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Artificial neural network-aided design of $Co/SrCO_3$ catalyst for preferential oxidation of CO in excess hydrogen

Kohji Omata *, Yasukazu Kobayashi, Muneyoshi Yamada

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai 980-8579, Japan

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Abstract

Preferential oxidation (PROX) of 0.7–1 vol.% CO using the stoichiometric amount of O_2 was investigated in excess hydrogen. Cobalt loading and preparation conditions of $Co/SrCO_3$ was optimized by using a full factorial design of experiment, an artificial neural network and a grid search. The optimum catalyst was 3.2 mol% $Co/SrCO_3$ pretreated at 345 °C and 97% CO conversion was achieved at 240 °C under dry and CO_2 free conditions. However CO_2 and H_2O vapor inhibited the activity, and the new additive to the $Co/SrCO_3$ catalyst was investigated in the next step for the high tolerance towards CO_2 and H_2O. Representative 10 elements (B, K, Sc, Mn, Zn, Nb, Ag, Nd, Re, and Tl) were selected to represent the physicochemical properties of all elements. Based on the relation between the physicochemical properties of element X and the catalytic performance of $Co–X/SrCO_3$, the elements such as Bi, Ga, and In were predicted to be promising additives. Finally, the catalytic performance of these additives was experimentally verified. Sixty-four percent CO conversion and 70% selectivity for PROX at 240 °C was achieved in the presence of excess carbon dioxide and steam by Co 3.2–Bi 0.3 mol%/$SrCO_3$ pretreated at 345 °C.

Keywords: PROX of CO; $Co/SrCO_3$ catalyst; Artificial neural network; Physicochemical property

1. Introduction

A polymer electrolyte membrane fuel cell (PEMFC) is promising fuel cell technology. Hydrogen as a fuel of the cell can be easily produced by steam reforming and/or partial oxidation of liquid fuels such as methanol, but CO concentrations in the hydrogen feed must be lowered below 10 ppm to avoid the poisoning of the metal electrode. Preferential oxidation (PROX) of CO in hydrogen is an effective method to remove CO, and the rapid development of catalyst for CO PROX reaction is required. While only few catalysts containing cobalt were reported [1–5], cobalt oxide is attractive because of its high activity for CO oxidation. We investigated selective oxidation by cobalt oxide in 1 vol.% hydrogen and 1 vol.% CO [6], and found that Co(III) species located in octahedral site in spinel structure of Co_3O_4 was the active site for selective CO oxidation, and that the selectivity was enhanced by using physical mixture of sodium-doped cobalt oxide and alkali earth metal carbonate. Formation and the stabilization of cobalt carbonate were suggested for the suppression of hydrogen oxidation. However the selectivity for CO oxidation of the bulk cobalt oxide was decreased in excess hydrogen.

In the present study, activity and selectivity of cobalt supported on alkali earth metal carbonate for PROX of 1 vol.% CO was investigated using the stoichiometric amount of O_2 in excess hydrogen. $Co/SrCO_3$ was discovered [7], and optimized to achieve high performance by means of data mining technique such as a full factorial design of experiment, an artificial neural network (ANN) and a grid search. Then, effect of additive was investigated to promote the activity of $Co/SrCO_3$ for PROX by means of the data mining technique because no criteria of effective additives are available for such a new catalyst. Recently, ANN is increasingly applied to the catalyst development through the prediction of catalyst performance such as activity, selectivity and durability, from the limited number of experimental results. ANN shows high ability to find out the non-linear relationship between the experimentally obtained parameters and catalytic parameters. A few successful cases have been reported where catalytic properties were predicted from physicochemical properties of the catalyst

* Corresponding author. Fax: +81 22 795 7293.
E-mail address: omata@erec.che.tohoku.ac.jp (K. Omata).

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elements instead of the experimentally determined parameters [8–10]. We also succeeded to predict an effective additive [9,10] based on the experimental results and physicochemical properties of the elements contained in the catalyst. In the second step of our catalyst development, 10 elements dispersing in the wide range of the physicochemical properties were selected. From the relation between the physicochemical properties of the selected element X and the activities for CO PROX at 240 °C, a few candidates of additives for high activity and high selectivity was determined. Finally, the promoting effect of these additives were experimentally verified.

