

Facile Tool for Prediction of Catalytic Activity - Cu-Lanthanoid Catalyst for Methanol Synthesis

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1. Introduction

Methanol (MeOH) and dimethyl ether (DME), which can be easily obtained from MeOH, are superior candidates for clean transportation fuel. A compact and simple process with good economy has been proposed to produce these fuels from dispersed unused carbon resources (Yamada, 2003). The key point of this process is development of a noble catalyst which is active for MeOH synthesis under mild reaction conditions. A number of new catalysts for MeOH synthesis from syngas were discovered and some of them are more active than the conventional Cu/Zn/Al catalyst. Cu-lanthanoid catalyst was reported as one of the alternative catalyst (Andriamasinoro et al., 1993; Nix et al., 1987; Walker et al., 1992). Under mild conditions Cu-Yb showed higher activity than Cu-Zn-Al (Sakata et al., 1998). Prediction of the characteristics of new catalysts or catalyst additives from the physicochemical properties of catalyst components would accelerate catalyst development. In the present study such prediction methodology was developed and applied for MeOH synthesis by Cu-Lanthanoid catalyst.

As reviewed in the introduction of reference (Valero et al., 2009), modeling methodologies were suggested in the research field of catalysis (Baumes et al., 2004; 2007; Farrusseng et al., 2005; Grubert et al., 2003; Holeňa & Baerns, 2003; Serra et al., 2003; Serra, Corma, Valero, Argente & Botti, 2007; Wolf et al., 2000). It was also reported that an artificial neural network, especially a radial basis function network (RBFN), (Omata et al., 2004; Umegaki et al., 2003) was successfully applied for the regression of catalytic phenomena instead of the conventional polynomial equation. Such methodology is effective for integrating the observation (Serna et al., 2008) and the characterization (Barr et al., 2004; Baumes et al., 2009; 2008; Gilmore et al., 2004; Takeuchi et al., 2005). Successful prediction of catalytic properties from the physicochemical properties of the catalyst elements was, however, reported only in few cases (Kito et al., 1992; 1994).

We recently succeeded in identifying an effective additive for Ni/active carbon (AC) catalyst for the carbonylation of methanol based on previous experimental results and the physicochemical properties of the elements (Omata & Yamada, 2004). The physicochemical properties of element X were correlated by means of RBFN to the catalytic selectivity

for vapor-phase carbonylation of methanol with a Ni-X/AC catalyst. Parameters of the RBFN were determined using the experimental results. As a result Sn was predicted and experimentally verified to suppress the methane formation. In the similar way, beryllium was predicted as the most effective additive of Cu/Zn for methanol synthesis from syngas, which was verified experimentally (Omata et al., 2005). In other case, La and Ce, Sc and Nd were predicted to promote the activity of Ni/ α -Al₂O₃ for oxidative reforming of methane. The experimentally observed activity of Ni-Sc/ α -Al₂O₃ was five times higher than that of unpromoted Ni/ α -Al₂O₃ catalyst (Omata et al., 2008).

In the present study, the activity of Cu-lanthanoid catalyst was correlated to the physicochemical properties by means of multiple regression analysis (model 1), RBFN (model 2), and support vector regression (SVR, model 3, 4, and 5). Through the prediction of activity of Cu-Sc and Cu-Pr catalyst, the generalization activity of these methods were compared and then the influential physicochemical properties were determined by the best methodology.

2. Experimental

Ethanol-oxalate method was employed for catalyst preparation. Ethanol solution of nitrates of Cu and lanthanoid was mixed with a given composition (Cu/lanthanoid = 5/1 molar ratio), and then an ethanol solution of oxalic acid was added to precipitate the mixed oxalic salts. The resulting mixed oxalates were washed with ethanol and dried at 353 K for 4 h in vacuo, and then were calcined at 573 K for 4 h into mixed oxide. The catalyst precursor oxide was activated at 403 K, 2.5 h, and 523 K, 1 h in the reaction gas. The reaction gas (syngas) composition was : 60% H₂, 30% CO, 5% CO₂ and 5% Ar (as internal standard). The reaction was conducted at 498 K, 1 MPa, W/F = 1 g·h/mol. Under these conditions, CO conversion is lower than equilibrium limit of methanol synthesis. Activity is shown as a space-time yield (STY, g-MeOH/kg-cat./h). Product gas was analyzed by micro-GC (Agilent, M-200, Molecular Sieve 5A/PoraPLOT U).

3. Prediction method

3.1 Dataset for parameter decision

Experimental results of the activity test are summarized in Fig. 1. The activity of Cu-Sc is much higher than those of Cu-La, Cu-Ce and Cu-Pr which were previously reported. The target of the present study is to predict the activity of Cu-Sc and Cu-Pr (black bars in Fig. 1) based on the experimental result in the figure other than the two catalysts.

As variables of regressions, physicochemical properties of lanthanoid (Periodic Table X , Synergy Creations) such as 1st ionization energy (1I [eV]), 2nd ionization energy (2I [eV]), electro negativity (EN [-]), electric dipole polarizability (ED [Å³]), boiling point (BP [K]), melting point (MP [K]), specific heat capacity (HC [J/g/K]), heat of fusion (HF [kJ/mol]), heat of vaporization (HV [kJ/mol]), thermal conductivity (TC [W/m/K]), covalent radius (CR [pm]), density (DS [g/cm³]), ionic radius (IR [pm]), and atomic weight (AW [g/mol]) were used with formation enthalpy of oxide (FE [kJ/mol])(Barin et al., 1993).

These primary properties should affect the secondary properties of catalyst such as surface area, surface composition, metal dispersion, electric state, morphology, thermal stability, and so on. These secondary properties then determine the catalytic activity. Therefore, properties of element should be correlated to the catalytic performance in complicated non-linear manner. Physicochemical properties of lanthanoid used for both the parameter decision and the activity prediction were normalized to 0~1 as shown in Table 1.

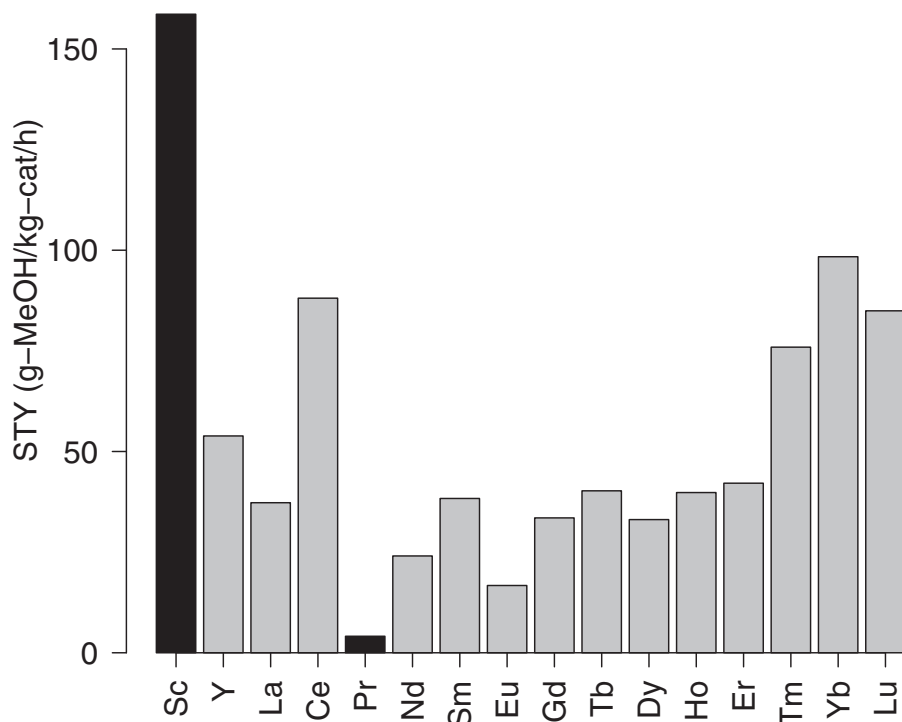


Fig. 1. Activity of Cu-Lanthanoid Catalyst for Methanol Synthesis from Syngas at 1 MPa. Data of black bars were only used for the validation of models.

