
Relative contributions of input data to catalytic activity of lanthanide oxides in the oxidation of butane

	Eq. (1)		Eq. (2)		Eq. (3)	
	C_{av}	σ	C_{av}	σ	C_{av}	σ
Series 1						
IP4	34	3	26	1	29	2
Z	24	8	25	2	26	6
r	29	4	26	1	27	3
Xi	13	3	23	2	18	4
Series 2						
IP4	51	6	36	2	39	3
Z	13	5	26	3	18	7
r	35	4	38	3	43	6

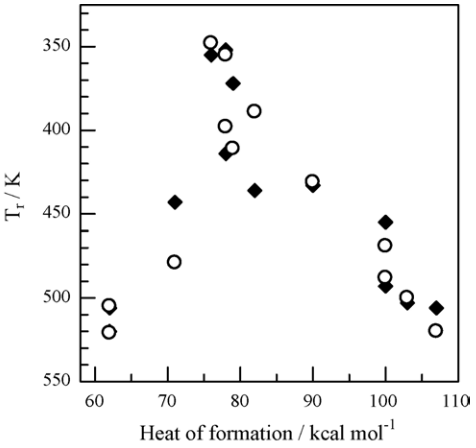

Fig. 4. Catalytic activities of metals in decomposition of formic acid: (○) experimentally observed [11]; (◆) estimated by ANN.

as input data. Fifteen runs were conducted by changing the number of hidden units from 2 to 30, and Table 3 summarizes the averaged contributions of input data and their standard deviations obtained in the runs with more than three hidden units. This is because the network with two hidden units seemed too simple to represent the volcano-type correlation: the estimation error and the relative contribution changed discontinuously as the number of hidden units decreased from three to two.

The relative contributions shown in Table 3 were quite similar to those in Table 1. Eq. (1) gave enough large contribution of ΔH_f so that it can be identified as the primary factor controlling catalytic activity. On the other hand, Eq. (2) gave only slightly larger contribution of ΔH_f. In case of Eq. (3), the relative contribution of ΔH_f depended on the number of hidden units: in the runs with 3 hidden units, it was as large as that calculated by Eq. (1), and with 30 hidden units it became close to that calculated by Eq. (2).

3.4. Oxidation of methane on lanthanide oxides

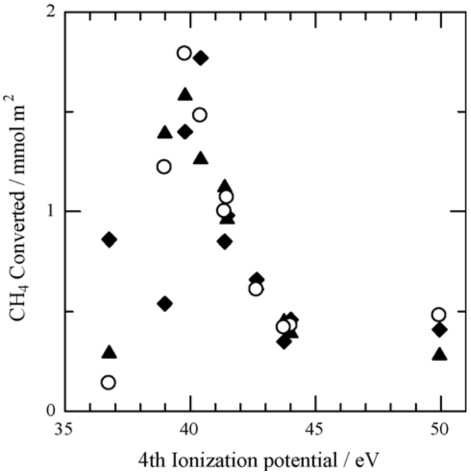

Fig. 5. Catalytic activities of lanthanide oxides in oxidation of methane by pulse method: (○) experimentally observed [12], (◆, ▲) estimated by ANN ((◆) with IP4, *r*, *Z*, and Xi; (▲) with IP4 and *Z* as input data, respectively).

The oxidation of methane on lanthanide oxides by pulse method resulted in very sharp volcano-type correlation between the catalytic activity and the fourth ionization potential, as shown by open symbols in Fig. 5 [13]. When *Z*, *r*, and Xi, as well as IP4, were used as input data, the estimated activities in the leave-one-out test agreed very well with the experimental values in a descending part, but only poorly in an ascending part, as shown by closed diamonds. It is interesting to note, however, that a good agreement was obtained even in the ascending part, when only IP4 and *Z* were adopted as input data, as shown by closed triangles.

Table 3
Relative contributions of possible factors to catalytic activity of metal in the decomposition of formic acid

	Eq. (1)		Eq. (2)		Eq. (3)	
	C_{av}	σ	C_{av}	σ	C_{av}	σ
ΔH_f	72	6	35	4	48	11
NND	7	3	23	2	19	5
d	20	5	22	1	18	4
mp	2	1	21	2	15	5

Table 4 summarizes the averaged relative contributions and their standard deviations in eight runs with more than 12 hidden units, because the contribution calculated by Eq. (1) decreased drastically with the decrease in the hidden units from 12 to 10. It would require more hidden units to represent very sharp volcano-type correlation shown in Fig. 5. As shown in Table 4, the relative contribution of IP4 calculated by Eq. (1) was much larger than the others, while the relative contributions of IP4 calculated by Eqs. (2) and (3) were less than those of *Z*. Thus, only Eq. (1) gave enough large relative contribution of IP4 for identifying it as the primary factor controlling catalytic activity.

4. Discussion

4.1. Identification of primary factor

In order to examine the possibility of estimating the importance of each input data leading to the identification of the primary factor controlling catalytic activity, Eqs. (1)–(3) were applied to four examples: oxidation of propene on metal oxides [9], oxidation of butane on lanthanide oxides [11], decomposition of formic acid on metals [12], and oxidation of methane on lanthanide oxides by pulse method [13]. The catalytic activities were revealed to change monotonously with

Table 4
Relative contributions of possible factors to catalytic activity of lanthanide oxides in the oxidation of methane by pulse reaction method

	Eq. (1)		Eq. (2)		Eq. (3)	
	C_{av}	σ	C_{av}	σ	C_{av}	σ
IP4	73	8	25	1	25	3
Z	14	8	27	2	31	5
r	5	3	24	1	22	4
Xi	8	2	24	1	22	2

the corresponding primary factors in the first and the second examples, and volcano-type correlations were established in the third and fourth examples. In all the examples, Eq. (1) gave reasonable results, as shown in Tables 1–4: the relative contributions of experimentally identified primary factors were the largest among those of input data. In the oxidation of butane on lanthanide oxides, the difference between the primary factor (IP4) and the other input data was not so large in Series 1, where IP4, *Z*, *r*, and Xi were used as input data. However, the difference was significant in Series 2, where Xi was excluded from the input data. On the other hand, the relative contributions calculated by Eqs. (2) and (3) did not always agree with the conclusions of experimental studies. In the first and third examples, the relative contributions of experimentally identified primary factors (ΔHo and ΔH_f) were larger than the others, though the differences were not so large as those in the case of Eq. (1). Only when the number of hidden units was very small, the relative contributions calculated by Eq. (3) were close to those calculated by Eq. (1). However, in the second example, the relative contribution of experimentally identified primary factor (IP4) was not larger than the others in Series 1, and further, in Series 2, it was smaller than that of *r*. In the fourth example, the relative contribution of IP4 was smaller than that of *Z*.

Finally, it may be concluded that only Eq. (1) can be used to calculate the ‘contribution’ of each input data to the output data and to identify the primary factor controlling catalytic activity. It should be noted that Eq. (1) was not theoretically derived, but rather intuitionally proposed. Therefore, further examination is necessary to establish the method.

4.2. Identification of secondary factor

The relative contributions of primary factors calculated by Eq. (1) in the H-series of first example and in the second example were smaller than those of the other examples, as shown in Tables 1–4. The smaller relative contribution of ΔHo in H-series of propene oxidation in comparison with that in L-series can be ascribed to possible experimental error: a scatter in H-series seems to be larger than that in L-series, as can be seen from open symbols in Fig. 2, and further, the estimation error in the leave-one-out test in H-series was almost twice as large as that in L-series.

On the other hand, the small relative contribution of IP4 in butane oxidation appeared to suggest the possibility that the catalytic activity was also affected by a secondary factor, *r*, ionic radius of trivalent lanthanide cation [7]. Although the difference in the contribution between *r* and *Z* was not so large in Series 1, the relative contribution of *r* was obviously larger than that of *Z* in Series 2. Further, the estimation error in leave-one-out test was the lowest, when only IP4 and *r* were used as input data. Closer inspection of experimental data indicated that, in Fig. 3, the activities of Sm to Gd oxides shown by squares were larger than those of Tm to Lu oxides shown by triangles. This difference seems to correspond to larger *r* of Sm to Gd than those of Tm to Lu; it is known that *r* monotonously decreases with the atomic number in the lanthanum-series. One possibility of explaining the effect of *r* is the hardness of lanthanide cation, which was proposed to affect the oxidation activity of lanthanide oxides [14].

However, this does not necessarily mean that *r* is a real factor controlling the catalytic activity of lanthanide oxides. It is possible that the ionic radius is a dummy parameter of real factor that changes along with *r*. It is also possible that the difference in the activity between two groups is due to an experimental error. In most of published data [15], the differences between two groups were within the reasonable experimental error, maybe because of low activities of these oxides. Therefore, in this particular example, it is quite difficult to propose *r* as a secondary factor without any further experimental study. However, above-mentioned result demonstrates the possibility of identifying the secondary factor, only if the experimental error is not serious. Further study is necessary to establish the method to identify the secondary factor.

5. Conclusions

In order to examine the possibility of analyzing the factors controlling catalytic activity by neural network, Eqs. (1)–(3) were proposed and applied to four examples including both monotonous and volcano-type correlations established experimentally. In all the examples, Eq. (1) successfully identified the primary factors that had been revealed in experimental studies. On the other hand, Eq. (2) could not identify at all, and Eq. (3) could only in limited cases of two examples. Further, it was demonstrated that even the secondary factor could be identified by Eq. (1), only if the experimental error is not serious.

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