2. Experimental

Supported cobalt (Co 3.2 mol% and additive 0.3 mol%) catalysts were prepared by an impregnation method using ethanol solution of metal nitrates. Alkali earth metal carbonate (Wako Pure Industry), γ-$A1_2O_3$, SiO_2 or CeO_2 was impregnated in ethanol solution of nitrates. After evaporation of ethanol, the precursor was calcined in air at 450 °C in some experiments. X-ray diffractogram was recorded by Mini Flex (Cu Kα, 30 kV, 15 mA, Rigaku).

Activity tests were conducted at atmospheric pressure with 120 mg catalyst diluted with 200 mg quartz sand. The reaction gas mixture consisted of 1 vol.% CO, 0.5 vol.% O_2, 5 vol.% N_2 in H_2, or 0.73 vol.% CO, 0.36 vol.% O_2, 18.0 vol.% CO_2, 10.0 vol.% H_2O, 4.7 vol.% N_2, 66.2 vol.% H_2. W/F was 1.5 g h mol^{-1}. The catalysts were pretreated in the reaction gas, and then the temperature was decreased. The product gas of preferential oxidation reaction was analyzed by gas chromatograph equipped with thermal conductivity detector. O_2, N_2, CH_4, and CO were separated in MS-5A column (4 m, 100 °C, hydrogen flow), and N_2 was used as internal standard. CO conversion, O_2 conversion, and methane yield were defined as Eqs. (1)–(3):

$$\text{CO conversion}\,(\%) = 100 \times (1 - \text{CO flow}_{\text{out}}/\text{CO flow}_{\text{in}}) \quad (1)$$

$$\text{O}_2\ \text{conversion}\,(\%) = 100 \times (1 - \text{O}_2\ \text{flow}_{\text{out}}/\text{O}_2\ \text{flow}_{\text{in}}) \quad (2)$$

$$\text{CH}_4\ \text{yield}\,(\%) = 100 \times \text{CH}_4\ \text{flow}_{\text{out}}/\text{CO flow}_{\text{in}} \quad (3)$$

Apparent oxygen conversion by CO oxidation could be defined as Eq. (4), because the amount of CO and O_2 in the reaction gas was stoichiometric, whereas oxygen conversion by H_2 oxidation was defined as Eq. (5).

The selectivity of catalyst can be evaluated by the two kinds of O_2 conversions:

$$\text{O}_2\ \text{conversion by CO oxidation}\,(\%) = \text{CO conversion} - \text{CH}_4\ \text{yield} \quad (4)$$

$$\text{O}_2\ \text{conversion by H}_2\ \text{oxidation}\,(\%) = \text{O}_2\ \text{conversion} - (\text{CO conversion} - \text{CH}_4\ \text{yield}) \quad (5)$$

Physicochemical properties of elements were collected in database software (Periodic Table X, version 3.5; Synergy Creation [11] and literature [12]). Two radial basis function networks (RBFN) were constructed by STATISTICA Neural Networks (version 6; Stat Soft Inc.), and they were used to correlate physicochemical properties with CO conversion and O_2 conversion by H_2, respectively. Subset of theses properties was used as input data, and the optimum combination of the properties were decided by validation data, which was used during the training to check the generalization ability and the precision of prediction by the RBFN. The RBFN was denoted like RBFN8-9-1. The numbers show the number of nodes in the input layer, hidden layer, and then output layer, respectively.

