Simultaneous Optimization of Preparation Conditions and Composition of the Methanol Synthesis Catalyst by an All-Encompassing Calculation on an Artificial Neural Network

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Design and Development of Cu−Zn Oxide Catalyst for Direct Dimethyl Ether Synthesis Using an Artificial Neural Network and Physicochemical Properties of Elements

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A hybrid catalyst consisting of Cu−Zn−X oxide and γ-alumina was prepared for single-stage dimethyl ether synthesis. An artificial neural network (ANN) was applied to find the effective additives for the hybrid catalyst. For the training of ANN, elements (X)—B, K, Nb, Re, Cd, Ce, Sm, and Tl—were selected. The activity change with time on stream of the hybrid catalyst was fitted to a generalized power law equation (GPLE). The resultant GPLE parameters and the physicochemical properties of the eight elements were used as training data for ANN. After the training, the trained ANN was used to predict the activity of the hybrid catalyst containing various X elements as Cu−Zn−X. Elements Al, Ti, V, and Nb were predicted as promising, and the composition of hepternary oxide catalyst was optimized by the combination of design of experiment, ANN, and grid search. The catalyst with the optimized composition showed stable and high activity.

Introduction

Dimethyl ether (DME), which can be easily derived from methanol, is a superior clean fuel for both transportation and power generation. A compact and simple process has been proposed to produce this fuel with a good economy from dispersed unused carbon resources.[1] The key point of this process is the development of a noble hybrid catalyst for one-stage DME synthesis from syngas. The hybrid catalyst is prepared by mixing Cu−Zn oxide for methanol synthesis and γ-alumina for methanol dehydration. In the present study, we searched for new additives for Cu−Zn oxide catalyst with the aid of the periodic table and an artificial neural network (ANN). Then the catalyst composition was optimized with the aid of design of experiment (DOE), ANN, and a grid search.

Recently, ANNs have been increasingly applied to catalyst development through the prediction of catalyst performance, such as activity, selectivity, and durability, from experimental results. Among them, a few successful cases have been reported where catalytic properties were predicted from physicochemical properties of the catalyst elements.[2,3] We also successfully predicted an effective additive both on Ni/active carbon catalyst for carbonylation of methanol[4] and on Cu−Zn oxide catalyst for methanol synthesis.[5] Our predictions were conducted based on the previous experimental results and physicochemical properties of related elements. Better selectivity was obtained in the case of Ni/active carbon catalyst using ANN trained by 11 pairs of training data. In contrast, the predictions for Cu−Zn oxide catalyst were not as good, although the ANN was trained by 22 pairs of training data. The range and dispersion of physicochemical properties included in the training data were important factors for the quality of the predictions.

Applications of ANNs to the prediction of activity, not only at steady-state activity but also at unsteady state, have been reported.[6,7] We fitted the activity change with time on stream of Co−MgO catalyst for dry reforming of methane to a simple power law equation (SPLE).[7] An artificial neural network learned the relationship between the catalyst preparation parameters and the SPLE parameters, and predicted the preparation parameters for stable catalyst.

We have reported the optimization of catalyst using DOE and ANN.[8,9] The activity of the catalysts, the compositions[8] or preparation parameters[9] of which were determined by the orthogonal array, was measured in a high-throughput screening manner[8] or in a conventional fixed bed reactor.[9] The ANNs were trained using the experimental results, and the optimum point in the ANN was searched for using a grid search. If an ANN was trained using 18 experimental data that were designed by DOE (L_{18} orthogonal array), the ANN gave predictions as good as those by an ANN trained by 94 data for which the parameters were determined randomly. In addition, a radial basis function network (RBFN) gave better prediction results than a back-propagation type ANN.[8] DOE gives an effective data set for ANN, especially RBFN training.

Each methodology, such as (i) prediction for new additives by ANN based on physicochemical properties,[4] (ii) GPLE and ANN for stable catalyst,[7] and (iii) DOE and ANN for optimization,[8,9] was reported separately. In the present study, all of them were used for the first time sequentially from the screening stage to the optimization stage of a catalyst development.

