[Regular Paper]

Screening Using Artificial Neural Network of Additives for Cu–Zn Oxide Catalyst for Methanol Synthesis from Syngas

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The activity of Cu–Zn oxide catalysts for methanol synthesis from syngas varies depending on the additives to the oxide, and optimum composition is sensitive to the reaction conditions. An artificial neural network (ANN) was applied to identify the most effective additives based on the experimental results already reported. The physicochemical characters of element X, such as ionic radii and ionization energy, and the activity of Cu–Zn–X oxide catalyst were correlated using the ANN. Twenty-two types of X were supplied for the training of the ANN, and 29 activities of Cu–Zn–X, the X of which was not included in the training data, were predicted. Beryllium was predicted as the most effective additive, which was verified experimentally.

Keywords

Methanol synthesis, Neural network, Physicochemical property, Copper zinc catalyst

1. Introduction

Methanol (MeOH) and dimethyl ether (DME), which can be easily obtained from MeOH, are superior candidates for use as clean transportation fuel. A compact and simple process with good economy has been proposed to produce these fuels from dispersed unused carbon resources[1]. The key point of this process is development of a noble catalyst which is active under mild reaction conditions. To identify the optimum catalyst, we have developed combinatorial tools consisting of a high-throughput screening reactor using a 96-well microplate, activity mapping using an artificial neural network (ANN), and optimization by a grid search[2]. We confirmed that design of experiment (DOE) is useful to determine the parameters of catalyst preparation for training of the ANN[3] and that DOE reduces the number of experiments.

Recently, ANNs have been applied to catalyst development through the prediction of catalyst characteristics such as activity, selectivity and durability, based on experimental results. Prediction of the characteristics of new catalysts or catalyst additives from the physicochemical properties of catalyst components would accelerate catalyst development. However, successful prediction of catalytic properties from the physicochemical properties of the catalyst elements has only been reported in few cases[4),5]. We recently succeeded in identifying an effective additive for Ni/active carbon catalyst for the carbonylation of methanol based on previous experimental results and the physicochemical properties of the elements[6]. We expect that this methodology, together with DOE, will contribute to more rapid catalyst development.

In the present study, ANN was applied to identify the most effective additive X from both the physicochemical properties of element X and the activity of Cu–Zn–X catalyst for methanol synthesis as experimentally determined[7]. A radial basis function network (RBFN), a type of ANN, was employed to correlate the physicochemical properties of the additive element to the activity. Then, the periodic table was surveyed to identify the optimum additives using the trained RBFN.

2. Experimental Procedures

2. 1. Catalyst Preparation and Testing

Cu–Zn–X oxide catalysts were prepared as described previously[7] by the oxalate-ethanol co-precipitation method. Ethanol solutions of nitrates of Cu, Zn and so on were mixed (Cu/Zn/X molar ratio 6/3/1), and then an ethanol solution of oxalic acid was added to precipitate the mixed oxalic salts. The precursors, except for that containing Be, were washed with ethanol, and ethanol was removed by vaporization fol-

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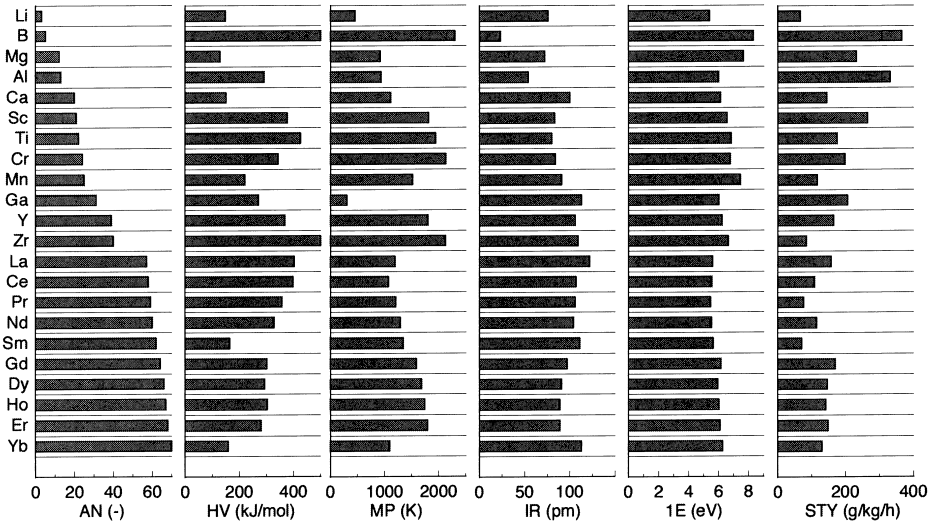


