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Application of neural network to estimation of catalyst deactivation in methanol conversion

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Abstract

The neural network was applied to the estimation of catalyst deactivation by taking, as an example, methanol conversion into hydrocarbons over ion-exchanged dealuminated mordenites. In the first series, it was attempted to estimate the deactivation rate constant, k_d defined in $-\mathrm{d}A/\mathrm{d}t = k_d A$ where A is the degree of conversion, from the amount of strong acid sites and the catalyst composition such as the Si/Al ratio and the degree of ion exchange. The estimated rate constant agreed well in most cases with the experimentally obtained constant. The most serious exception was Ba ion-exchanged dealuminated mordenite which experimentally exhibited the slowest deactivation. Better agreement was obtained when the first-order reaction rate constant was used as A in the above equation instead of the degree of conversion. In the second series, it was shown that the neural network has a strong ability to extrapolate the catalyst decay curve even without knowing catalyst composition and properties, especially when the first-order reaction rate constant was used to represent the catalyst activity. All of these results clearly demonstrate that the neural network is a powerful tool to estimate the deactivation behaviour of catalysts.

Keywords: Neural network; Deactivation; Decay curve; Methanol conversion; Modified zeolite

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1. Introduction

Although catalyst lifetime is one of the most important properties that industrial catalysts should possess, not many papers have been devoted to the problem in comparison with the activity and selectivity. Therefore, it is still quite difficult to estimate the catalyst lifetime and/or the deactivation rate because of the lack of knowledge about the relation between deactivation rate and controlling factors. The present study aims at examining the possibility of an artificial neural network to estimate the deactivation rate by taking methanol conversion over cation-exchanged mordenite catalysts as an example. The neural network, which arose from attempts to model the functioning of the human brain, is structured to learn the relationship between a set of factors and the results, even if the relation between them is theoretically undefined and is non-linear. Actually, the neural network has been successfully applied predictively in various fields of chemistry, such as structure–activity relationships, structure–spectrum correlations, and so on [1,2]. In catalysis, the present authors successfully applied the neural network for the estimation of the acid strength of mixed oxides [3] and of the catalytic activity and selectivity of oxide catalysts in the oxidative dehydrogenation of ethylbenzene [4] and in the oxidation of butane [5], and proposed that the neural network can be a powerful tool for the design of catalysts [6]. Actually, the neural network was applied to the design of a multicomponent catalyst for propane ammoxidation, and it was demonstrated that the optimum catalyst was obtained after three trial-and-error cycles aided by the neural network [7]. A similar attempt was made for methane oxidative coupling, and it was indicated that the optimum catalyst predicted by the neural network was actually better than any other catalysts in the training set [8]. The design method was further improved by combining the neural network with genetic algorithms. Cundari et al. [9] applied the method for propane ammoxidation and obtained acrylonitrile yield of 79%. Omata et al. [10] also indicated that the

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combination of the neural network and genetic algorithm is a promising method for highly efficient catalyst screening by taking methanol synthesis catalyst as an example. But, so far, no attempt was made to apply the neural network for the deactivation problem.

It is well known that methanol conversion into hydrocarbons on zeolites is followed by catalyst deactivation due to coke deposition formed through the polymerisation of aromatic molecules such as polyalkylbenzenes [11]. H-ZSM-5 zeolite is known to exhibit a durable activity because of the pore structure that retards the coke formation. Another method to obtain durable activity is the modification of acidic properties of zeolites. Although mordenite catalyst was deactivated very quickly in methanol conversion, a durable activity was obtained by Ba ion exchange of highly dealuminated mordenite [12,13].

The present study aims at examining the possibility of an artificial neural network to estimate the deactivation rate by taking, as an example, methanol conversion over modified mordenite catalysts for two cases: the estimation of the deactivation rate constant and the extrapolation of the activity decay curve.

2. Experimental

H-mordenite with a SiO_2/Al_2O_3 ratio of 15.9, referred to as HM15, was a Reference Catalyst of the Catalysis Society of Japan, JRC-HM-15 [14]. The dealumination and the ion exchange were conducted according to the procedures reported previously [12,13]. Dealuminated mordenite, DM, was prepared by leaching HM15 in hydrochloric acid, followed by filtration and washing. Highly dealuminated mordenites were prepared by repeating this procedure. Materials thus obtained were dried, pelleted, crushed, and sized to 28–48 mesh. Ion exchange was conducted with an aqueous solution of corresponding acetate, followed by filtration, washing, and drying. These samples were calcined at 673 K in an O_2 flow. Table 1 lists the catalysts thus prepared. The numerals following 'DM' and 'Ba or La' in the catalyst symbols stand for the SiO_2/Al_2O_3 ratio and the degree of ion exchange, respectively.

