Applied Catalysis A: General 407 (2011) 112–117

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Screening of new additives to heteropoly acid catalyst for Friedel–Crafts reaction by microwave heated HTS and by Gaussian process regression

Kohji Omata*

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

ARTICLE INFO

Article history:
Received 4 February 2011
Received in revised form 18 August 2011
Accepted 20 August 2011
Available online 26 August 2011

Keywords:
Friedel–Crafts reaction
High-throughput screening
Microwave heating
Principal component analysis
Nonlinear regression
Gaussian process regression

ABSTRACT

Activity of heteropoly acid (HPA) catalyst for Friedel–Crafts reaction was promoted by Pt addition of which effect was discovered by means of microwave heated high-throughput screening (HTS) and Gaussian process regression (GPR). In the screening, activities of Na, Mg, Mn, Zn, Pd, Cs, Pr and W promoted HPA were measured, and every activity test using microwave irradiation required only 150 s. The results and physicochemical properties of these 8 elements were used to construct regression models by a radial basis function network (RBFN), a support vector machine, and GPR. The regression model by GPR predicted that Pt is an effective additive, which promotes the activity, and the activity was experimentally verified to be 8 times higher than that of the unpromoted HPA catalyst. The performance of the regression model by GPR was superior to those by RBFN or by SVM because an excellent effect of Pt addition was discovered only by GPR. In addition to the extrapolative prediction, advantages of GPR model are that the performance and accuracy of the regression model are increased by using *expected improvement* which can suggest the additional experiments necessary for the improvement of the regression model.

1. Introduction

Physicochemical properties of elements can be used as explanatory variables for understanding catalytic phenomena. For example, Kito et al. [1–3] used an artificial neural network (ANN) with a backpropagation algorithm in their pioneering works to build a non-linear regression model. I also reported that a radial basis function network (RBFN) without a backpropagation algorithm, or a support vector machine (SVM), can be used for the model to predict a catalytic activity [4–7]. These results suggest that ANN, RBFN and SVM are nice tools to find correlations in non-linear catalytic phenomena.

Recently, activity of a heteropoly acid (HPA) catalyst was predicted by a regression models constructed by RBFN or by SVM [7]. The inner parameters of the models were determined by the physicochemical properties of Na, Mg, Mn, Zn, Pd, Sn, Cs, Pr, W and the activities of HPAs promoted by these additives. When properties of the 64 elements were input to the models, both RBFN and SVM predicted that Sn-HPA would show the highest activity and Bi-HPA is the second. It was confirmed experimentally that Bi-HPA showed the second highest activity among the tested catalysts. The weak point of the regression models was that they could not find an additive with which the activity of HPA was higher than that of Sn-HPA. Another problem of the screening is that the exploration was terminated when the predicted optima was verified experimentally, and the further screening was not performed, because the criteria of the termination is not clear. Recently Gaussian process regression (GPR) attracts much attention to solve these problems. Actually, GPR succeeded in finding a new additives to HPA catalyst supported on active carbon, and showed a superior performance to those of RBFN and SVM [8].

In the present study GPR was applied to construct a regression model to predict a catalytic activity from physicochemical properties of an element. A small amount of samples of the catalytic test of Friedel–Crafts reaction with non-supported heteropoly acid were used for the model. Because GPR can show the accuracy of the predictions during the modeling, and can suggest the additional experiments, it is applicable to the data analysis of a small dataset. From the view point of hardware of the activity test, on the other hand, it usually demands large amounts of cost, labor and time. High-throughput screening (HTS) attracts much attention as a useful tool to reduce them. In the present study HTS using test tubes as reactor was conducted. Microwave irradiation was also applied for heating the reaction media quickly.

2. Experimental

In the former report [7], 9 training data (Na-, Mg-, Mn-, Zn-, Pd-, Sn-, Cs-, Pr-, W-HPA) were used to construct models by RBFN and SVM. In the present study, after another model was constructed

* Corresponding author. Present address: Department of Materials Science, Interdisciplinary Faculty of Science and Engineering, Shimane University, Matsue 690-8504, Japan.
E-mail address: omata@riko.shimane-u.ac.jp

0926-860X/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2011.08.030

by GPR using the same training data for the comparison among RBFN, SVM and GPR, data of Sn-HPA were excluded for the models. Thus, Na, Mg, Mn, Zn, Pd, Cs, Pr and W were selected as training elements in the second step. By narrowing the training data, the better performance of GPR was highlighted. Additional experiments were conducted according to the same procedure of the report. Iron (II) acetate (Aldrich), 12 tungsto (VI) phosphoric acid n-hydrate (HPA, $H_3(PW_{12}O_{40})\cdot nH_2O$) and hydrogen hexachloroplatinate (IV) hexahydrate (Wako Pure Chemical Industries, Ltd.) were used as received without further purification. The charged amount of cation was 2.5 equivalent amounts as hydrogen of HPA. An aqueous solution of the salt of additive element in 2 ml of water, and an aqueous solution of 0.5 g of HPA in 2 ml of water were mixed with vigorous stirring. The solution was dried up at 100 °C and then used in the reaction without pretreatment. All the cationic species in the precursor remains in a test tube at activity test.

