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Combinatorial Catalysis Tool Under High Pressure For Heterogeneous Catalyst Consisting of Multi-Well Microplate System, Neural Network and Genetic Algorithm — Optimization of Cu-Zn-Al-Ga Oxide Catalyst

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A kind of an artificial neural network, a radial basis function network (RBFN) with/without genetic algorithm (GA) was applied for optimization of the composition of Cu-Zn-Al-Ga oxide catalyst for methanol synthesis. In the present study, 61 data obtained by 96 line HTS (high-throughput screening) reactor under high pressure, was used as RBFN training data. In the optimization process with GA, the trained RBFN could be used as a fitness function of GA. The 96 line HTS reactor was used only to obtain the training data and the convergence was almost achieved at 8th generation without the repetition of catalyst preparation and reaction. The optimized catalyst by GA was compared with the result obtained by all-encompassing calculation. The catalyst was proved to have be the global maximum activity in the neural network. The optimum catalyst included the small amount of Ga, and showed higher activity than conventional Cu-Zn-Al oxide catalyst.

Key words: combinatorial catalysis, HTS, artificial neural network, genetic algorithm, 96 well microplate

1. INTRODUCTION

Methanol and dimethyl ether synthesized from methanol are the good candidates for clean transport fuel. Compact and economic process using a dispersed unused carbon resources has been proposed [1]. Since the conventional Cu-based catalysts for methanol synthesis shows insufficient activities to realize the compact and economic process, the discovery or development of catalyst with high activity is important. For rapid discovery and development of high performance catalysts, combinatorial method attracts much attention [2-5]. The method has been developed hitherto from two major points of view; the development of rapid analytical systems for HTS (high-throughput screening) [6-9] and the development of the method to reduce the number of catalyst tests. Soft computing like genetic algorithm (GA) and neural network has been applied for the latter purpose [10-16]. On the other hand, it should be also emphasized that high pressure HTS apparatus is important for catalyst development because catalysts are used under pressure in almost industrial processes like methanol synthesis. Nevertheless only few have been reported [17, 18]. We have reported the optimization by GA under pressure and have obtained successful results [14-16]. In the optimization process with GA, most laborious and time-consuming steps were catalyst preparation and assessments of catalytic activity by HTS reactor. In order to reduce the number of repetition of such steps, radial basis function network (RBFN) was used as fitness function in GA program [15, 16]. In this method, the experimental data obtained by HTS reactor was only used as training data for RBFN, and the activity used in the optimization process by GA was calculated by the RBFN. Therefore, the catalyst composition can be optimized using small number of catalyst preparation and experiments by HTS reactor.

In the previous study, we reported the synergistic effect of Al and Sc on the activity of Cu-Zn-Al-Sc oxide catalyst for methanol synthesis and optimized the composition. The optimum catalyst includes small amount of Sc with high specific surface area of metallic Cu. Kubo et al. have suggested from the results of their computational approach that excess electrons of ZnO particle are localized on ZnO particle surface by Al addition and the aggregation of ZnO particles are prevented by the effect of electrostatic repellence between ZnO particles [19]. Therefore, the resulting ZnO particles are ultra fine and the specific surface area of ZnO increases. They have also suggested that doping of Al^{3+} with Sc^{3+} or Ga^{3+} enhances the effect of Al dopant. In the present study, the effect of Ga addition to Cu-Zn-Al oxide catalyst for methanol synthesis is investigated

using combinatorial tool to clarify the synergism of Al-Ga.

2. EXPERIMENTAL

2.1 Catalyst Preparation and Activity Test

Catalysts were prepared by oxalate-ethanol co-precipitation method described in the previous paper [14]. Metal nitrates were used as the precursors of metal components. The oxide precursors calcined at 573 K were reduced in reaction gas ($H_2/CO/CO_2/Ar$ = 60/30/5/5) by temperature-programmed heating up to 523 K. Methanol synthesis was conducted at 498 K, 1 MPa using high pressure 96 line HTS system [9] to obtain the training data for RBFN. The activity of the optimum catalyst obtained by GA with RBFN was compared with that of Cu-Zn-Al oxide catalyst using both the HTS reactor and the conventional fixed bed reactor [14]. In HTS system, a colorimetric method of $K_2Cr_2O_7$ solution reported previously [9] was used in order to assess 96 catalysts activities at the same time. On the other hand, gas chromatograph (Simadzu GC-14B) equipped with TCD was connected on-line to the conventional reactor. CO, CO_2, and Ar were separated in active carbon column. The catalytic activity was expressed in terms of space time yield (STY) of methanol using direct quantitative analysis of methanol by the colorimetric method or using CO_x conversion (x = 1, 2) by gas chromatography.