The acid amount and strength were measured by temperature programmed desorption of ammonia in the same way as described previously [13,15], except that the samples were evacuated for 5 h after the equilibration of ammonia-adsorption in order to minimmize a low-temperature desorption peak. The amount of strong acid sites thus determined is also shown in Table 1. Methanol conversion was conducted using a conventional continuous flow reactor at atmospheric pressure in a similar way to that described previously [12,13]. Methanol ($68.2 \times 10^{-6}\,\mathrm{mol\,min^{-1}}$) in helium gas ($40\,\mathrm{cm^3\,min^{-1}}$) was fed over zeolite catalyst (50 mg) at 623 K. Only a small amount of catalyst was used so as to evaluate more exactly the rate of deactivation.

3. Catalyst deactivation in methanol conversion

Fig. 1 shows the decline of catalytic activity of HM15 and some modified mordenites with time on stream. On HM15, the total yield of hydrocarbons decreased rapidly, and it became almost negligible after the reaction for 4 h. A dealuminated mordenite, DM104, exhibited similar deactivation behaviour except that the initial yield, measured after the reaction for 5 min, was higher than that on HM15. Further dealumination not only retarded the deactivation but also lowered the initial activity: The hydrocarbon yield on DM328 was significant even after the reaction for 5 h, though the initial yield was much lower than that on DM104. The lower initial activity of DM328 can be attributed to a smaller amount of strong acid sites shown in Table 1. The lowest initial activity of HM15, however, cannot be interpreted in terms of the amount of strong acid sites, because HM15 has a much larger amount of strong acid sites than the dealuminated mordenites.

On the other hand, Ba ion exchange had a remarkable effect on the deactivation behaviour: Ba32DM104 exhibited very slow deactivation, which indicates that the deactivation rate was remarkably retarded by the introduction of a rather small amount of Ba ion. Further increase in Ba ion led to considerable decrease of initial yield, maybe because of the smaller amount of strong acid sites.

The deactivation process is frequently described by the following power rate expression:

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = k_d A^n \tag{1}$$

where k_d is the deactivation rate constant and A is the relative activity of the catalyst [16]. When n is equal to unity and the total yield or the conversion, X, is used as A, the integration of Eq. (1) gives the following equation:

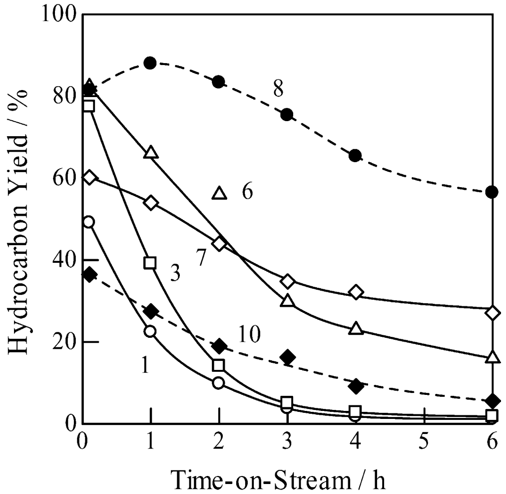

Fig. 1. Deactivation of unmodified and modified mordenites in methanol conversion. (1) HM15; (3) DM104; (6) DM164; (7) DM328; (8) Ba32DM104 and (10) Ba80DM104.

Table 1
List of catalysts used in the present study

No.	Catalyst	Si/Al_2	Ion exchange (%)		Acid amount ($mmol\,g^{-1}$)	k_d (h^{-1}) Eq. (2)[a]	k_d (h^{-1}) Eq. (5)[a]
			Ba	La			
1	HM15	15.9	0.0	0.0	0.82	0.85	0.93
2	DM50	50.4	0.0	0.0	0.29	0.96	1.08
3	DM104	104.0	0.0	0.0	0.21	0.89	1.04
4	DM107	107.0	0.0	0.0	0.23	0.92	1.06
5	DM126	126.0	0.0	0.0	0.17	0.82	0.95
6	DM164	164.0	0.0	0.0	0.14	0.30	0.50
7	DM328	328.0	0.0	0.0	0.11	0.14	0.24
8	Ba32DM104	104.0	32.4	0.0	0.15	0.09	0.23
9	Ba52DM104	104.0	52.3	0.0	0.12	0.25	0.31
10	Ba80DM104	104.0	79.5	0.0	0.04	0.32	0.35
11	Ba29HM15	15.9	28.7	0.0	0.31	0.52	0.55
12	Ba47HM15	15.9	47.3	0.0	0.20	0.50	0.52
13	Ba64HM15	15.9	64.3	0.0	0.05	0.25	0.25
14	Ba70HM15	15.9	70.0	0.0	0.01	0.31	0.28
15	La31DM107	107.0	0.0	30.6	0.23	0.71	0.85
16	La47DM107	107.0	0.0	46.9	0.20	0.54	0.73
17	La76DM107	107.0	0.0	76.1	0.19	0.50	0.62

[a] Defined by Eqs (2) and (5), respectively.

$$\ln\left(\frac{X}{X_0}\right) = -k_d t \qquad (2)$$

As previously reported [13], this equation fitted the experimental results fairly well as shown in Fig. 2. The assumption that the total yield represents the catalytic activity means that the reaction is assumed to be a zero-order reaction. The deactivation rate constant obtained from the slope of the straight line in Fig. 2 was also shown in Table 1: The deactivation rate constant was decreased by the dealumination, and it was remarkably decreased by the Ba ion exchange of dealuminated mordenites. On the other hand, the Ba ion exchange of the parent mordenite, HM15, and La ion exchange of dealuminated mordenite decreased the rate constant to some extent, but not remarkably.

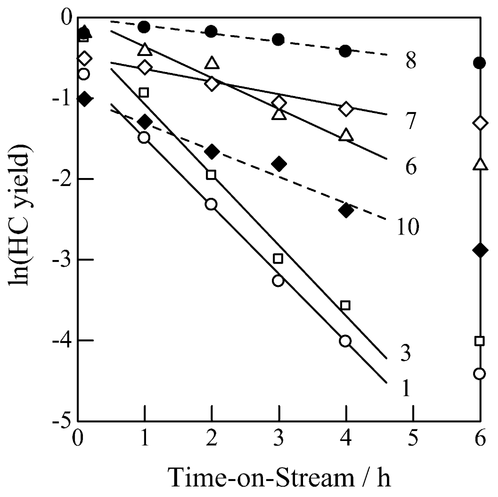

Fig. 2. Plot of the first-order deactivation of unmodified and modified mordenites in methanol conversion on the assumption of the zero-order reaction. (1) HM15; (3) DM104; (6) DM164; (7) DM328; (8) Ba32DM104; and (10) Ba80DM104.

4. Overview of the neural network

In the present study, an artificial neural network based on an error back propagation model is used because of its strong learning capability. Fig. 3 schematically shows an overview of the structural organisation of the neural network used for the estimation of the deactivation rate constant defined as above. 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 deactivation, i.e., the Si/Al2 ratio, the degree of Ba ion exchange, the degree of

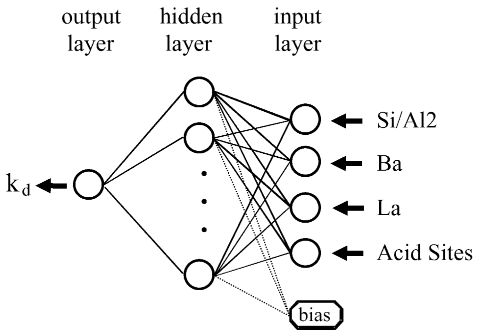

Fig. 3. Construction of the neural network used for the estimation of the deactivation rate constant (k_d) by using Si/Al2 ratio, degree of Ba ion exchange, degree of La ion exchange, and amount of strong acid sites as possible factors controlling k_d.

La ion exchange, and the amount of strong acid sites in this case. The output layer, on the other hand, contains one unit representing the output data to be estimated, i.e., the deactivation rate constant in this case.