Methods

Activity Test. Cu−Zn−X oxide catalysts were prepared by an oxalate−ethanol coprecipitation method. Ethanol solutions of nitrate of Cu, Zn, and one additive except V and Be were

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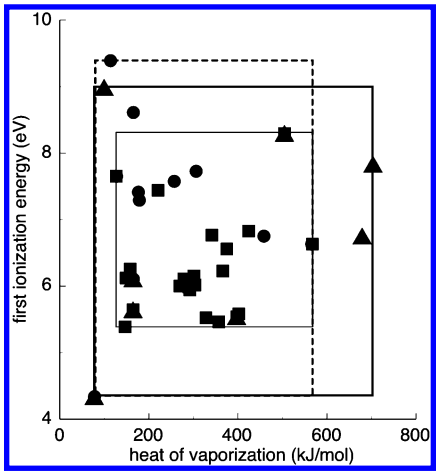

Figure 1. Dispersion of training data set: ■, 22 elements for methanol synthesis; ●, 11 elements for methanol carbonylation; ▲, 8 elements for dimethyl ether synthesis.

mixed (Cu/Zn/X molar ratio was 65/35/5), and then an ethanol solution of oxalic acid was mixed to precipitate the mixed oxalic salts. Vanadium acetyl acetone was solved in a mixed solvent (acetone:methanol = 1:1), and it was used as the V source. Nitrate in 50 wt % aqueous solution was used as the Be source. Ethanol was removed by vaporization followed by calcination in air at 623 K for 4 h. The oxide was mixed with γ-alumina granules to use as a hybrid catalyst. The weight ratio of γ-alumina was 1.2 times the catalyst oxide. The hybrid catalyst was activated in situ in a conventional fixed bed reactor at 0.1 MPa and 523 K using reaction gas ($H_2/CO/CO_2/N_2$ = 60/30/5/5). Methanol synthesis was conducted at 498 K, 1 MPa, W/F = 8 g of cat. h/mol to measure CO_x (CO and CO_2) conversion. The unreacted syngas was analyzed by a micro gas chromatograph (Micro-GC, M-200, Agilent Technologies, Inc.). After catalytic activity was measured, the activity change with time on stream was fitted to a generalized power law equation (GPLE).[10] The activity was expressed as eq 1, where t (min) is time on stream and a, b, c, and d are GPLE parameters.

$$CO_x \text{ conversion} = a/(b + t) \wedge c + d \qquad (1)$$

Each catalyst was featured by the four parameters, and this kind of parametrization was necessary because a variety of additives were used to obtain training data for ANN even if the unsteady state activity was sometimes obtained.

Methodology. Artificial neural networks were applied to correlate physicochemical properties with the GPLE parameters. Among many types of ANNs, a radial basis function network (RBFN) was used becasue it is robust and tolerant of experimental errors. STATISTICA Neural Network (version 6; StatSoft, Inc.) was used for constructing an RBFN, which was trained by the eight pairs of physicochemical character−activity data. Physicochemical properties of additives (X) were collected from database software (Periodic Table X, version 3.5; Synergy Creations).

After five effective additives to Cu−Zn oxide catalyst were determined, the catalyst composition was designed by an L_{18} orthogonal array of the Taguchi method for the optimization. ANN was again used to correlate catalyst composition with the GPLE parameters. Then, a grid search was conducted to find the global maximum of the ANN. The grid search program was coded using macro commands of STATISTICA. Response surfaces as functions of Cu and Zn content can be obtained using the predictions of the ANN. When other compositions are different, the response surfaces differ from each other. If all the response surfaces are overlapped, the top view represents a so-called envelope of the response surfaces and we can find the global maximum on the envelope. Finally, the activity of the predicted optimum catalyst was confirmed in a conventional fixed bed reactor for a long time.

