

[Regular Paper]

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 ($\text{CO} + \text{H}_2$). 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 L_9 orthogonal array. After 9 data sets 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 Today*¹⁾ and *Applied Catalysis A*²⁾ 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 GA^{5)–8)} or a grid search (formerly reported as all-encompassing calculation^{9)–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 conditions^{12)–15)}. The quantitative influence of the parameters was estimated using a polynomial model and a regression technique¹⁴⁾. The apparent complexity of the statistical method can be simplified by the Taguchi method^{13),15),16)}. 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 training^{17)–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 search^{18)–20)}. More precise predictions are of course possible by ANNs trained by a large

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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 pressure²¹⁾. 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-MgO²²⁾, Mo, W carbide²³⁾, Ni-MgO²⁴⁾, Co/TiO₂²⁵⁾, and Co-MgO²⁶⁾ are effective non-noble metal catalysts under pressure. The Co-MgO catalyst prepared by the oxalate co-precipitation method showed high activity^{26a)}, whereas the H₂/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 H₂ at 850°C for 10 min under 0.1 MPa, reactant gas (CH₄/CO₂ = 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/CH₄ + CO₂ 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 L₉ orthogonal array as shown in Table 1 was used for DOE¹⁶⁾. Only nine experiments as shown in Table 2 are necessary for four factors with three levels instead of 81 (= 3⁴) 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

Table 1 L₉ Orthogonal Array

No.	Level of Parameter			
	A	B	C	D
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 2 Parameter Levels for DOE and Intervals for a Grid Search

Parameter		DOE			Grid search		
		Level 1	Level 2	Level 3	Range	Interval	Samples
A. Co content	[mol%]	7	10	12	7-12	0.5	11
B. Calcination temp.	[°C]	400	550	700	400-700	10	31
C. Citric acid	[eq.]	1.0	1.5	2.0	1-2	0.1	11
D. Pelletization	[kg/cm ²]	0	300	600	0-600	100	7

Table 3 Activity of Catalysts Prepared According to DOE

No.	Co content [mol%]	Calcination temperature [°C]	Citric acid [eq.]	Pelletization pressure [kg/cm ²]	CO yield [%]	Carbon deposition [mg/g]
1	7	400	1.0	0	24.2	63
2	7	550	1.5	300	16.5	19
3	7	700	2.0	600	0	95
4	10	400	1.5	600	22.3	47
5	10	550	2.0	0	32.2	244
6	10	700	1.0	300	0	106
7	12	400	2.0	300	23.9	70
8	12	550	1.0	600	28.6	2332
9	12	700	1.5	0	0	55
10	9	400	1.7	0	33.8 ^{a)}	52 ^{a)}

a) Predicted values were 35.8%, 1.2 mg/g, respectively.

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 search²⁰⁾ was conducted using the macro commands of STATISTICA to find the global maximum of the ANN^{9)~11)}. All combinations of parameters were generated. Calculation intervals for Co content, calcination temperature, amount of citric acid, and pelletization pressure were 0.5 mol%, 10°C, 0.1 equivalent, and 100 kg/cm², respectively, as shown in **Table 2**. The number of possible combinations was 26,257. Then the trained ANN predicted CO yields using each parameter set. The global maximum could then be predicted. Similar methods have been reported as “all-encompassing calculation”^{9~11)} or “computational

scanning”¹⁸⁾. Then the predicted CO yields were plotted as a function of a key parameter. The plots represent the activity envelope from the view point of the key parameter and the optimum key parameter for the global maximum catalyst, and the shape around the maximum can easily be displayed. The next important feature of the target catalyst is carbon deposition during dry reforming of methane. Therefore, the optimum catalyst will be discovered among catalysts with small amounts of carbon deposition. Catalysts with more than 5 mg/g carbon deposition and less than 30% CO yield were removed from the 26,257 catalysts formed by a grid search and then the same optimization procedure was repeated to find the optimum catalyst.