Fig. 1 Effect of Additives on STY at 1 MPa, 498 K

lowed by calcination in air. The mixed oxides were 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 and 1 MPa to measure the space time yield (STY, g-MeOH/kg-cat./h). The products were analyzed by on-line gas chromatography. The activity test of the catalyst predicted as optimum was conducted in a high pressure HTS reactor using low-cost piping[8]. In this case, the methanol was analyzed by the color reaction of chromium ion as described elsewhere[9].

2. 2. Artificial Neural Network

STATISTICA Neural Network, version 6 (StatSoft) was used for constructing the RBFN, which was trained using 22 pairs of physicochemical character-activity (STY) data. Physicochemical properties of additives (X) were collected from database software (Periodic Table X, version 3.5; Synergy Creations). The candidate physicochemical properties for the input data were selected based on the function of catalyst additives according to the previous results[6]. The properties were used for preliminary training of the RBFN, and if the results were good, the properties were selected as the final training data. First ionization energy (*1E*, eV) was used to represent the electric effect of additives. Heat of vaporization (*HV*, kJ/mol), ionic radii (*IR*, pm) and melting point (*MP*, K) were used to represent geometrical effects. The ionic valency of the elements used for the ionic radii was: + 1 = Li, Na, K, Rb, Ag, Cs, Au, Tl; + 2 = Be, Mg, Ca, Mn, Co, Ni, Cu, Zn, Sr, Pd, Cd, Ba, Pb; + 3 = B, Al, Sc, Cr, Fe, Ga, Y, Rh, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Bi; + 4 = Ti, Ge, Zr, Ru, Sn, Hf, Os, Ir, Pt; + 5 = V, Nb, Ta; + 6 = Mo, W; and +7 = Re. In all, five properties including atomic number (*AN*) were entered in the input layer of the RBFN.

Only space time yield (STY, g-MeOH/kg-cat./h) was obtained from the output layer. The association layer contained 21 nodes. To find the best additive, the parameters of elements not included in the training data were input to the trained RBFN, and the STYs predicted by the RBFN were compared.

3. Results and Discussion

3. 1. Effect of Additives

The activities of the Cu–Zn–X catalysts are illustrated in **Fig. 1** according to the physicochemical properties of element X. The catalysts containing B, Al, Sc and Mg had high activities, whereas those containing Li, Nd, and Ce had quite low activities.

3. 2. Training of the RBFN

Activity as a function of the physicochemical properties of additives is shown in **Fig. 2(a)-(e)**. Clearly, additives with small ionic radii formed active catalysts, but no other clear relationship was observed. The RBFN was trained using the 22 datasets in **Fig. 1**, and applied to obtain quantitative information. After the RBFN was successfully trained, the predicted activity was almost identical to the experimental results as shown in **Fig. 2(f)**. The activity of catalysts containing elements not included in the training data could be mapped as a function of the physicochemical properties.

3. 3. Prediction of STY

The properties used for the prediction of STY are shown in **Fig. 3**. These elements were selected for the prediction if each property of the elements was lower than the maximum + 20% of the property in **Fig. 1** and higher than the minimum − 20% of the property in **Fig. 1**. These constraints were necessary because the range of physicochemical properties in the training