Results and Discussion

Selection of Elements and Physicochemical Properties for Training. In our previous studies, the number of training data for ANN was not closely related to the quality of its prediction.[4,5] In both cases, RBFN was used as ANN to correlate the physicochemical properties with the catalytic activity. The properties used in the former case were first ionization energy (IE, eV), heat of vaporization (HV, kJ/mol), melting point (MP, K), and atomic radius (AR, pm). A total of four properties were given to the input layer of the RBFN. In the latter case, there were five: IE, HV, MP, ionic radii (IR, pm) instead of AR, and atomic number (AN). Thus, the structures of RBFN and the type of input data were similar.

On the contrary, the kind of elements included in the training data was naturally different because the elements were selected as promising ones for each reaction. The physicochemical properties of these elements were compared, and clearly, the range of the properties was influential in the prediction of ANN. As representatives of the properties, HV and IE of each element are plotted in Figure 1 with a square showing the boundary of each group. The area for methanol carbonylation shown by the broken line and filled circles is wider than that for methanol synthesis shown by the thin solid line and filled squares.

Generally, ANN works as an interpolatory function, and a training data set with a wide range is desirable for the prediction over a wide range. A similar result was reported for the prediction of catalyst activity from the catalyst composition. The accuracy of ANN trained using an 18 data set designed by an L_{18} orthogonal array was almost same as that of ANN trained using a 94 data set that was randomly determined.[8]

If this is the case, we can expect an accurate prediction from a small data set whose properties are well dispersed like a "virtual" orthogonal array hidden in the periodic table. For example, an L_4 orthogonal array dealing with three factors with two levels is shown in Table 1a. When AN, HV, and IP are used as three factors, and each value 3−44 of AN, 9−165 of HV, and 3.8−5.6 of IE are decided as level 1 whereas 45−88 of AN, 166−824 of HV, and 5.6−10.5 of IE are decided as

Table 1. Sample of Orthogonal Array

(a) L_4 orthogonal array				(b) "virtual" orthogonal array in periodic table			
	level				level		
expt no.	factor 1	factor 2	factor 3	element	AN	HV	IE
1	1	1	1	K	1	1	1
2	1	2	2	B	1	2	2
3	2	1	2	Cd	2	1	2
4	2	2	1	Re	2	2	1

level 2, the orthogonal array can be realized using K, B, Cd, and Re as shown in Table 1b.

According to the above discussion, eight elements including B, K, Nb, Re, Cd, Ce, Sm, and Tl were selected in the present study. No orthogonal array was realized using these elements because the salts of the elements should be dissolved in ethanol for catalyst preparation, and the combinations of properties are limited and distorted. HV and IE values of these elements are also plotted in Figure 1 by filled triangles and the thick solid line. Clearly, the eight elements are dispersed in a wider area.

As the training data, the linear expansion coefficient (per degree), magnetic susceptibility (cm^3/mol), atomic radius (pm), atomic volume (cm^3), fourth ionization energy (eV), and resistivity (ohm m) of the eight elements were not used because of the lack for the eight elements. Furthermore, when some physicochemical properties of the eight elements have high correlation coefficients with each other, we can use only one representative property. In conclusion, nine physicochemical properties of the eight elements, or their subset, could be included in the training data set. The properties were AN, HV, IR, IE, covalent radius (CR, pm), density (DS, g/cm^3), thermal conductivity (TC, W/(m K)), photoelectric work function (PW, eV), and second ionization energy (SI, eV).

Activity Test of Cu−Zn−X Oxide Catalyst and Determination of GPLE Parameters. The activity change of a hybrid catalyst of Cu−Zn−X oxide and γ-alumina with time on stream is shown in Figure 2. Activities with Cu−Zn oxide (shown as none) and Cu−Zn−Al, which is the typical industrial catalyst, are also shown in the figure. The latter result was used as validation data during ANN training. Open triangles are experimental results, and solid lines are the fitting results to GPLE. In the case of B addition, only the experimental result before 400 min was fitted to GPLE, because the increase of the activity after 400 min of reaction is the effect of B escape from the catalyst surface.[11] The fitted GPLE parameters are listed in Table 2.

The interesting point in Table 2 is the effect of B addition. Whereas B was reported as an effective additive to Cu−Zn oxide catalyst for methanol synthesis,[11,12] the GPLE parameters suggest the low activity of Cu−Zn−B oxide when mixed with γ-alumina as a hybrid catalyst. The difference is the formation of water during the reaction. In single-stage DME synthesis, a stoichiometric amount of water or carbon dioxide is formed. The effect of water addition was compared in Figure 3. All the activities of Cu−Zn oxide catalyst were suppressed by water addition. The degree of the degradation was Cu−Zn > Cu−Zn−B > Cu−Zn−Al. The result suggests that B is not an excellent additive to Cu−Zn oxide for single-stage DME synthesis.

Search for New Additives on Trained RBFN. After training using the physicochemical properties of the eight elements and the GPLE parameters, the validation error of RBFN7-8-4 with one hidden layer was the lowest among various kind of RBFNs. The number of nodes in the input layer, hidden layer, and output layer of RBFN7-8-4 is 7, 8, and 4, respectively. Seven properties—AN, HV, CR, DS, PW, IE, and SI—were used for the input layer, and IR and TC were not included in the RBFN. Parameter *d* of GPLE, the residual activity, as a function of each input datum is shown in Figure 4a−g, and no clear relation was observed between the value of *d* and each property. The *d* predicted by the RBFN was almost the same as the experimental *d*.

The effects of elements, which were not included in the training data set, was predicted by the trained RBFN7-8-4. The

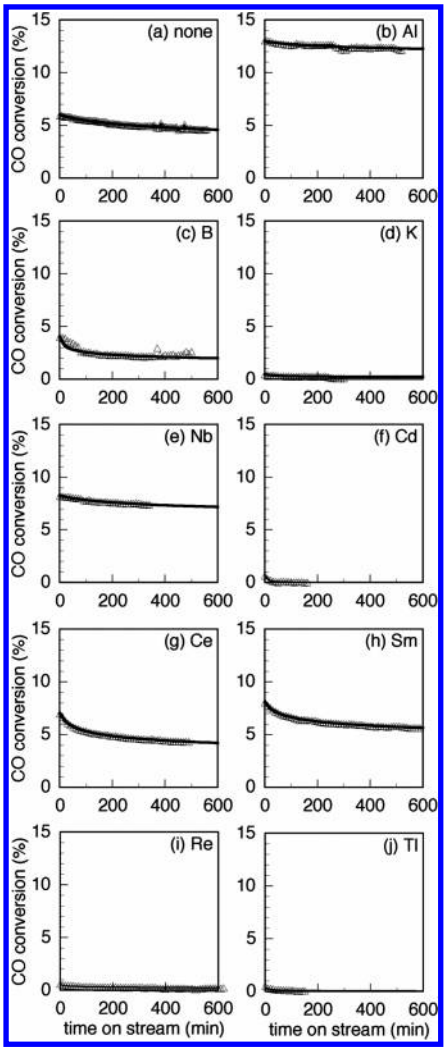

Figure 2. Effect of additives on activity of Cu−Zn oxide. 1 MPa; 498 K; Cu/Zn/additive = 65/30/5 molar ratio.

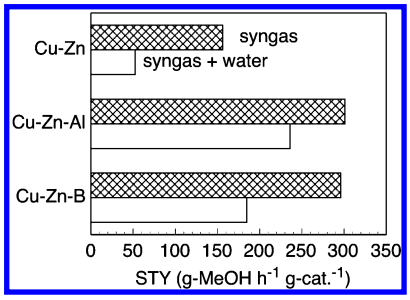

Figure 3. Effect of water addition on activity of methanol synthesis. 1 MPa; 498 K; syngas feed 500 mmol h^{-1} g of cat.$^{-1}$; water feed 6.7 mmol h^{-1} g of cat.$^{-1}$; Cu/Zn = 2/1 molar ratio; additive 10 mol %.

activity after 1000 h time on stream was calculated using the predicted parameters and GPLE. The four highest activities in the training data, the validation data, and the predicted result were Al > V > Ti > Nb. Among them, Al was used as validation, and Nb was used as training. V, Ti, and Nb were, for us, entirely new additives to Cu−Zn oxide catalyst for methanol synthesis.

Cu−V ultrafine particle catalyst has been reported as an active catalyst for methanol synthesis in a liquid phase.[13] The activity was higher than that of Cu−Zn. Addition of a small amount of V was also reported as effective in an early review.[14] Ti has been reported as an effective additive to silica supported Cu catalyst.[15] We found only negative effects of Nb in the

Table 2. GPLE Parameters by Fitting to Experimental Result

	GPLE parameters			
additive	*a*	*b*	*c*	*d*
none	11.81	112.6	0.190	1.19
Al	10.71	60.1	0.034	3.66
B	4.79	5.3	0.174	0.43
K	9.93	42.5	0.988	0.22
Nb	8.29	79.6	0.114	3.25
Cd	18.30	13.9	1.295	0.00
Ce	10.40	20.7	0.212	1.54
Sm	9.44	20.7	0.164	2.33
Re	0.85	11.7	0.238	0.06
Tl	1.05	8.7	0.502	0.01

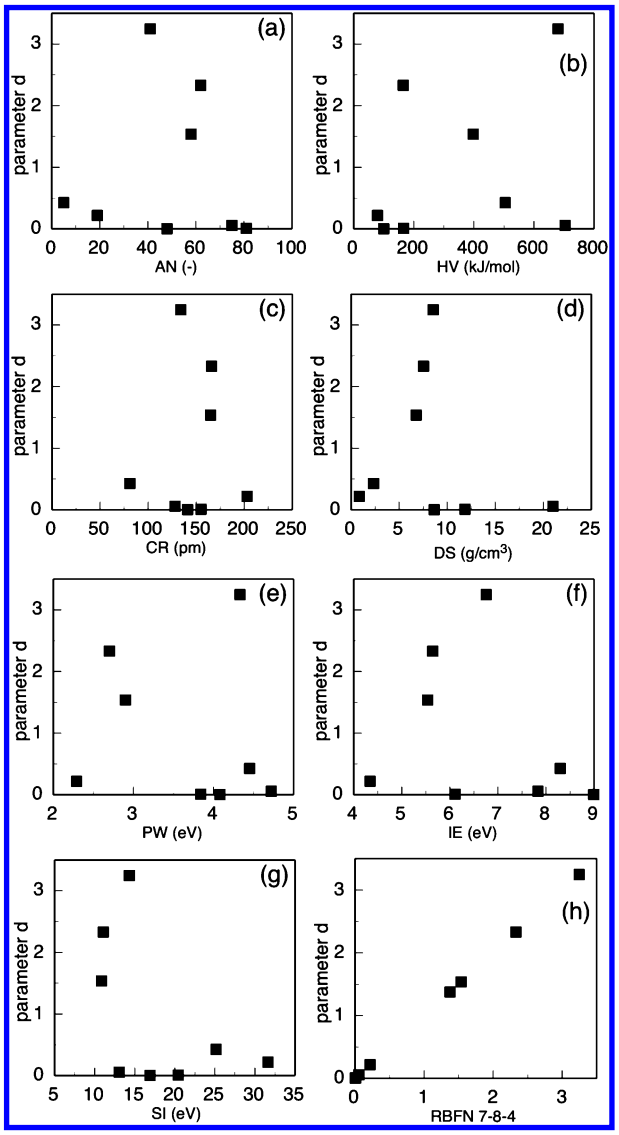

Figure 4. Parameter *d* as a function of physicochemical properties.

literature.[16] In that case, the activity of Raney Cu−Nb was lower than that of Cu−Zn catalyst for methanol synthesis.