If a training set of known pairs of input data (SiO_2/Al_2O_3 ratio, degrees of Ba and La ion exchange, and amount of strong acid sites) and output data (observed deactivation rate constant) is given to the neural network, 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 weight of connections (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. The final set of weight of connection may be compared to a 'mathematical function' representing the relation between the output and input data through a medium of hidden layer units (y_j):

$$k_d = f_1(y_1, y_2, \dots) \tag{3}$$

$$y_j = f_2(\mathrm{Si/Al2, Ba, La, Acid\,amount}). \tag{4}$$

Then, the deactivation rate constant of a target catalyst can be calculated by substituting the corresponding input data, i.e., the Si/Al2 ratio, the degrees of Ba and La ion exchange, and the amount of strong acid sites of target catalyst, in the network pattern thus trained.

The estimation ability of the neural network was examined through a leave-one-out test. First, the neural network was trained to learn the 'function' by using a training set of the input and output data, in which both of the input and output data of one catalyst were left-out. Then, the deactivation rate constant on the left-out catalyst was calculated by introducing the input data of the left-out catalyst into thus trained network. This procedure was repeated for all the catalysts, and the calculated constants were compared with the experimentally observed ones.

The back propagation neural network is known to overfit the training set, bringing sometimes rather large error in predicted values after the training with too many iterations. Because of its strong learning capability, the neural network is said to learn not only the tendency of target phenomena but also various noise such as errors involved in the given set of input and output data, particularly after training with an excess number of iterations. This problem was solved as follows: In the leave-one-out test mentioned above, the errors in the calculated output values were recorded as a function of training iterations. First, the mean error for all the catalysts decreased steeply with the training iteration, reached a minimum, and then increased because of the overfitting. The output values calculated by using the network giving a minimum error were taken as the predicted values in the present study.

For each case, more than 20 runs of the leave-one-out test were conducted by changing the initial weight of connections to avoid being trapped in the local minimum and by changing the numbers of hidden layers and units to attain an efficient estimation without overfitting. Generally speaking, the estimated values were reproduced within a reasonable error except for those obtained with too-simple network structure. The estimated results shown here are those of minimum errors, because the local minimum results in larger error.

5. Estimation of the deactivation rate constant

First, the possibility of estimating the deactivation rate constant, defined by Eq. (2), was examined by using the neural network with the construction shown in Fig. 3. The SiO_2/Al_2O_3 ratio, the degree of Ba ion exchange, the degree of La ion exchange, and the amount of strong acid sites were used as the input data, i.e., the possible factors controlling the deactivation rate constant. Open symbols in Fig. 4 show the comparison of deactivation rate constants estimated by the leave-one-out test with those obtained experimentally. As shown, the estimated constants agreed with the experimental values within probable experimental error, except for HM15, DM50, DM164, and Ba32DM104. This agreement with a few exceptions suggests the possibility of the neural network to estimate the deactivation rate constant, but it also suggests that further examination is necessary to obtain better agreement without exceptions.

In the case of DM164, the experimental data seemed to contain some experimental error, because the catalyst decay curve shown in Fig. 1 was not monotonic and the plot in Fig. 2 did not give a good straight line in comparison with the other catalysts. In the cases of HM15 and DM50, the de-

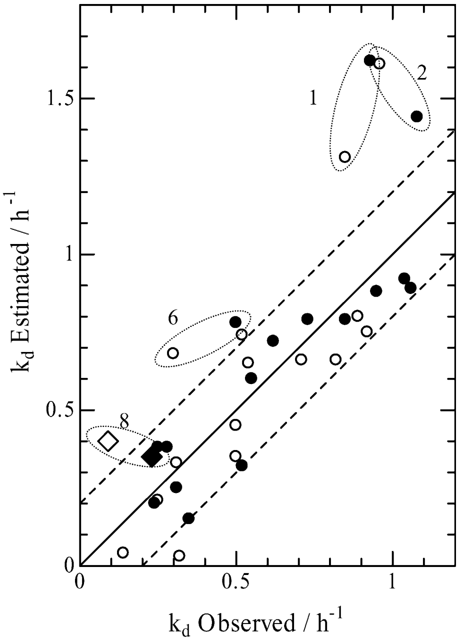

Fig. 4. Comparison of estimated deactivation rate constants defined by Eq. (2) (open symbols) and Eq. (5) (closed symbols) with those experimentally observed. (1) HM15; (2) DM50; (6) DM164; and (8) Ba32DM104.

tailed inspection of the experimental results suggested that the experimentally obtained deactivation rate constants are underestimated and that the estimated deactivation rate constants are rather valid. In the case of HM15, for example, the initial HC yield on HM15 was much lower than those on the other catalysts, though HM15 had much larger amount of strong acid sites. This result can be rationalized, if HM15 was significantly deactivated even in the initial 5 min. Actually, the amount of coke deposited in the initial 5 min attained 4.4% of catalyst weight, which was much larger than those on, for example, DM104 (0.16%) and Ba32DM104 (0.09%). As for DM50, although the initial activity was close to those on DM104 and Ba32DM104, the amount of coke deposited (1.01%) was also much larger. All of these indicate that HM15 and DM50 were deactivated much faster than expected from the deactivation rate constant calculated from the slope of the line in Fig. 2. In the case of Ba32DM104, which was the best catalyst in the present study, the disagreement between the estimated and the experimental deactivation rate constants, shown by an open diamond, could not be explained.

Another attempt was made on the assumption that the methanol conversion is a first-order reaction with respect to methanol partial pressure. The integration of Eq. (1) on this assumption gives the following equation:

$$\ln\left(\frac{k_1 W}{F}\right) = -k_d t + \text{constant} \qquad (5)$$

where $k_1 W/F = -\ln(1-X)$. Fig. 5 shows that this equation fitted the experimental results to an extent similar to Eq. (2) shown in Fig. 2. The deactivation rate constant calculated from this figure was also indicated in Table 1. By using this deactivation rate constant as the output data of the training set, the leave-one-out test was conducted with the neural network of the same structure shown in Fig. 3 and with the same input data as above. Closed symbols in Fig. 4 show the comparison of the deactivation rate constant thus estimated with the experimental constant. In the cases of HM15, DM50, and DM164, for which the experimental deactivation rate constant seemed to contain some experimental error, the estimated deactivation rate constant did not agree well with the experimental rate constant. The estimation error in these cases seemed close to that of the deactivation rate constant defined by Eq. (2), or, in other words, the estimation error was not essentially affected by the definition of the deactivation rate constant. This is because a main cause of error seemed to be attributed to the experimental error but not to the estimation error. For the other cases, the estimated deactivation rate constant agreed well with the experimental rate constant within a reasonable error. It should be noted that, as shown by closed diamond, a close agreement was also obtained in the most important case of Ba32DM104, which is in marked contrast to the result that only a poor agreement was obtained on the basis of Eq. (2) as shown by an open diamond. Or, in other words, high estimation accuracy was obtained only when the result of the catalytic run was represented by the reaction rate constant, but not by the total yield or the conversion. This clearly indicates that the estimation accuracy strongly depends on the representation mode of the output data to be estimated.

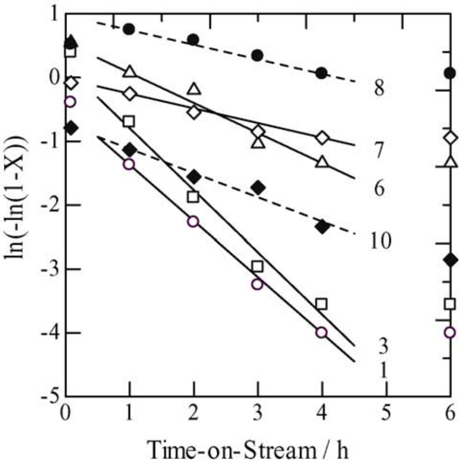

Fig. 5. Plot of the first-order deactivation of unmodified and modified mordenites in methanol conversion on the assumption of the first-order reaction. (1) HM15; (3) DM104; (6) DM164; (7) DM328; (8) Ba32DM104; and (10) Ba80DM104.

6. Extrapolation of catalyst decay curve

In the second series, it was attempted to extrapolate the catalyst decay curve, i.e., to estimate the catalytic activity after a prolonged run from the initial decay data. In the first run of this series, the total yield after the catalytic run for a certain period was estimated from the result of a catalytic run showing initial decay and the composition and properties of catalysts. As shown in Fig. 6, the input data included not only the Si/Al2 ratio, the degree of Ba ion exchange, the degree of La ion exchange, and the amount of strong acid sites of catalysts but also the HC yields at 5 min, 1, 2, and 3 h, and the output data included the HC yields at 4 and 6 h.