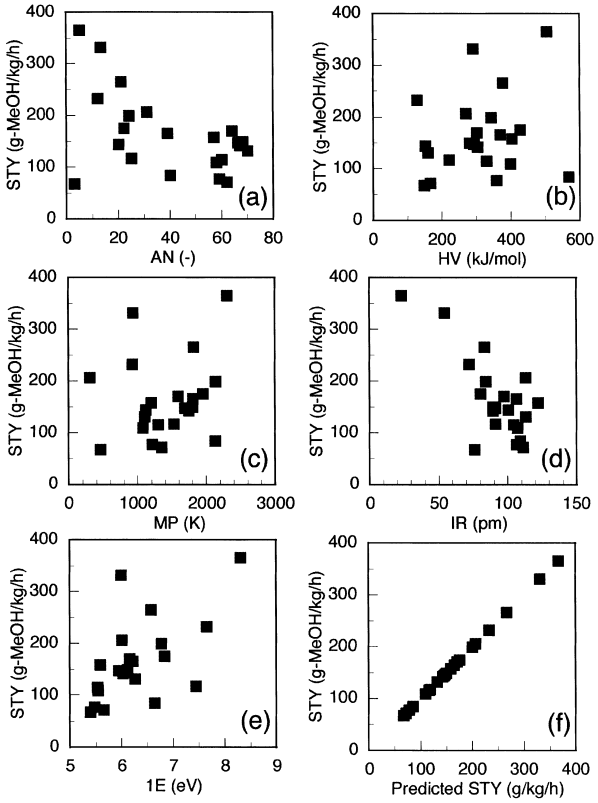
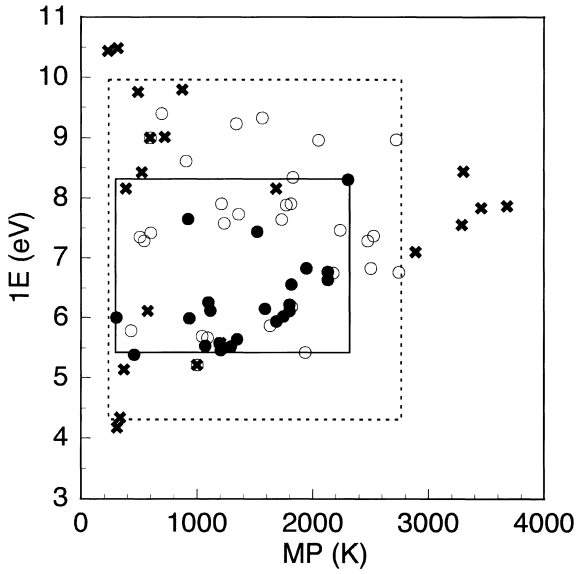


Fig. 2 Catalytic Activity of Cu–Zn–X as a Function of Atomic Number (*AN*), Heat of Vaporization (*HV*), Melting Point (*MP*), Ionic Radii (*IR*), and Ionization Energy (*1E*)



Data for training (●), data for prediction (○), excluded data (×). Solid line shows boundary of data for training. Broken line shows limits of ± 20% for prediction.

Fig. 3 Range of Physicochemical Properties

data was narrow, so training of the RBFN was less effective, otherwise, Hg and I were the best additives. The predicted STYs and properties used for the prediction are shown in **Fig. 4**.

Be, Zn, and Au showed the best predicted activity, so we concentrated further investigations on beryllium, because Zn is used as a main component and Au shows low activity for methanol synthesis by CO_2 hydrogenation[10]. Because the preparation procedure was different for Be additive, the effect of Al addition was also checked in **Fig. 5** as a function of the amount of additive. The Cu–Be system is reported to be as effective as the Cu–Zn system[11]. The effect of Be content was also clearly confirmed: the activity of Cu–Zn–Be was higher than that of Cu–Zn–Al across the entire range of content in **Fig. 5**.

4. Conclusion

The ANN was used to find an effective additive to Cu–Zn oxide for methanol synthesis from syngas. The ANN showed that the physicochemical characters of element X, such as ionic radii and ionization potential, had a nonlinear relationship to the activity of Cu–Zn–X oxide. Twenty-two elements X were supplied for the training of ANN whereas 29 activities of Cu–Zn–X catalysts, the X of which was not included in the training data, were predicted. Beryllium was predicted as the most effective additive, which was verified experimentally. This ANN methodology to predict the effectiveness of new catalysts or catalyst additives from the physicochemical properties of catalyst components will accelerate catalyst development.

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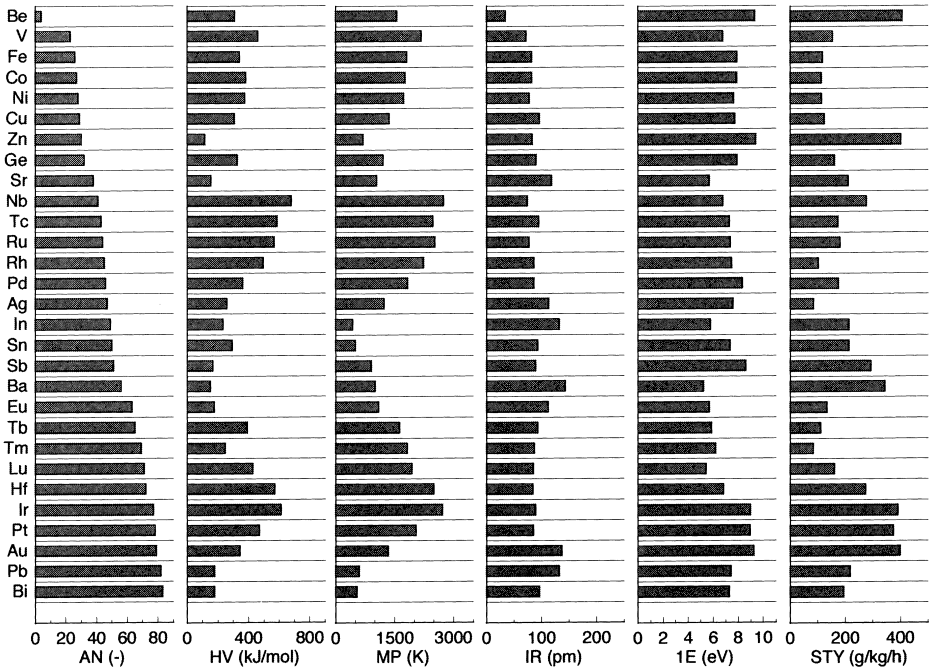
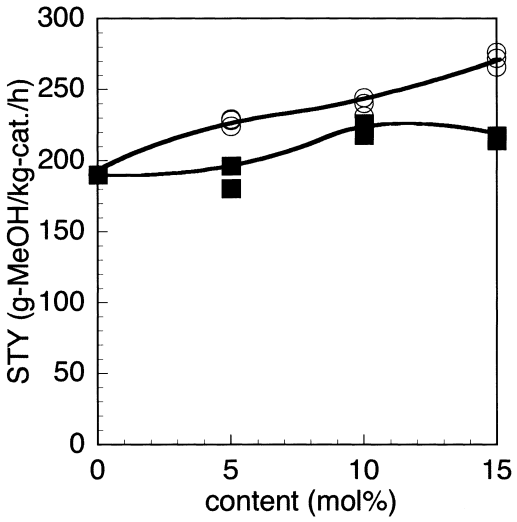


Fig. 4 Predicted STY and the Physicochemical Properties Used for the Prediction



Cu/Zn = 2/1, Al (■), Be (○).

Fig. 5 Effect of Be and Al Content at 498 K, 1 MPa

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要　　旨

合成ガスからのメタノール合成に用いるCu-Zn酸化物触媒用新規添加物の人工ニューラルネットワークにおける探索

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銅-亜鉛酸化物触媒のメタノール合成活性は添加物によって大きく変わり，また最高活性を示す触媒組成は反応条件により敏感に変化することが知られている。人工ニューラルネットワーク（ANN）を用いて実験結果を再解析することにより新規添加物を探索した。元素Xのイオン半径，イオン化ポテンシャルなどの物性値とCu–Zn–X酸化物触媒の活性の関係をANNで学習した。22種の添加物の実験結果を学習に用い，学習データには含まれない29種の元素の添加効果を予想した。Beの優れた添加効果が予想されたが，この予想は実験的にも確認された。