The effect of V and Ti as the third additive to Cu−Zn oxide was examined. As shown in Figure 5 as open triangles, they showed high activity. The GPLE parameters are listed in Table 3. The parameter *d* of Ti-containing catalyst is higher than that of all catalysts in Table 2. From this result, we confirmed that this methodology is useful to discover new catalysts and can promote the catalyst development process.

Optimization of Catalyst Composition Using an Orthogonal Array and an Artificial Neural Network. The binary Cu−

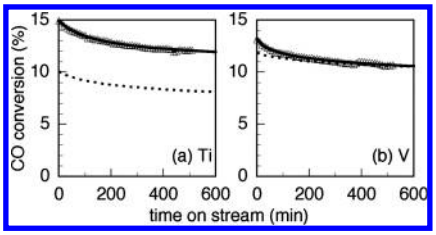

Figure 5. Effect of candidate elements on activity of Cu−Zn oxide. 1 MPa; 498 K; Cu/Zn/additive = 65/30/5 molar ratio. Broken line is the predicted activity.

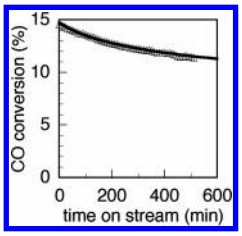

Figure 6. Effect of Be on activity of Cu−Zn oxide. 1 MPa; 498 K; Cu/Zn/Be = 65/30/5 molar ratio.

Table 3. Experimental GPLE Parameters of Candidate Elements

	GPLE parameters			
additive	*a*	*b*	*c*	*d*
Ti	40.88	88.6	0.476	10.09
V	13.61	26.1	0.095	3.19

Be oxide had been reported to be more active than Cu−Zn,[17] and in the previous study, Be was predicted from the experimental results of 22 elements to promote the activity of Cu−Zn oxide for methanol synthesis. However, in the present study, Be was not recommended as an effective additive from the experimental results of eight elements. Probably the low activity of B-containing catalyst reflected the prediction for the neighboring element in the periodic table. The activity test of Be-containing catalyst for DME synthesis was conducted. The activity change is shown in Figure 6. The GPLE parameters *a*, *b*, *c*, and *d* are 37.93, 164.1, 0.244, and 3.78, respectively. The estimated activity after 1000 h time on stream was higher than that of Nb-containing catalyst, and Be was confirmed to be effective also for DME synthesis. The result suggests that RBFN7-8-4 cannot find the inhibiting effect of water peculiar to B from the physicochemical properties. Additional physicochemical properties, which are different between B and Be, should have been included in the training data set to distinguish the activity of B- and Be-containing catalysts. Although Be is effective, Cr was selected from the literature instead of Be because an allowable concentration of beryllium oxide is much lower than that of chromium oxide.

From these results, Cu−Zn−Al−Ti−Nb−V−Cr oxide catalyst was proposed for the composition optimization in the next step. An orthogonal array of L_{18} was applied to the optimization of the catalyst composition. The factors are molar compositions of Cu, Zn, Al, Ti, Nb, V, and Cr. Levels of each factor and the designed catalyst compositions are listed in Table 4. Catalysts 1−18 were prepared and tested. The fitting parameters to GPLE are also summarized in the table.

Because of the exceptionally high value of *a* for no. 11 in Table 4, training of RBFN using catalyst composition and all the GPLE parameters themselves was not accomplished. Instead, the residual activity, parameter *d* of GPLE, was used to construct RBFN. After training of the ANN, a grid search was conducted on the ANN. The grid was set at every 10 mol %; then the total 8008 activities were predicted. The response surfaces as

Table 4. L_{18} Orthogonal Array, Catalyst Composition, and Experimental GPLE Parameters

	L_{18} Orthogonal Array						
	factor						
	Cu	Zn	Al	Ti	Nb	V	Cr
level 1	20	7.5	5	0	0	0	0
level 2	40	15	12.5	7.5	7.5	7.5	7.5
level 3	60	22.5	20	15	15	15	15

	level							catalyst composition (mol %)							GPLE parameter[a]			
catalyst no.								Cu	Zn	Al	Ti	Nb	V	Cr	*a*	*b*	*c*	*d*
1	1	1	1	1	1	1	1	61.5	23.1	15.4	0.0	0.0	0.0	0.0	4.79	5.2	0.272	7.57
2	1	2	2	2	2	2	2	25.8	19.4	16.1	9.7	9.7	9.7	9.7	48.34	120.9	0.709	0.44
3	1	3	3	3	3	3	3	16.3	18.4	16.3	12.2	12.2	12.2	12.2	13.36	32.2	0.655	0.16
4	2	1	1	2	2	3	3	41.0	7.7	5.1	7.7	7.7	15.4	15.4	2.52	35.7	0.152	0.12
5	2	2	2	3	3	1	1	41.0	15.4	12.8	15.4	15.4	0.0	0.0	5.79	15.5	0.571	0.18
6	2	3	3	1	1	2	2	41.0	23.1	20.5	0.0	0.0	7.7	7.7	10.18	33.4	0.337	3.4
7	3	1	2	1	3	2	3	51.1	6.4	10.6	0.0	12.8	6.4	12.8	1.37	2.8	0.072	0.45
8	3	2	3	2	1	3	1	51.1	12.8	17.0	6.4	0.0	12.8	0.0	9.63	24	0.922	2.8
9	3	3	1	3	2	1	2	51.1	19.1	4.3	12.8	6.4	0.0	6.4	11.13	14.9	0.394	4.62
10	1	1	3	3	2	2	1	25.8	9.7	25.8	19.4	9.7	9.7	0.0	7.55	5.5	0.684	0.01
11	1	2	1	1	3	3	2	25.8	19.4	6.5	0.0	19.4	19.4	9.7	8089	76	1.9998	0.01
12	1	3	2	2	1	1	3	25.8	29.0	16.1	9.7	0.0	0.0	19.4	6.09	27.9	0.171	2.3
13	2	1	2	3	1	3	2	41.0	7.7	12.8	15.4	0.0	15.4	7.7	48.15	45.5	0.841	1.57
14	2	2	3	1	2	1	3	41.0	15.4	20.5	0.0	7.7	0.0	15.4	19.71	28.5	0.751	1.22
15	2	3	1	2	3	2	1	41.0	23.1	5.1	7.7	15.4	7.7	0.0	3.73	4	0.258	1.53
16	3	1	3	2	3	1	2	51.1	6.4	17.0	6.4	12.8	0.0	6.4	90.15	22.8	1.594	0.91
17	3	2	1	3	1	2	3	51.1	12.8	4.3	12.8	0.0	6.4	12.8	73.04	52.5	1.045	1.82
18	3	3	2	1	2	3	1	51.1	19.1	10.6	0.0	6.4	12.8	0.0	5.11	19.9	0.347	0.53

[a] CO_x conversion $= a/(b + \text{time (min)}) \wedge c + d$.

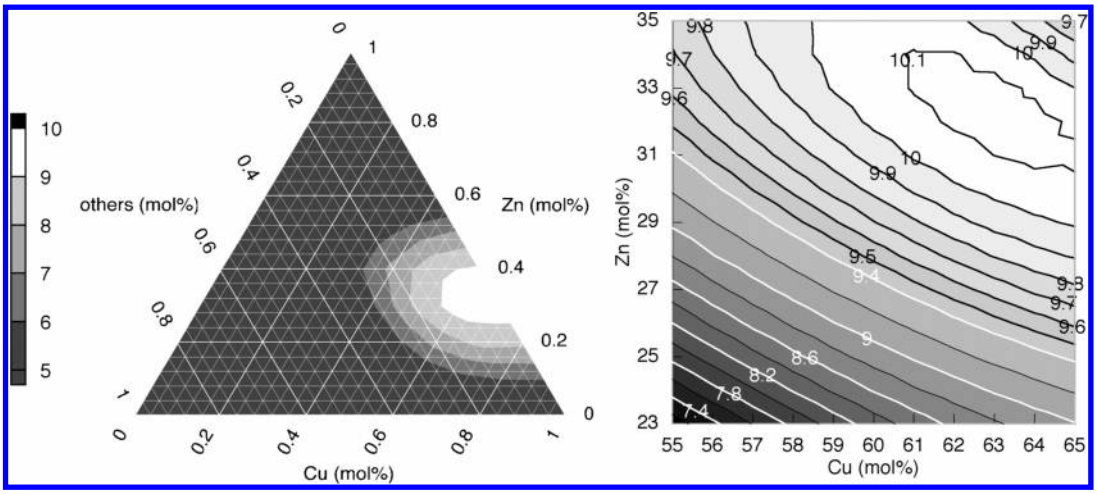

Figure 7. Top view of overlapped response surfaces of residual activity.

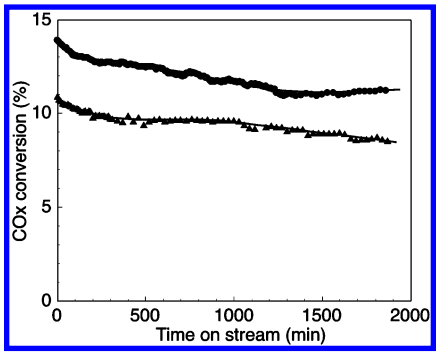

Figure 8. Activity test of optimized catalyst. 1 MPa; 498 K. ●, Cu/Zn/Ti = 63/32/5; ▲, Cu/Zn/Al = 60/30/10.

functions of Cu and Zn content were overlapped, and the top view is presented in Figure 7 as a ternary graph. The global optimum is clearly located, and the minute grid search with 1 mol % digit was repeated in the range of Cu, 55−65, and Zn, 23−35. The resultant top view is shown in Figure 7. The predicted optimum catalyst composition was Cu/Zn/Al/Ti/Nb/V/Cr = 63/32/0/5/0/0/0. In this case, no synergy was observed between Ti and four other additives. Titanium alone enhanced the residual activity of Cu/Zn catalyst. This is the conspicuity of Ti compared with Sr/B[12] or Al/Ga[18] with which synergy on activity promotion was observed.

The catalyst was prepared and mixed with γ-alumina. The activity for DME synthesis was compared with those of Cu/Zn/Al (6/3/1) catalyst as shown in Figure 8. The activity of the optimum catalyst was stable after 20 h and higher compared with those of the ternary component catalysts containing Al.

Conclusion

An artificial neural network (ANN) was applied to find the effective additives for Cu−Zn oxide in the hybrid catalyst mixed with γ-alumina, for single-stage dimethyl ether synthesis. Eight elements (X)—B, K, Nb, Re, Cd, Ce, Sm, and Tl—were selected. These were selected to be dispersed in the wide range of

physicochemical properties. The activities of Cu−Zn−X + γ-alumina hybrid catalyst and the physicochemical properties of the eight elements were used as training data for ANN. The trained ANN predicted the promising additives Al, Ti, V, and Nb. Using design of experiment (DOE), ANN, and a grid search, the composition of heptarnary oxide catalyst was optimized. From the final long run, the catalyst was confirmed to be an active and stable catalyst.

We concluded that the methodology of ANN based on physicochemical properties, GPLE parameters, DOE, and grid search will accelerate the catalyst development process. With the assistance of DOE, the number of experiments was reduced, and a specially designed reactor for high-throughput screening was not used in the present study. This methodology can be applied to demanding reactions at high temperature and/or high pressure.

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