Microwave irradiation was applied for accelerating a heating step. A 15-mm diameter test tube charged with anisole (2.0 g), benzyl alcohol (0.2 g), and 5 mg of catalyst was placed in a 200-ml beaker, which was heated in a domestic microwave oven (700 W) for 150 s. The test tube was picked up after the reaction as soon as possible and cooled in water. The products were separated by centrifugation after calcium carbonate addition, and analyzed by a gas chromatograph (Shimadzu GC-8A, Ar carrier, Dexil 300 GC packed column at 170 °C) equipped with a flame ionization detector. The main products were benzyl anisoles, and small amounts of dibenzyl ether were formed. The combination of a test tube reactor and microwave heating resulted in *environmentally benign* activity test: 5 mg-catalyst, 2 g-anisole for 150 s reaction [7] in comparison with those of the same reaction as: 0.1 g-catalyst, 10 g-anisole for 3 h reaction [9], or 1 g-catalyst, 10 g-anisole for 3 h reaction [10]. Temperature of liquid during microwave irradiation was estimated in the former report [11] as shown in Fig. 1(a). The temperatures of bottom of the test tube and those at top liquid level are shown. The temperature increased gradually with increasing the irradiation time, but was below 150 °C after 3 min irradiation. Fortunately boiling points of the reactants and products are over 150 °C excluding water. Thus, it can be concluded that the experiments can be conducted safely in 3 min reaction. Not only the reaction time but also the period between the irradiation slightly influenced on the activity as shown in Fig. 1(b). If temperature of a magnetron of a microwave oven is low, the irradiation is stronger. Thus the period between the reactions was set to 10–20 min.

Regression models were built by statistic language R [12]. Regression by RBFN was conducted by homemade R codes. The details such as the principles and all the R codes are explained in the former report [7]. The main functions used in the present study were **prcomp** for principal component analysis, **svm** in *e1071* library for SVM, and **bgp** in *tpg* library for GPR developed by Gramacy [13,14]. Physicochemical properties [15,16] such as oxide formation enthalpy, 1st ionization energy, 2nd ionization energy, electronegativity, electric dipole polarizability, boiling point, melting point, specific heat capacity, heat of fusion, heat of vaporization, thermal conductivity, covalent radius, density, ionic radius, atomic weight, and valence of ion were used to feature 64 elements which were used as a candidate for a HPA catalyst promoter. Properties and activities were recorded in a 'data.csv' file with element symbols. Properties were stored in the 1–16th columns. Because every property was normalized in the step of principal component analysis, selection of the units of properties make no differences for regression models. Activities and symbols were stored in the 17th and 18th column, respectively.

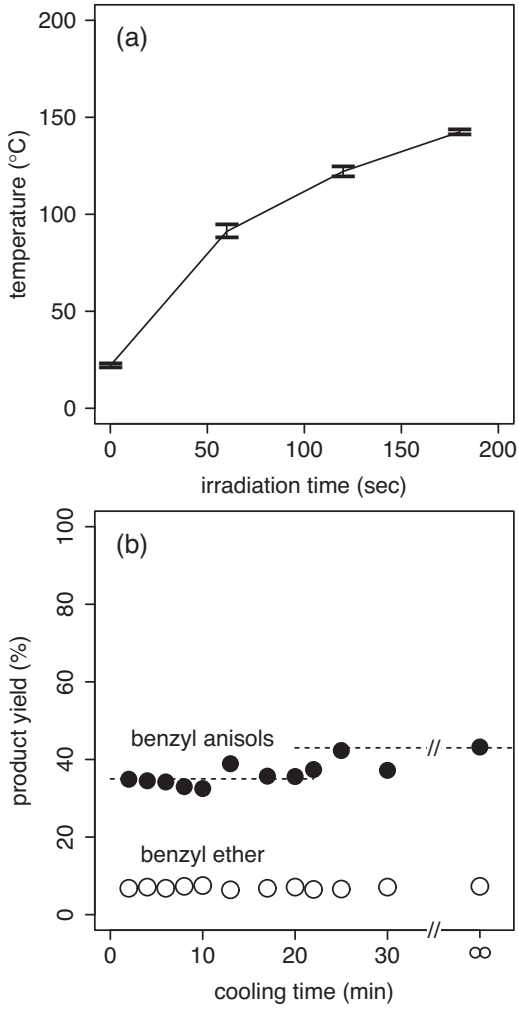

Fig. 1. (a) Temperature of bottom and upper part of the reactant liquid after microwave irradiation (anisole 2.0 g, benzyl alcohol 0.2 g). (b) Effect of cooling time on product yield with HPA catalyst (HPA 5 mg, irradiation 150 s).

3. Results and discussion

3.1. Performance of GPR using 9 training data

At first, the number of explanatory variables (16 physicochemical properties) were reduced by using principal component analysis. Scree plot of the result is shown in Fig. 2 with the cumulative eigenvalues. Both the Scree plot and the cumulative eigenvalues suggest that 5 components are enough to summarize the feature of 16 physicochemical properties. Thus, 5 principal components were used for regression models, and listed in Table 1 with the all experimental activities.

The 5 principal components of the 9 elements and activity of HPA catalyst containing one of the 9 elements listed in the top of Table 1 were used for the regression model by GPR. The procedure of GPR will be explained in detail later. The prediction was compared with those of RBFN or SVM reported in the former report. In the former report, the predicted activities were as follows listed in comparison with the top two of the training data (Sn-HPA and Mn-HPA):

by RBFN:Sn-HPA > 60% > Bi-HPA > 50% > Mn-HPA,

by SVM:Sn-HPA > 60% > Bi-HPA > 50% > . . . > Mn-HPA.

The both method concluded that no additive gives higher activity then that of Sn-HPA, and that of Bi-HPS is the second. On the other hand, the order of activity predicted by GPR is: