Development of a Co-MgO Catalyst for High-pressure Dry Reforming of Methane Based on Design of Experiment, Artificial Neural Network and Grid Search

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Dry reforming of methane is a potentially important process to convert the greenhouse gases carbon dioxide and methane simultaneously to syngas (CO + H₂). The most serious problem with the dry reforming of methane is carbon deposition, so preparation parameters of the citric acid method were surveyed to prepare an active Co-MgO catalyst with low carbon deposition using design of experiment, artificial neural network and grid search. The preparation parameters such as Co loading, amount of citric acid, calcination temperature, and pelletization pressure were determined according to an L₉ orthogonal array. After 9 datasets of the parameter activity were designed and measured in a conventional pressurized fixed bed reactor, an artificial neural network was constructed. The optimum composition was determined by a grid search and verified experimentally to be active with a small amount of carbon deposition. Design of experiment combined with an artificial neural network and grid search was useful for catalyst development.

Keywords
Methane dry reforming, Combinatorial catalysis, Design of experiment, Artificial neural network, Grid search, Cobalt magnesia catalyst

1. Introduction

Combinatorial catalysis is now commonly used as a promising tool for catalyst research and development. Various tools were demonstrated in special issues of Catalysis Today¹ and Applied Catalysis A² in 2003. Combinatorial and rapid library synthesis with high-throughput screening (HTS) is the main technology accelerating every step of the R&D of catalysts. Considering the complexity of advanced materials, however, the two tools are not sufficient. If 76 non-radioactive elements can be applied to the catalysts, there are 2,850 binary but 18,474,840 quinary combinations of these elements³. Such a number of combinations is clearly too much for even the most advanced HTS system at present. Therefore, data mining tools such as the artificial neural network (ANN) and genetic algorithm (GA) are used to compensate.

We reported optimization of the Cu-Zn oxide catalyst for methanol synthesis using HTS with 96 parallel reaction lines⁴, ANN to correlate catalyst parameters with activities, and GA⁵–⁸ or a grid search (formerly reported as all-encompassing calculation⁹–¹¹) to find the global maximum on the artificial neural network. Random parameters for the catalyst were used in these previous experiments to obtain training data for the ANN because such dispersed data were thought to give better networks. Rather large numbers of datasets are necessary in this method and additional data are sometimes required for re-training of the ANN for more precise prediction. A better and well-designed dataset for effective training of ANN is necessary.

Statistical design of the experiment was applied for a few catalysts to identify the important factors among catalyst composition, preparation parameters and reaction conditions¹²–¹⁵. The quantitative influence of the parameters was estimated using a polynomial model and a regression technique¹⁶. The apparent complexity of the statistical method can be simplified by the Taguchi method¹⁷,¹⁸,¹⁹. The orthogonal array can reduce the number of necessary experiments, while maximizing the amount of information derived from the reduced experiment set. Such arranged datasets seem suitable for ANN training¹⁷–¹⁹. The resulting ANN gives good predictions for the output parameter of the ANN such as activity and selectivity. The global optimum on the ANN was found rapidly with the assistance of a grid search¹⁸–²⁰. More precise predictions are of course possible by ANNs trained by a large...
numbers of datasets if HTS is available at data-gathering. Otherwise, the combination of DOE, ANN and a grid search can be applied as a substitute for HTS.

Experimental design with an orthogonal array was implemented to identify better conditions of Co-MgO preparation for high pressure dry reforming of methane in this study. The reaction converts greenhouse gases (methane and carbon dioxide) at the same time to useful syngas with a low hydrogen/carbon monoxide ratio, which is suitable for the oxo-reaction and Fischer-Tropsch synthesis. Dry reforming of methane should be carried out under high pressure for correct evaluation of the catalyst because methane pressure is high in a natural gas field and Fischer-Tropsch synthesis is performed at high pressure\(^{21}\). If the experiment is run at high pressure, rate of carbon formation is high and the most serious problem with the dry reforming of methane is carbon deposition, which causes catalyst deactivation, plugging of the reactor, and breakdown of the catalyst. Only a few catalysts, such as Ni-CaO-MgO\(^{22}\), Mo, W carbide\(^{23}\), Ni-MgO\(^{24}\), Co/TiO\(_2\)^{25}, and Co-MgO\(^{26}\) are effective non-noble metal catalysts under pressure. The Co-MgO catalyst prepared by the oxalate co-precipitation method showed high activity\(^{26,26a}\), whereas the H\(_2\)/CO ratio of the product gas was about 0.8, lower than that expected from the stoichiometry of dry reforming because of the reverse water gas shift reaction\(^{26b}\). Furthermore, we found carbon deposition on the Co-MgO catalyst was suppressed if prepared using the citric acid method. Preparation parameters for this method were evaluated to obtain a catalyst with higher activity and lower carbon deposition.