3. Results and discussion

3.1. Optimization of $Co/SrCO_3$ under dry and CO_2 free atmosphere

Activity of 3.2 mol% $Co/SrCO_3$ is shown in Fig. 1(a) without CO_2 and H_2O. In the range of A (160–200 °C), the CO conversion is low whereas mainly preferential CO oxidation proceeds. In the range C (over 260 °C), selectivity to CO

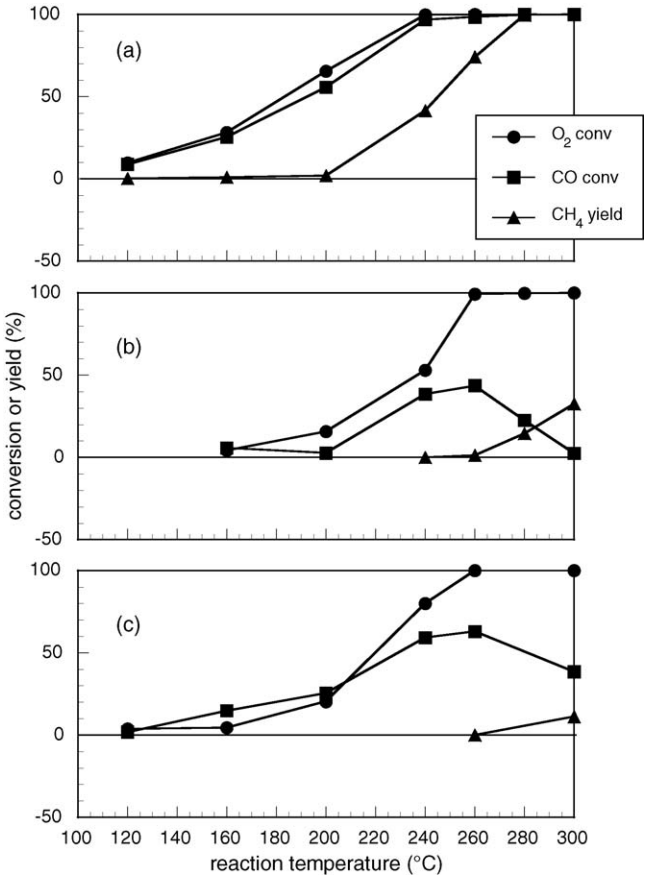

Fig. 1. O_2 (●) and CO (■) conversion and CH_4 yield (▲) of $Co/SrCO_3$ catalyst for CO PROX. (a) 3.2% $Co/SrCO_3$ pretreated at 345 °C was used under CO_2 and H_2O free gas, (b) 3.2% $Co/SrCO_3$ pretreated at 345 °C was used under CO_2 and H_2O, and (c) 3.2% Co 0.3% $Bi/SrCO_3$ pretreated at 345 °C under CO_2 and H_2O.

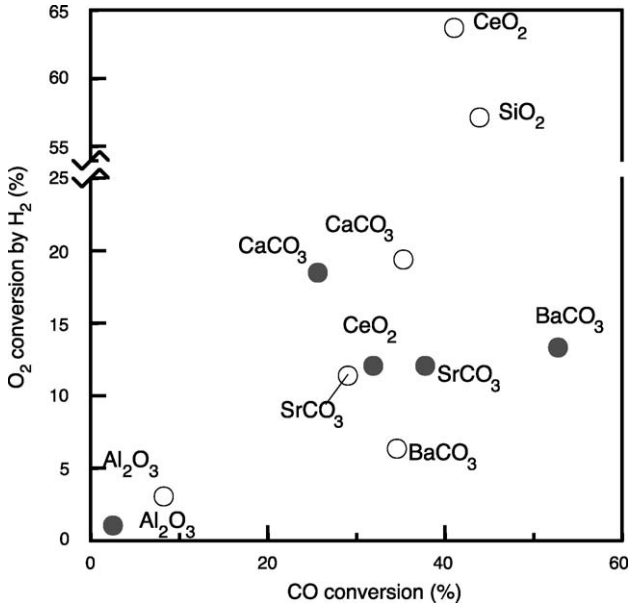

Fig. 2. Effect of support and calcination for referential oxidation and methanation of CO with 5 mol% Co. Support is shown in the figure. (●) calcined at 450 °C and (○) uncalcined.

oxidation is quite low because of CO methanation and reverse water gas shift reaction. Oxygen is used mainly for hydrogen oxidation. In the range B (200–260 °C), the oxidation of CO and hydrogen proceed simultaneously. Thus, CO conversion and O_2 conversion by H_2 oxidation at 200 °C were used to optimize the Co loading and pretreatment temperature.

The activity of uncalcined 5 mol% Co catalyst is presented in Fig. 2 as open circle to show the effect of support. The order of CO PROX selectivity of 5 mol% Co/alkali earth metal carbonate was: $Co/BaCO_3 > Co/SrCO_3 > Co/CaCO_3$ whereas the PROX activity is almost same. $Co/BaCO_3$ removed CO with the lowest loss of hydrogen. The catalytic performance of Co/CeO_2 was higher than that of $Co/CaCO_3$. The present results suggest that CeO_2 can be a good support for copper and cobalt based catalyst, whereas selectivity is not enough. CO conversion was over 99% at high temperature with Co/SiO_2 by the methanation reaction but both the activity and the selectivity of CO PROX with Co/SiO_2 were not satisfactory. CO conversion proceeded at low temperature as 160 °C with Co/Al_2O_3, and the competitive hydrogen oxidation brought the lack of oxygen. Thus, the maximum CO conversion was below 30% with Co/Al_2O_3. Effect of catalyst calcination was also investigated in the figure as closed circle. Calcination at 450 °C resulted in the decrease of the oxidation activity of both CO and H_2 of Co catalyst supported on Al_2O_3, SiO_2, CeO_2, $CaCO_3$ whereas those on $BaCO_3$ and $SrCO_3$ increased.

In order to prepare $Co/BaCO_3$ with higher CO oxidation activity and lower H_2 oxidation activity at 200 °C, Co loading, Na addition, temperature of calcination and pretreatment in the reaction gas were optimized. L_9 orthogonal array was used to design the experiments and the results were used for the training of ANN. The predicted optimum catalyst (1.2 mol% Co, 0 mol% $Na/BaCO_3$ calcined at 300 °C, pretreated at 480 °C) showed quite low activity (28% CO conversion) probably because of the inadequate design of experiments. In the next step uncalcined $Co/SrCO_3$ was optimized with respect to Co loading and pretreatment temperature using full factorial design. Levels for Co content was: 1, 2.5 and 5 mol% and pretreatment was: 360, 400, and 480 °C. CO conversion and O_2 conversion by H_2 oxidation in Fig. 3 were determined experimentally.

Response surfaces for each result can be easily built as contour lines from Fig. 3. ANN was applied, however, to find the direct relation between CO conversion and O_2 conversion by H_2. The preparation conditions and the experimental results were used as training data for an RBFN. The number of node in input layer, hidden layer, and output layer are 2, 9, and 2, respectively. In grid search, search range of each parameter was set as follows—Co loading: 1–5 mol% at every 0.1 mol%, pretreatment temperature: 340–480 °C at every 5 °C. All CO conversion and O_2 conversion by H_2 oxidation (total 1189) catalysts were predicted by the trained RBFN. The predicted CO conversions are illustrated in Fig. 4. Gray plot shows the activity of those pretreated at 345 °C with a variety of Co content.

The highest CO conversion (49%) was predicted with 3.2 mol% $Co/SrCO_3$ pretreated at 345 °C. Fortunately, the O_2 conversion by H_2 is not so high (10%) as predicted in Fig. 4.

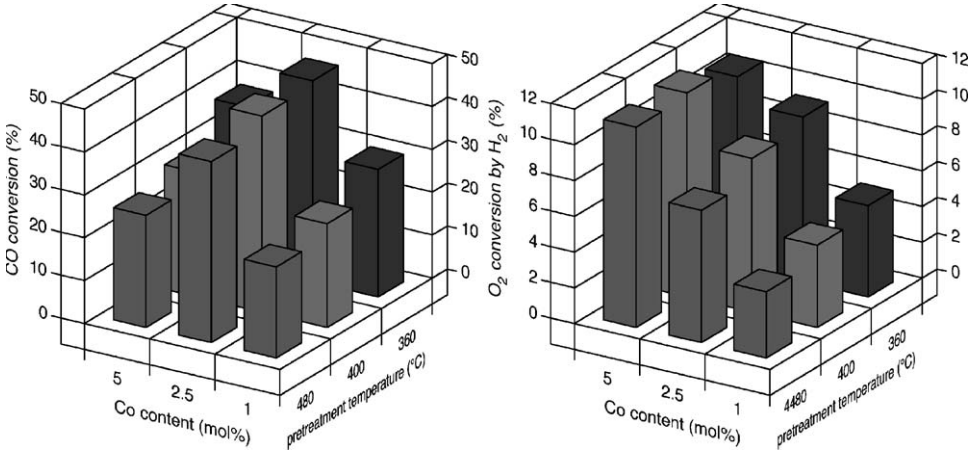

Fig. 3. Full factorial design and the experimental results with $Co/SrCO_3$ catalyst.

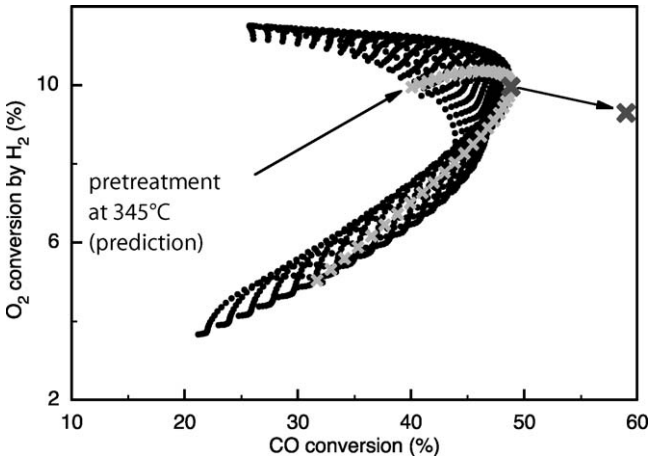

Fig. 4. Result of grid search. O_2 conversion by H_2 oxidation as a function of CO conversion with $Co/SrCO_3$ catalyst.

The results were confirmed experimentally to be 59 and 9.3%, respectively as shown with large cross in the figure and the effect of reaction temperature is shown in Fig. 1(a). X-ray diffractograms of the optimum catalyst before and after reaction are compared in Fig. 5. Strontium carbonate was stable during the CO PROX reaction, and clearly it works as catalyst carrier.

3.2. Effect of CO_2 and H_2O addition on CO PROX

In the reformed gas, large amount of carbon dioxide and steam are usually contained, and the influences of these gases on the catalytic performance are to be checked. The best catalyst reported in the previous section, Co 3.2 mol%/$SrCO_3$ pretreated at 345 °C, showed quite low activity in the presence of CO_2 and H_2O as shown in Fig. 1(b). The activity with CO_2 and H_2O at 240 °C was at the same level as those at 200 °C without CO_2 and H_2O and the negative effect of reverse water gas shift reaction is serious at high temperature. The aim of next step is, therefore, the improvement of the tolerance towards CO_2 and H_2O by new additives to $Co/SrCO_3$ and by optimization of the catalyst preparation.

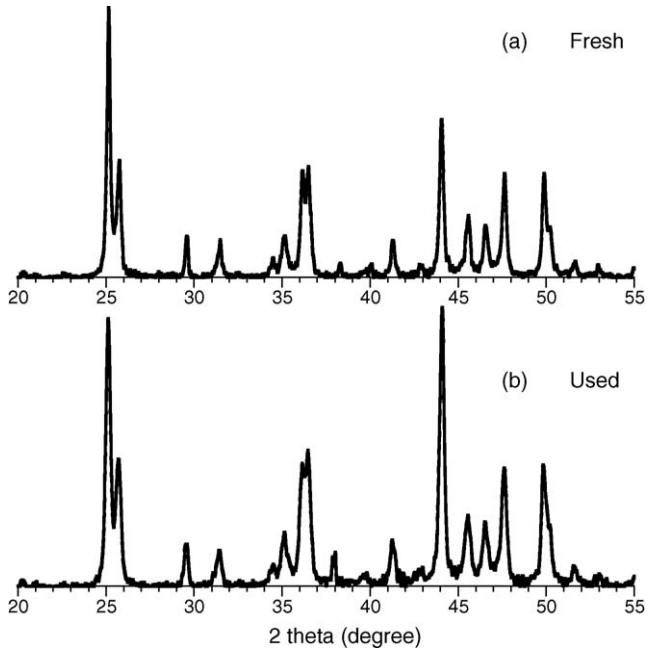

Fig. 5. X-ray diffractogram of fresh and used 3.2 mol% $Co/SrCO_3$ catalyst.

Selection of physicochemical properties for input of ANN is the most influential factor for the quality of the prediction. If the kind of selected properties is not adequate, or the number is too few, the resulting ANN cannot express the diversity of catalysts. Too many properties, on the contrary, can be the cause of confusion during the ANN training. From the viewpoint of simplicity of ANN training, the similar properties are not necessary to be included at the same time for the prediction. In order to find the similar properties, Kohonen neural network was used to find the representative, because it is a robust tool for mapping a variety of data based on the similarity of the data and it is useful to reduce the number of descriptors of an artificial neural network by mapping the parameters [13]. However, the predictions of additives by ANN constructed based on the restricted number of physicochemical properties were not successful. Therefore, all the available physicochemical properties were used for the training of ANN. Excluding rare gases, radioactive atoms, and so on, 63 elements were selected as candidates of additives to solid catalyst. Because all of the data was available for the selected 63 elements, 15 physicochemical properties of these elements were selected as: atomic number (AN), atomic weight (AW, g/mol), melting point (MP, K), boiling point (BP, K), heat of vaporization (HV, kJ/mol), heat of fusion (HF, kJ/mol), specific heat capacity (HC, J/g/K), covalent radius (CR, pm), ionic radius (IR, pm), electronegativity (EN), first ionization energy (1I, eV), second ionization energy (2I, eV), electric dipole polarizability (ED, cm^3), density (DS, g/cm^3), and thermal conductivity (TC, W/m/K). In the catalytic oxidation reaction, formation enthalpy of metal oxide (FE, kJ/mol) [11] is one of the most influential parameters on the redox property of the catalyst, and was also used for the training of ANN. The elements were ordered with respect to each property, and top 5, middle 5 and bottom 5 elements for these properties were selected among the 63 elements. The range and dispersion of physicochemical properties included in the training data were important factors for the quality of the predictions. The minimum number of elements were newly selected dispersing in the wide range of the properties. High solubility of nitrates, acetates, or alkoxides in ethanol or acetone, low decomposition temperature, low toxicity, and so on, are the selection criteria. The minimum dataset of element X was selected as: B, K, Sc, Mn, Zn, Nb, Ag, Nd, Re, and Tl. The activity of $Co/SrCO_3$ and $Co–X/SrCO_3$ is shown in Fig. 6(a).

The activities of closed circles and physicochemical properties of these elements were used as training data of RBFN. The data of Tl was used for validation of CO conversion, and that of Re was used for validation of O_2 conversion by H_2, and two ANNs were constructed for each output, because ANN with two node for output resulted in bad prediction. Using the RBFNn-9-1 with the lowest validation

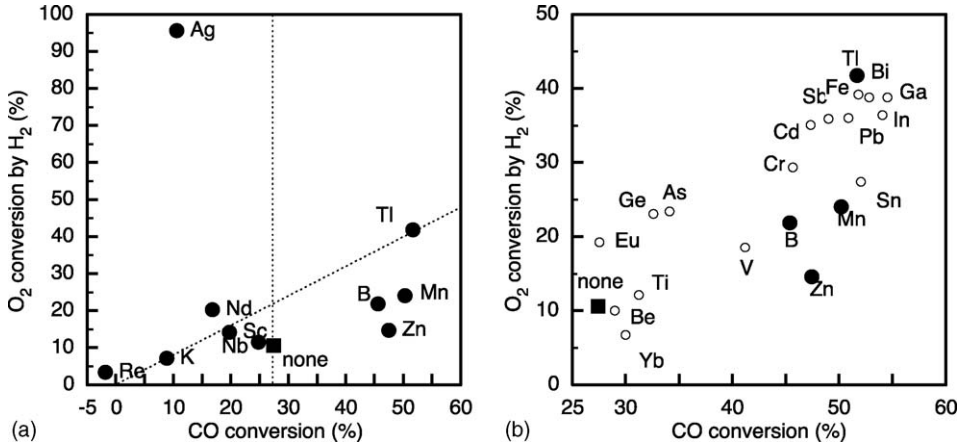

Fig. 6. (a) Experimental catalytic activity of $Co/SrCO_3$ (■) and $Co–X/SrCO_3$ (●) for ANN training and (b) predicted catalytic activity of $Co–X/SrCO_3$ (○).