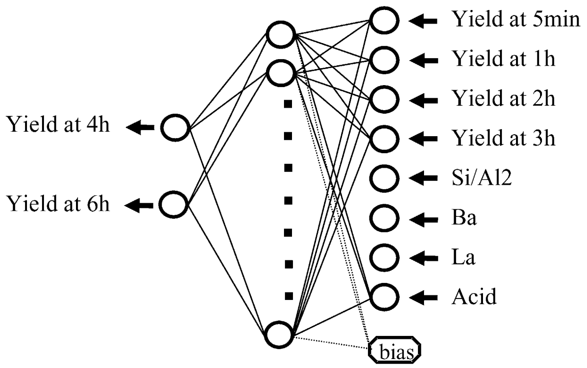

Fig. 6. Construction of the neural network used for the extrapolation of the decay curve by using Si/Al2 ratio, degree of Ba ion exchange, degree of La ion exchange, amount of strong acid sites, and yields at 5 min, 1, 2 and 3 h as input data.

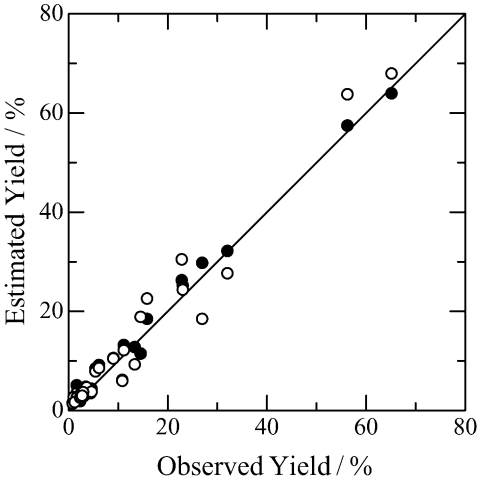

Fig. 7. Comparison of HC yields at 4h and 6h estimated by the neural network with experimentally observed yields. Closed circles, estimated from the input data shown in Fig. 6; and open circles, estimated from the input data including only the yields at 5 min, 1, 2 and 3 h but not the composition and properties of catalyst.

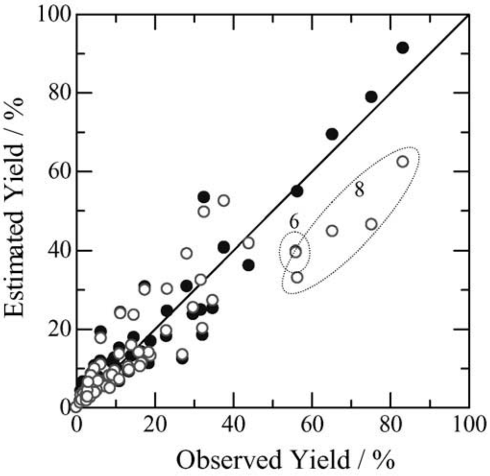

Fig. 8. Comparison of HC yields at 2, 3, 4 and 6 h estimated by neural network with experimentally observed yields. Input data included only the yields (open circles) and the first-order reaction rate constant (closed circles) at 5 min and 1 h. (6) DM164 and (8) Ba32DM104.

The result of the leave-one-out test was shown by closed circles in Fig. 7. As shown, the estimated HC yields agreed very well with the experimental values. It should be noted that the estimation accuracy was much higher than that for the estimation of deactivation rate constant shown in Fig. 4. Especially, even in the cases of HM15 and DM50 for which the deactivation rate constants could not be estimated well, the estimated yields agreed very well with the experimental values.

Open circles in Fig. 7 show the result of the leave-one-out test conducted by excluding the composition and properties of catalysts from the input data: The HC yields at 4 and 6 h were estimated only from the HC yields at 5 min, 1, 2, and 3 h. As shown, although the estimation accuracy in this case was slightly lower than the above-mentioned error shown by closed circles, the accuracy was also higher than that for the estimation of deactivation rate constant shown in Fig. 4. These results suggest that the neural network has a strong capability of extrapolation of the catalyst decay curve even without knowing the composition and properties of the catalyst.