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

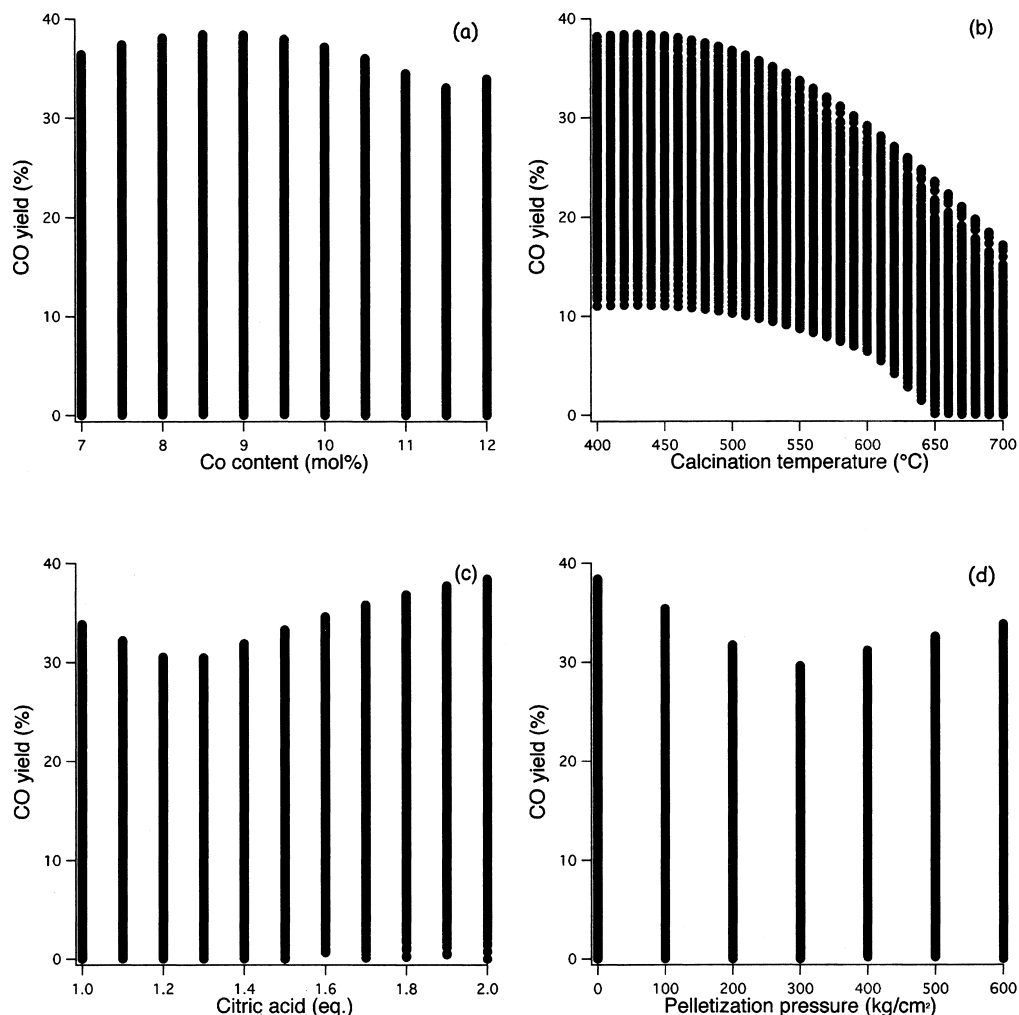


Fig. 1 Projected CO Yield for All Catalysts against (a) Co Content, (b) Calcination Temperature, (c) Citric Acid, (d) Pelletization Pressure

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 conditions^{26c)}. 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 stoi-

chiometric 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 deposition⁵⁾.

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 L_9 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

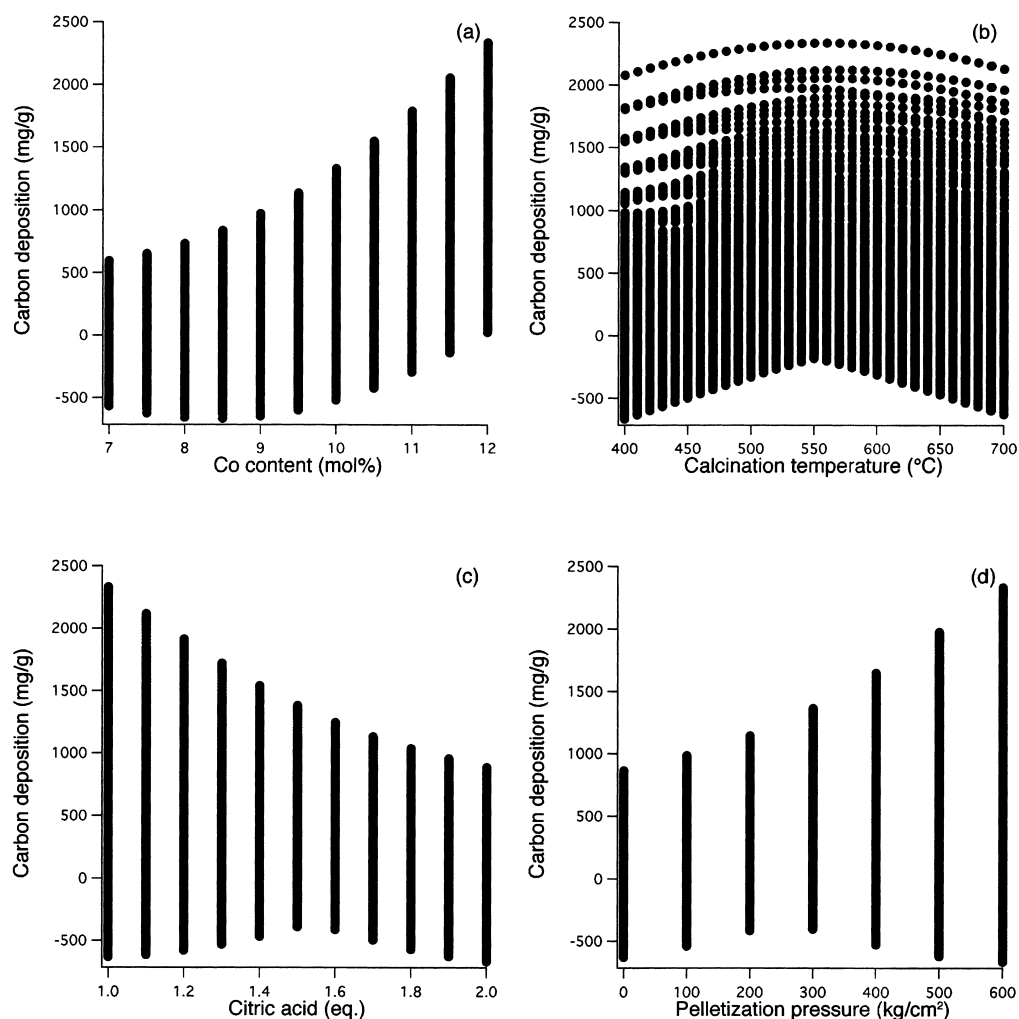


Fig. 2 Projected Carbon Deposition on All Catalysts against (a) Co Content, (b) Calcination Temperature, (c) Citric Acid, (d) Pelletization Pressure

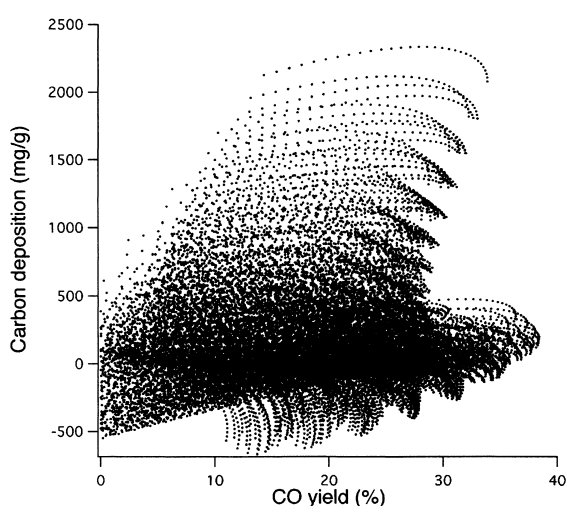


Fig. 3 Total Plot of Carbon Deposition on All Catalysts and CO Yield

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

- 1) Maier, W. F., *Appl. Catal. A: General*, **254**, (1), 1 (2003).
- 2) Baerns, M., Mirodatos, C., Perego, C., *Catal. Today*, **81**, (3), 307 (2003).
- 3) Cawse, J. N. in Cawse, J. N. (ed.), "Experimental Design for Combinatorial and High Throughput Materials Development," Wiley-Interscience, New Jersey (2003), Chap. 1, p. 1.
- 4) Omata, K., Watanabe, Y., Umegaki, T., Hashimoto, M., Yamada, M., *J. Jpn. Petrol. Inst.*, **46**, (5), 328 (2003).
- 5) Umegaki, T., Omata, K., Ishiguro, G., Watanabe, Y., Yamada, M., *J. Jpn. Petrol. Inst.*, **46**, (3), 181 (2003).
- 6) Omata, K., Umegaki, T., Watanabe, Y., Nukui, N., Yamada, M., *J. Jpn. Petrol. Inst.*, **46**, (3), 189 (2003).

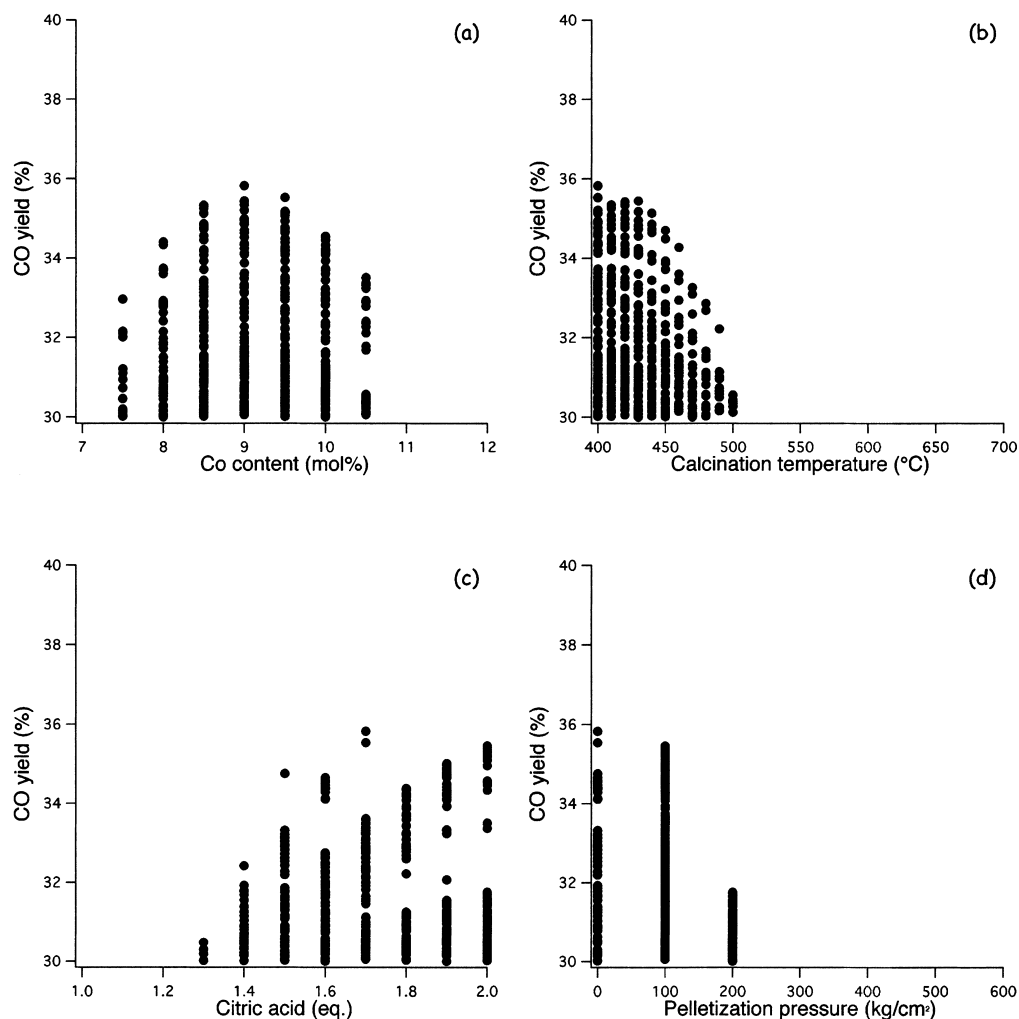
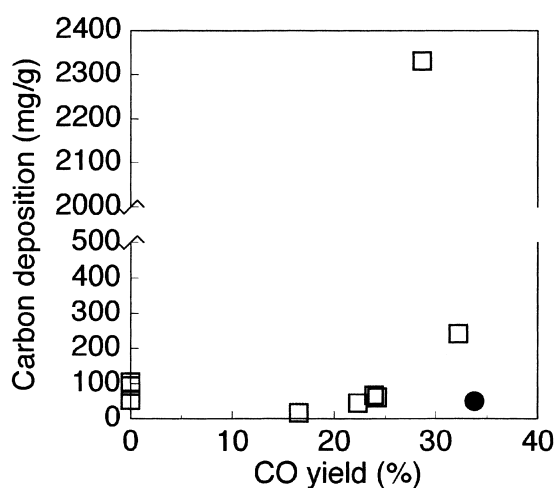