error, CO conversion of $Co/SrCO_3$ catalyst with one additive from 62 elements was predicted, and RBFNm-9-1 was used for the prediction of O_2 conversion by H_2. The predictions were combined and are shown in Fig. 6(b) for better activity then "none" and better selectivity than Tl addition. Among them, Ga, In and Bi are the best three additives.

Cobalt catalyst with 3.2 mol% Co and 0.3 mol% additive on $SrCO_3$ was prepared and tested. The result is shown in Fig. 7. In accordance of the prediction, addition of Bi promoted CO conversion. CO conversion with $Co–Bi/SrCO_3$ was even higher than the highest conversion among the ANN training data by $Co–Tl/SrCO_3$ catalyst. Effect of reaction temperature is shown in Fig. 1(c) and activity at 240 °C was 2 times and selectivity was 1.5 times better when Co 3.2–Bi 0.3 mol%/$SrCO_3$ was used.

The selected physicochemical properties as input of RBFNn-9-1 for CO conversion was 1I, EN, HV, MP, BP, HF, 2I, CR, ED, TC, and those of RBFNm-9-1 for O_2 conversion by H_2 was AW, 1I, EN, HC, 2I, DS, ED. Besides the common properties, mainly electronic factors such as 1I, 2I, and ED, thermal factors are important for CO oxidation activity, whereas morphology is a predominant factor for suppression of H_2 oxidation. The result should be related to the mechanism of the CO PROX with $Co/SrCO_3$ catalyst, and the detailed characterizations are required to clarify the mechanism of activity and selectivity changes by the additives.

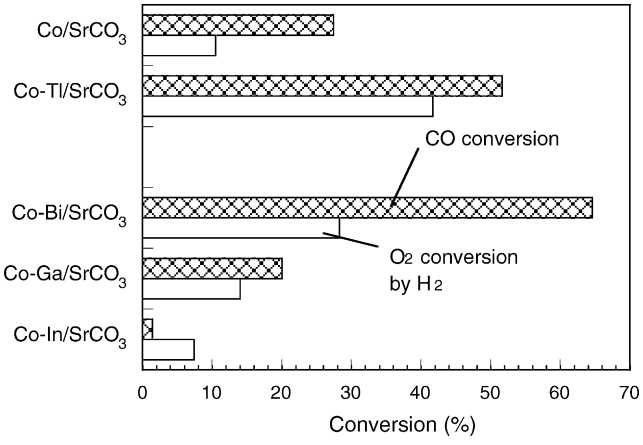

Fig. 7. Experimental verification of $Co–Bi/SrCO_3$ catalyst.

4. Conclusions

Preferential oxidation (PROX) of 1 vol.% CO was investigated using the stoichiometric amount of O_2 (0.5 vol.%) in excess hydrogen. $Co/SrCO_3$ (3.2 mol% $Co/SrCO_3$ pretreated at 345 °C), optimized by using a full factorial design, an artificial neural network and a grid search, showed 97% conversion at 240 °C. Effect of additive was then investigated to promote the activity of $Co/SrCO_3$ at 240 °C and the tolerance towards CO_2 and H_2O. Ten elements (B, K, Sc, Mn, Zn, Nb, Ag, Nd, Re, and Tl) were selected as representatives for the physicochemical properties. An artificial neural network was trained to predict the catalytic activity of $Co–X/SrCO_3$ based on the physicochemical properties of element X. $Co–Bi/SrCO_3$ was predicted to show the highest activity, and the result was experimentally confirmed. Thus, virtual screening of new additive to $Co/SrCO_3$ was successfully performed on an neural network which correlates physicochemical properties with catalytic activities.

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