2. Experimental

2.1. Catalyst Preparation

Cobalt nitrate and magnesium nitrate were dissolved in melting citric acid monohydrate in a beaker heated on a hot-plate. The resulting mixture was treated in a vacuum oven at 70°C for 3 h and then calcined in air at 170°C for 1 h and at 400-700°C for 4 h.

2.2. Activity Tests

Dry reforming of methane was conducted in a fixed bed flow reactor. A reactor tube made of quartz was inserted in a stainless steel tube. Catalyst was packed inside the quartz tube to prevent direct contact of the reaction gas with the stainless tube. Nitrogen was fed between the two tubes. After the catalysts were reduced with H\(_2\) at 850°C for 10 min under 0.1 MPa, reactant gas (CH\(_4\)/CO\(_2\) = 1) was introduced into the catalyst bed at 750°C under 1 MPa, and the SV (space velocity) was set to 400,000 ml/g/h. Analysis of the reaction products was performed with an on-line gas chromatography (micro-GC, M-200, Agilent Technologies, Inc.). The catalytic activity was indicated as the yield of CO (CO production rate/CH\(_4\)+ CO\(_2\) feed rate). The amounts of carbon depositions on the catalysts were quantified by carbon dioxide produced during temperature programmed oxidation (TPO) in an air flow after the reforming reaction.

3. Methodology

3.1. Design of Experiment (DOE)

An L\(_9\) orthogonal array as shown in Table 1 was used for DOE\(^{16}\). Only nine experiments as shown in Table 2 are necessary for four factors with three levels instead of 81(= 3\(^4\)) experiments. One of the advantages of the Taguchi method is the modest requirement for experiments. The three levels of each parameter are listed in Table 2.

3.2. Artificial Neural Network (ANNs)

Artificial neural networks were applied to correlate the preparation parameters with the catalytic activity. Among the many types of ANNs, the back propagation network (BPN) has been applied successfully to catalyst design. The BPN is a supervised learning and feed-forward type network which is modified by an epoch-by-epoch backward calculation minimizing errors between the target and predicted data. The important
checkpoint of BPN application is to avoid overtraining, which causes loss of generalizability of the BPN. Usually extra validation data is used to avoid the overtraining and the structure of the BPN is optimized to reduce the errors. Recently, the radial basis function network (RBFN) has also attracted much attention as an optimization tool in a variety of engineering fields because it is robust and suffers only slightly from overtraining. The apparent structure of the RBFN is similar to that of the BPN with only one hidden layer, in which a radial basis function is used instead of an S-shaped sigmoid function. During training, the center points of the radial basis functions are decided by training data, so the input datum for the RBFN is a vector. Then weights between the hidden layer and the output layer are determined to fit the output data to the training data. The RBFN was constructed using STATISTICA Neural Network 6.0 software (StatSoft).

Normalized catalyst preparation parameters, such as Co content, amount of citric acid, calcination temperature, and pelletization pressure, were given to the input layer. Catalytic performance, such as CO yield and carbon deposition after 4 h reaction, were issued from the output layer. The number of nodes in a hidden layer was set as identical to that of the training data. We determined 9 catalyst parameter sets for RBFN training as described above.

3. 3. Optimization Using the ANN

A grid search\textsuperscript{19} was conducted using the macro commands of STATISTICA to find the global maximum of the ANN\textsuperscript{20}. All combinations of parameters were generated. Calculation intervals for Co content, amount of citric acid, calcination temperature, and pelletization pressure, were given to the input layer. Catalytic performance, such as CO yield and carbon deposition after 4 h reaction, were issued from the output layer. The number of nodes in a hidden layer was set as identical to that of the training data. We determined 9 catalyst parameter sets for RBFN training as described above.