Fig. 4 Projected CO Yield by Catalysts of CO Yield > 30% and with Carbon Deposition < 5 mg/g against (a) Co Content, (b) Calcination Temperature, (c) Citric Acid, (d) Pelletization Pressure



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

Fig. 5 Comparison of Catalytic Performance

- 7) Umegaki, T., Watanabe, Y., Nukui, N., Omata, K., Yamada, M., *Energy & Fuels*, **17**, 850 (2003).
- 8) Watanabe, Y., Umegaki, T., Hashimoto, M., Omata, K., Yamada, M., *Catal. Today*, **89**, (4), 455 (2004).
- 9) Omata, K., Hashimoto, M., Watanabe, Y., Umegaki, T., Yamada, M., *J. Jpn. Petrol. Inst.*, **46**, (6), 383 (2003).
- 10) Omata, K., Hashimoto, M., Watanabe, Y., Umegaki, T., Wagatsuma, S., Ishiguro, G., Yamada, M., *Appl. Catal. A: General*, **262**, 207 (2004).
- 11) Omata, K., Watanabe, Y., Hashimoto, M., Umegaki, T., Yamada, M., *Ind. Eng. Chem. Res.*, **43**, 3282 (2004).
- 12) Baker, J. E., Burch, R., Golunski, S. E., *Appl. Catal. A: General*, **53**, 279 (1989).
- 13) Dawson, E. A., Barnes, P. A., *Appl. Catal. A: General*, **90**, 217 (1992).
- 14) Lima, A. A. G., Nele, M. N., Moreno, E. L., Andrade, H. M. C., *Appl. Catal. A: General*, **171**, 31 (1998).
- 15) Ozdemir, C., Nilgun, A., Yildirim, R., *Appl. Catal. A: General*, **258**, 145 (2004).
- 16) Hirose, K., Ueda, T., "Introduction to Taguchi Method Analysis," Doyukan, Tokyo (2003).
広瀬健一, 上田太一郎, "タグチメソッド解析法入門," 同友館, 東京 (2003).
- 17) Huang, K., Chen, F.-Q., Lu, D.-W., *Appl. Catal. A: General*,

- 219, 61 (2001).
- 18) Kompany-Zareh, M., Tavallali, H., Sajjadi, M., *Anal. Chim. Acta*, **469**, 303 (2002).
- 19) Omata, K., Watanabe, Y., Hashimoto, M., Umegaki, T., Yamada, M., *J. Jpn. Petrol. Inst.*, **46**, (6), 387 (2003).
- 20) Nascimento, C. A. O., Giudici, R., *Comp. Chem. Eng.*, **22**, S595 (1998).
- 21) Armor, J. N., Martenak, D. J., *Appl. Catal. A: General*, **206**, 231 (2001).
- 22) Yamazaki, O., Nozaki, T., Omata, K., Fujimoto, K., *Chem. Lett.*, 1953 (1992).
- 23) York, A. P. E., Claridge, J. B., Brungs, A. J., Tsang, S. C., Green, M. L. H., *Chem. Commun.*, 39 (1997).
- 24) Tomishige, K., Himeno, Y., Matumoto, Y., Yoshinaga, Y., Fujimoto, K., *Ind. Eng. Chem. Res.*, **39**, 1891 (2000).
- 25) Nagaoka, K., Takanabe, K., Aika, K., *Chem. Commun.*, 1006 (2002).
- 26a) Nukui, N., Omata, K., Hottai, T., Yamada, M., 91st Annual Meeting of Catalysis Society of Japan, Yokohama, March 2003, Abstr., 1P15.
- 26b) Omata, K., Nukui, N., Hottai, T., Yamada, M., unpublished data.
- 26c) Nukui, N., Hottai, T., Omata, K., Yamada, M., 45th Annual Meeting of Japan Petroleum Institute, Tokyo, May 2003, Abstr., B08.
- 27) Nakayama, T., Sato, S., Nozaki, F., *Bull. Chem. Soc. Jpn.*, **69**, 2107 (1996).

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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)，グリッドサーチにより探索した。コバルト含有量，クエン酸量，焼成温度，成型圧力を L₉ 直交

表により設定し，9 種類の触媒を調製し，高圧固定床流通式反応装置により活性と炭素析出量を測定した。その結果を ANN で学習してグリッドサーチにより ANN 中の最適点を得た。さらに，高活性低炭素析出の触媒が得られたことを実験的に検証した。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。

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