Further examination, however, indicates that such high estimation accuracy cannot always be attained, but it depends on the representation mode of the output data. Open circles in Fig. 8 show the HC yields at 2, 3, 4, and 6 h estimated from those at 5 min and 1 h: The output data were the HC yields at 2, 3, 4, and 6 h, and the input data included only the yields at 5 min and 1 h, but not the composition and properties of catalysts. As shown, the estimated yields did not agree well with the experimental yields. The disagreement was remarkable on DM164 and Ba32DM104, which exhibited slow deactivation. Then, the first-order reaction rate constant, k_1W/F, was used as the input and output data instead of the yield: The first-order reaction rate constants at 2, 3, 4, and 6 h were estimated from the rate constants at 5 min and 1 h, as shown in Fig. 9. Closed circles in Fig. 8 show the yields at 2, 3, 4 and 6 h calculated from the first-order reaction rate constants thus estimated. As shown, the calculated yields agreed very well with the experimentally obtained yields, forming a good contrast to the poor agreement shown by open circles. It should be emphasized that such high estimation accuracy can be attained, even when the composition and properties of the catalyst were excluded from the input data. Fig. 10 shows some examples of the estimated results in the form of the catalyst decay curve in order to demonstrate a high capability of the neural network for the extrapolation of the catalyst decay curve. As shown in the figure, the estimated decay curves agreed well with experimentally observed decay curves, indicating that the decay curves from 2 to 6 h could be well estimated from the initial data at 5 min and 1 h. It should be added that, as shown by inverted triangles, only a poor agreement was obtained, when the total yield was used instead of the reaction rate constant to represent the results of the catalytic run.

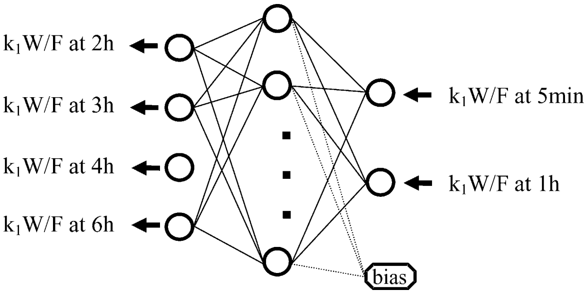

Fig. 9. Construction of the neural network used for the estimation of the rate constants of the first-order reaction, i.e., $-\ln(1-X)$, at 2, 3, 4, and 6 h from the rate constants at 5 min and 1 h as input data.

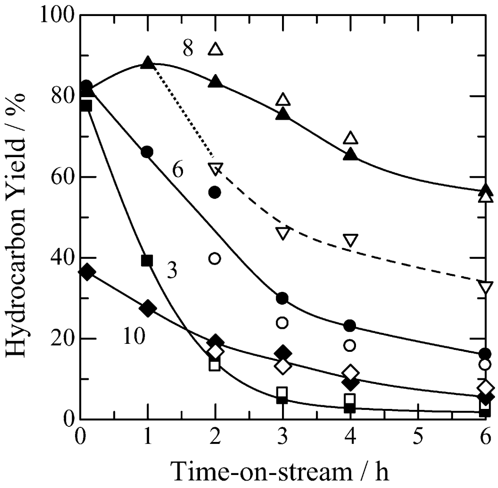

Fig. 10. Comparison of the decay curve estimated by using the neural network shown in Fig. 9 (open symbols) with the experimentally observed curve (closed symbols). (3) DM104, (6) DM164, (8) Ba32DM104, and (10) Ba80DM104. Inverted triangles stand for the decay curve estimated by using HC yield as input and output data.

7. Conclusions

The ability of the neural network to estimate catalyst deactivation was examined by taking, as an example, methanol conversion into hydrocarbons over ion-exchanged dealuminated mordenites. First, the neural network was applied for the estimation of the deactivation rate constant from the amount of strong acid sites and the catalyst composition such as the Si/Al ratio and the degree of ion exchange. It was revealed that the representation of output data to be estimated, i.e., the definition of the deactivation rate constant, has a large effect on the estimation accuracy, and that a main cause of estimation error seemed to be attributed to the experimental error. Second, it was attempted to extrapolate the catalyst decay curve. The estimated values agreed very well with the experimental values, even in the case where the experimental data seemed to contain some experimental error. The estimation accuracy was high, even when the input data included only the initial decay data but not the composition and properties of the catalysts. Higher estimation accuracy was attained when the reaction rate constant was used to represent the result of the catalytic run instead of the total yield or the conversion.

These results lead to the conclusion that the neural network can be a powerful tool for the estimation of catalyst life through the deactivation rate constant and/or the extrapolation of the catalyst decay curve.

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