2.2 Optimization Method

The compositions of 95 catalysts were decided randomly, and then the activities of the 95 catalysts were assessed twice using HTS system. The activities of the 34 catalysts were of great differences between the STYs obtained by the two times tests. These data was excluded from training data of RBFN, and the mean values of the activities of the 61 catalysts used as the training data. A Software package, STATISTICA Neural Network (Stat Soft) were used for the training of RBFN. The calculation was performed on a personal computer equipped with 2.0 GHz Intel Pentium 4 processor. The trained NN included 4 neurons in input layer corresponding to each catalyst component, 61 neurons in hidden layer, and 1 neuron in output layer corresponding to catalyst activity (STY). The theories of GA and NN, the scheme of optimization process, and the details of the program, such as the coding, the method and probabilities of cross-over and mutation, were described in detail in refs. [14-16]. To check if the maximum found by the RBFN and GA is global or local, all-encompassing calculation was conducted using macro commands of STATISTICA [20]. At first all the combination of parameters were generated (resolution of catalyst composition: 1 %). Then the trained RBFN predicted the STY from each input. At this moment the global maximum can be located. In the second stage the predictions were sorted by key parameters (Cu and Zn composition) and STY. Thus at the edge of the key parameters local maximum can be found. The plots of the local maximum vs. the key parameters represent the activity envelope.

2.3 Characterization of the Optimum Catalysts

The specific surface area of Cu metal after reaction was measured by in situ N_2O frontal chromatography [14]. The particle size of metallic copper was also calculated by the data of XRD measurement after reaction [14]. BET surface area was obtained from N_2 adsorption at liquid nitrogen temperature (77 K) using Monosorb MS-19 (Quantachrome). XPS was recorded by ESCA 750 (Shimadzu) with Mg Kα radiation source.

3. RESULTS AND DISCUSSION

3.1 Optimization of the Composition of Cu-Zn-Al-Ga Catalyst by GA with RBFN

61 data for RBFN training is shown in Fig. 1 as a function of Cu and Zn composition. All the quaternary composition were decided randomly and each catalyst was prepared automatically using liquid handler. Activity was measured in HTS reactor. The result is shown as gray scale in the figure. Clearly, Cu rich catalysts tend to show high activity. RBFN was trained using these data.

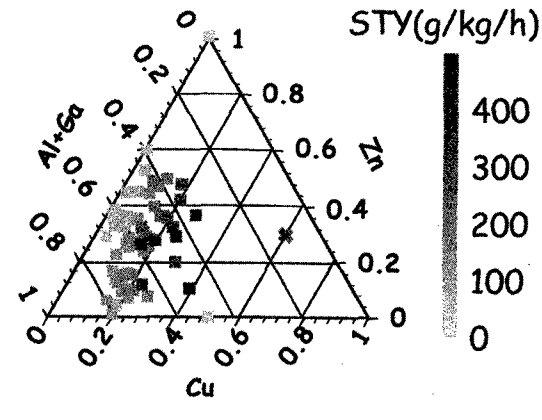

Fig. 1 Training Data for RBFN. (×) Reliability check point.

Prior to the optimization, reliability of the trained RBFN was checked. As described in experimental section, the evaluation in the optimization process is performed using the RBFN. The reliability of the optimized results, therefore, depends on the RBFN itself. Effect of Ga addition was first predicted by the RBFN as shown by solid line in Fig. 2. Activity slightly depends on the Al/Ga ratio. The prediction was confirmed by HTS experiment. Closed circles in the figure are

experimental result showing good agreement to the predictions. As shown in Fig. 1, the check point (×) is located far from the training data area. This result suggests the good generalization ability of RBFN.

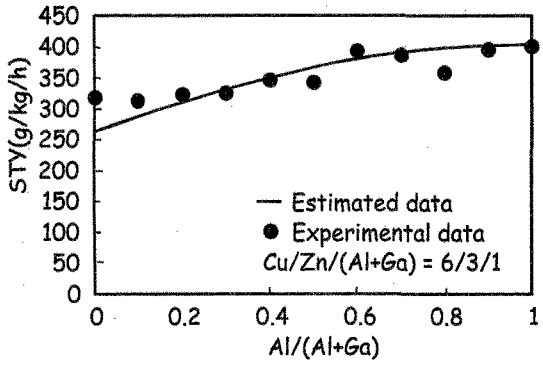

Fig. 2 Reliability Checks of the Trained RBFN.

Optimization was processed based on the RBFN. Fig. 3 shows the compositional distribution of Cu-Zn-Al-Ga catalysts generated in the process of GA assisted by RBFN. While the 95 catalysts of 1st generation distribute randomly (Fig. 3(a)), the catalysts composition converges to the maximum point in the optimization process. The optimum catalyst appeared at 8th generation. The optimum catalyst composition was Cu/Zn/Al/Ga = 66/21/12/2, and the STY of the catalyst (433 g-MeOH /kg-cat. /h) is much higher than that of the conventional catalyst (250 g-MeOH/kg-cat. /h).

3.2 All-encompassing calculation with the trained RBFN

One of the serious problems of optimization by GA is so-called "premature convergence" where genes converge to local maximum and lose diversity. To avoid the local maximum, the all-encompassing calculation was used [20]. The resolution of the calculation is much rough compared with GA program because the minute calculation demands more computing resources. If the resolution is 1% for quaternary system, the number of the possible combination is 176,851. For visualization of the result, envelope of the activity is illustrated in Fig. 4 as a contour map. The figure shows there are two peaks. The global maximum is in the region with higher Cu composition, and thus the predicted optimum by GA was proved to be global.

3.3. Effect of Ga Additive

The optimum catalysts described in Section 3.1 include 2 mol% Ga. The result indicates that Ga is an effective additive to Cu-Zn-Al oxide catalyst for methanol synthesis. Kubo et al. has suggested that the role of Ga additive is a dopant, and the electronic structure of Cu-Zn-Al oxide catalyst is modified [19]. They have also suggested that the physicochemical

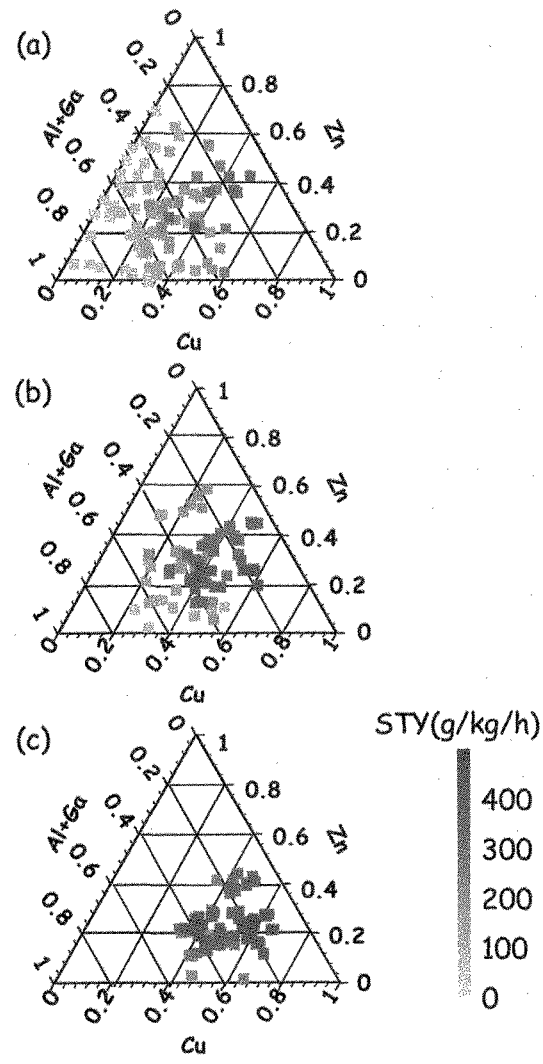

Fig. 3 Distribution of Catalysts in the Optimization Process with GA. (a) 1st, (b) 4th, (c) 8th Generation.

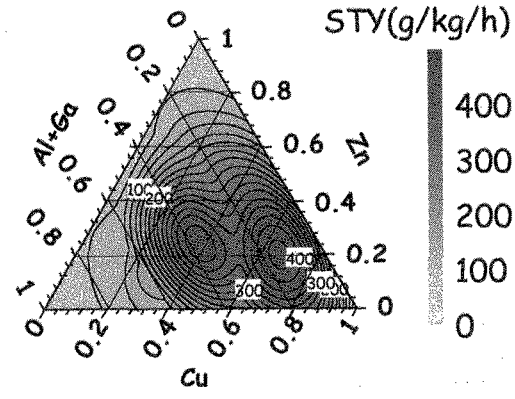

Fig. 4 Contour Map of Cu-Zn-Al-Ga Oxide Catalyst.

structure of Cu-Zn-Al catalyst is modified by Ga addition. Table I summarizes the activities examined by the conventional fixed bed reactor [14] and the physicochemical data of the catalysts with/without Ga

additive. The catalyst with Ga additive is the optimum catalyst found by the optimization with GA and RBFN. The activity of the optimum catalyst is higher than the catalyst without Ga additive. Shift of Zn B.E. suggests the positive charge of Zn ion by Ga addition as predicted [19]. Both increase of surface areas and decrease of crystallite size are consistent with the prediction. The results of activity tests and characterizations have shown that the change of the electronic structure of ZnO by Ga addition to Cu-Zn-Al oxide catalyst induce the change of the catalyst structure and metallic copper structure resulting in high activity and thus synergistic effect of Al-Ga was confirmed from both experimental and computational approach.

Table I The Activities Examined by Conventional Reactor and Physicochemical Data before and after Reaction.

	max comp.	without Ga
Cu/Zn/Al/Ga	66/21/12/2	66/21/14/0
STY(g/kg/h)	433	411
S_{Cu^0} (m^2/g)	34	33
Cu^0 Crystallite size(Å)	79	91
Scat (m^2/g)	124	113
B.E. of Zn $2p_{3/2}$ peak (eV)	1023.5	1023.3

4. CONCLUSION

In the present study, we investigated the effect of Ga addition to conventional Cu-Zn-Al oxide catalyst predicted by our combinatorial catalysis tool on the catalytic activity for methanol synthesis. The catalyst composition of Cu-Zn-Al-Ga catalyst was optimized by GA with RBFN and all-encompassing calculation in a quite short time with small amount of time-consumption and labor. The optimized catalyst included the small amount of Ga . The combinatorial method is available to efficient catalyst development under pressure.

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