4. Results and Discussion

The results of activity test using a conventional fixed bed reactor are summarized in Table 3. Training of the RBFN was easily achieved and the all-encompassing calculation was performed using the RBFN. All the predicted 26,257 CO yields are plotted as functions of Co content, calcination temperature, citric acid, and pelletization pressure in Fig 1. The optimum Co content for the highest activity in the RBFN was found quite easily as 8.5 mol%. In the same way, other optimum parameters could be identified. Carbon deposition on the catalysts is shown in Fig 2. The effect of preparation parameters on carbon deposition can be predicted from these figures. However, the relationship between CO yield and carbon deposition is rather complicated as shown in Fig 3. To identify the preparation conditions for high activity and low carbon deposition, parameters for catalysts with CO yield less than 30% and carbon deposition more than 5 mg/g were removed from Fig 1. The result is illustrated in Fig 4. Preparation conditions for the optimum catalysts are very limited by the above constraints. From Fig 4(a), for example, it is clear that all catalysts containing more than 11 mol% Co yield more than 5 mg/g.

<table>
<thead>
<tr>
<th>No.</th>
<th>Co content [mol%]</th>
<th>Calcination temperature [°C]</th>
<th>Citric acid [eq.]</th>
<th>Pelletization pressure [kg/cm²]</th>
<th>CO yield [%]</th>
<th>Carbon deposition [mg/g]</th>
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<tr>
<td>1</td>
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<td>400</td>
<td>1.0</td>
<td>0</td>
<td>24.2</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
<td>7</td>
<td>550</td>
<td>1.5</td>
<td>300</td>
<td>16.5</td>
<td>19</td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td>700</td>
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<td>600</td>
<td>0</td>
<td>95</td>
</tr>
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<td>33.8\textsuperscript{a}</td>
<td>52\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Predicted values were 35.8%, 1.2 mg/g, respectively.
carbon deposition. The predicted optimum catalyst is listed in Table 3 (No. 10), and the activity and carbon deposition were experimentally verified according to the prediction.

Usually an active catalyst with a high CO yield tends to develop a large amount of carbon deposition as shown in Fig 3 and in Fig 4. The optimized catalyst shown as the closed circle in Fig 5 achieved both high activity and low carbon deposition at the same time. We previously reported that CO yield and carbon deposition after 4 h reaction of 7 mol% Co-MgO prepared by an oxalate co-precipitation method was 37% and 630 mg/g, respectively, under the same reaction conditions26c). The result shows that modification of the preparation conditions of the citric acid method succeeded in preparing an active catalyst with much less carbon deposition. The surface area of MgO prepared by the citric acid method was increased if excess citric acid was used27). The target catalyst (No. 10 in Table 3) was prepared with excess citric acid over the stoichiometric amount, so high surface area of the catalyst may be the cause of the high activity. More detailed experiments, however, are necessary for understanding the mechanism of high activity and low carbon deposition27).

5. Conclusion

Development of a Co-MgO catalyst for dry reforming of methane was conducted using a DOE, an ANN and a grid search. The preparation parameters such as Co loading, amount of citric acid, calcination temperature, and pelletization pressure were evaluated to develop a catalyst with a high activity and low carbon deposition. The nine sets of preparation parameters were designed using an L9 orthogonal array. After performance of the nine catalysts were measured in a conventional pressurized fixed bed reactor, an ANN was constructed to find the global maximum with low carbon deposition by a grid search. The resulting catalyst
was verified by experiment. The activity was higher than those of the nine catalysts designed by DOE, and the carbon deposition was at the lowest level except two. The ANN trained by the DOE data identified a superior catalyst to those prepared based on the DOE data. DOE combined with ANN and a grid search is useful for catalyst development.

References


Fig. 4  Projected CO Yield by Catalysts of CO Yield > 30% and with Carbon Deposition < 5 mg/g against (a) Co Content, (b) Calcination Temperature, (c) Citric Acid, (d) Pelletization Pressure

Open square: DOE catalysts, closed circle: optimum catalyst.

Fig. 5  Comparison of Catalytic Performance
26b) Omata, K., Nukui, N., Hottai, T., Yamada, M., unpublished data.

要 旨
実験計画法，人工ニューラルネットワーク，グリッドサーチによるメタンの高圧ドライリフォーミング用Co-MgO触媒の開発

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メタンのドライリフォーミング反応は温暖化ガスを合成ガスへ転換する反応として注目されるが，高圧における炭素析出の抑制が課題となっている。高活性低炭素析出のCo-MgO触媒が得られるクエン酸調製法の調製条件を実験計画法，人工ニューラルネットワーク（ANN）で最適化し，グリッドサーチにより探索した。これら三つの手法の組合せにより触媒の迅速な改良が可能となった。