3.2 Multiple regression analysis (Model 1)

Multiple regression analysis was performed by using statistical language R as model 1. R provides many functions such as *lm()* and *step()* available for statistical analysis. Because correlation coefficients of MP to HF, BP to HV, and EN to 2I were over 0.9, respectively, these properties (MP, BP, EN) were eliminated from the analysis to reduce the number of the variables. Then, *step()* function of R was used to find the influential variables, and HF, 2I, and DS were not included in the final model because of their high AIC (Akaike's Information Criterion (Akaike, 1974)) score. Predicted STYs by the final model are plotted in Fig. 2 and the regression coefficients were determined as shown in Table 2. The activities of Cu-Pr and Cu-Sc were predicted by the regression equation.

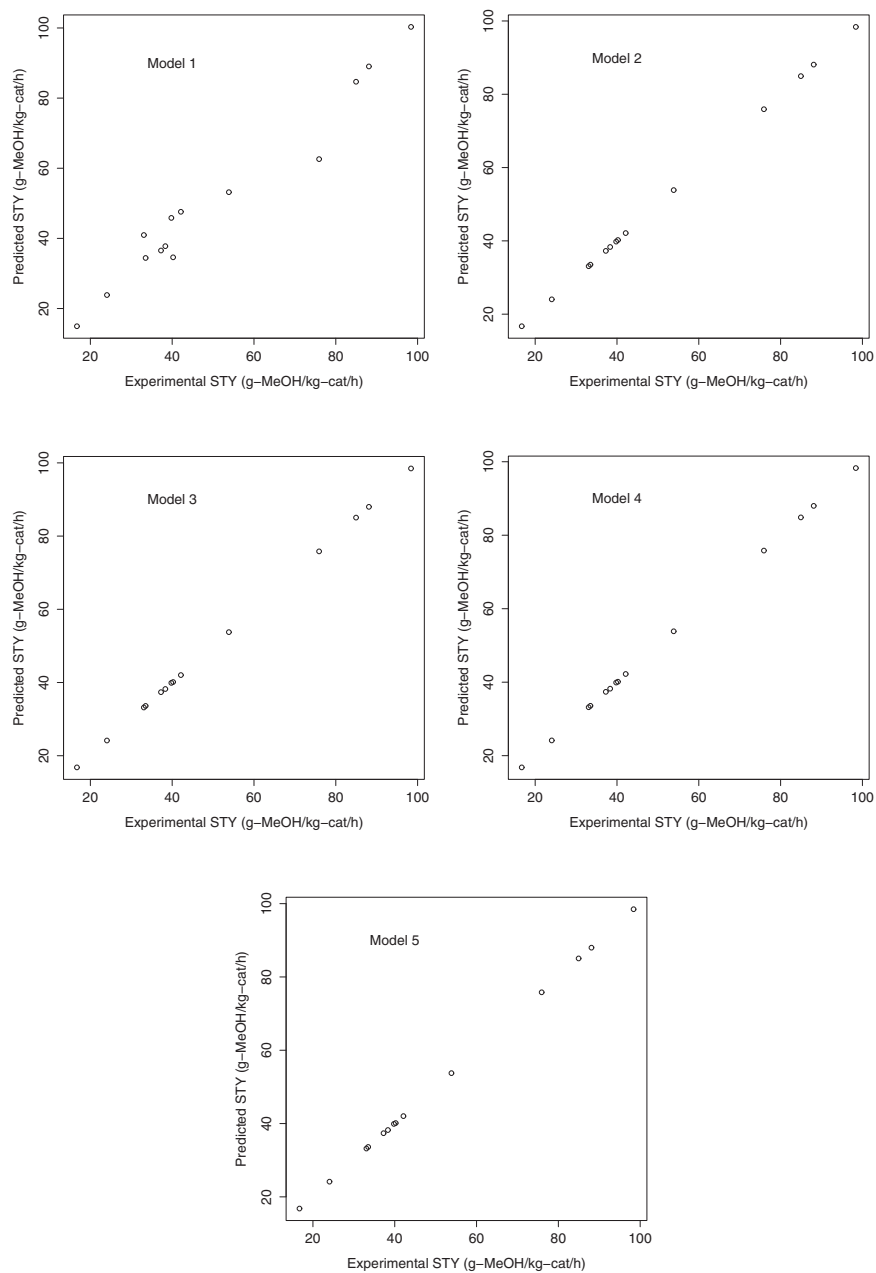


Fig. 2. Predicted STY by optimized model 1–5.

Symbol	AW	MP	BP	HV	HF	HC	CR	IR	EN	1I	2I	ED	DS	T
Y	0.338	0.842	0.925	0.775	0.835	0.357	0.439	0.590	0.500	0.699	0.504	0.360	0.219	0.2
La	0.646	0.141	0.976	0.904	0.242	0.119	0.610	1.000	0.000	0.133	0.152	0.978	0.541	0.1
Ce	0.732	0.000	0.963	0.888	0.146	0.095	0.512	0.615	0.000	0.097	0.090	0.868	0.553	0.0
Nd	0.764	0.252	0.808	0.628	0.000	0.095	0.488	0.538	0.000	0.088	0.054	1.000	0.585	0.2
Sm	0.811	0.317	0.258	0.022	0.313	0.119	0.537	0.718	0.500	0.186	0.155	0.809	0.664	0.1
Eu	0.823	0.022	0.174	0.063	0.280	0.071	1.000	0.744	0.000	0.212	0.206	0.728	0.330	0.1
Gd	0.864	0.594	0.894	0.528	0.694	0.214	0.415	0.359	0.500	0.637	0.460	0.419	0.715	0.0
Tb	0.877	0.646	0.875	0.862	0.760	0.071	0.366	0.256	0.500	0.381	0.290	0.566	0.770	0.0
Dy	0.905	0.706	0.590	0.498	0.835	0.048	0.366	0.205	0.500	0.451	0.334	0.493	0.810	0.0
Ho	0.923	0.777	0.648	0.535	0.835	0.048	0.341	0.154	0.500	0.522	0.373	0.426	0.848	0.2
Er	0.941	0.837	0.720	0.450	0.835	0.048	0.317	0.154	0.500	0.602	0.412	0.360	0.885	0.1
Tm	0.954	0.864	0.325	0.327	0.934	0.024	0.293	0.103	0.500	0.664	0.448	0.294	0.925	0.2
Yb	0.985	0.030	0.000	0.000	0.173	0.024	0.732	0.769	0.500	0.726	0.487	0.235	0.538	1.0
Lu	1.000	1.000	0.950	1.000	1.000	0.000	0.293	0.051	1.000	0.000	1.000	0.301	1.000	0.2
Pr	0.738	0.154	1.000	0.736	0.347	0.095	0.512	0.590	0.000	0.027	0.000	0.765	0.551	0.0
Sc	0.000	0.857	0.706	0.807	0.727	1.000	0.000	0.000	1.000	1.000	0.672	0.000	0.000	0.2

a) STY (g-MeOH/kg-cat/h)

The data in this table was saved in 'table_csv' as csv file and used in the R programs (R Development

```
(zz<-read.csv(table_csv))
(training<-zz[1:14,2:17])
(check<-zz[1:14,2:16])
(prediction<-zz[1:16,2:16])
(symbol<-data.frame(zz[,1]))
```

Table 1. Normalized Physicochemical Properties of Lanthanoid

	Estimate	Std. Error	t value	Pr(> t)
(Intercept)	352.9520	83.8388	4.21	0.0136
HV	-11.5397	14.0399	-0.82	0.4573
HC	-166.8569	97.6436	-1.71	0.1627
CR	-257.3117	57.7042	-4.46	0.0112
IR	100.9706	29.2293	3.45	0.0259
X1I	-53.1008	21.2195	-2.50	0.0666
ED	-139.1426	30.6455	-4.54	0.0105
DS	-78.1877	52.0711	-1.50	0.2076
TC	29.8160	24.2563	1.23	0.2864
FE	-82.7350	16.3662	-5.06	0.0072

Residual standard error: 9.319 on 4 degrees of freedom

Multiple R-squared: 0.9596, Adjusted R-squared: 0.8687

F-statistic: 10.55 on 9 and 4 DF, p-value: 0.01837

Table 2. Regression Coefficient of Model 1

3.3 Radial basis function network (Model 2)

Activity of methanol synthesis (response) was expressed by a RBFN as functions of the physicochemical properties in model 2:

$$\text{response} = \sum_{i=1}^{14} w_i \exp\left(-\frac{(\mathbf{x} - \mathbf{c}_i)^2}{2\sigma_i^2}\right) \quad (1)$$

where \mathbf{c}_i is the centers, σ_i is the radii, and w_i is the weights of the radial basis functions and \mathbf{x} is the physicochemical properties. σ_i was defined as the average of the distance to the two nearest-neighbors in the training data, and \mathbf{c}_i was determined as an input vector of the physicochemical properties of elements used as the training data. Of course data of Cu-Sr and Cu-Pr are not included in the training data. The RBFN was coded and constructed by R as below where predicted STY was plotted as shown in Fig. 2 and then the activities of Cu-Pr and Cu-Sc were predicted by the RBFN. The number of nodes in the input layer, in the hidden layer, and in the output layer of the RBFN was 15, 14, and 1 respectively.

```

model2<-function(t,p) {
  p<-as.matrix(p)
  response<-t[,ncol(t)]
  center<-as.matrix(t[, -ncol(t)])
  sigma2<-apply(apply(as.matrix(dist(center))^2,1,sort)[2:3,],2,mean)
  weight<-t(solve(exp(as.matrix(dist(center))^2)/(-2)/sigma2))%*%response
  pre<-NULL
  tt<-NULL
  for (i in 1:nrow(p)) {
    tt<-matrix(data=p[i,],nrow=nrow(center),ncol=ncol(center),byrow=T)
    pre[i]<-exp(apply((tt-center)^2/(-2)/sigma2,1,sum))%*%weight}
  return (pre)}
plot(training$response, model2(training,check))
cbind(symbol,model2(training,prediction))

```

3.4 Support vector regression (Model 3)

Recently support vector machine (SVM) attracts much attention because of its high generalization capability. SVM was first reported in the field of solid catalysis as a classifier (Baumes et al., 2006; Serra, Baumes, Moliner, Serna & Corma, 2007). It can be used also for regression, and by SVM the inputs are mapped into a high-dimensional space in nonlinear manner and then the modified inputs are correlated linearly with the output (Fan et al., 2005; Nandi et al., 2004). These reported results show clearly the superior generalization capability of a SVM and better availability through open source program makes SVM more applicable than an artificial neural network.

In the present study, SVR was performed using *libsvm* library (Fan et al., 2005) through *svm()* function in package *e1071* of R. A radial basis function was used as the kernel function and the normalized physicochemical properties and STY in Table 1 other than Cu-Pr and Cu-Sc were used.

In model 3, only cost parameter of SVM (the penalty parameter of the error term) was optimized as below using a trial-and-error method. By increasing cost parameter, the residual sum of squares was decreased as shown in Fig. 3. The predicted STY was in the steady state when cost parameter was larger than 10000. Predicted STY by the final model (cost=10000, gamma=1/15 as default) was plotted in Fig. 2 and then the activities of Cu-Pr and Cu-Sc were predicted by the SVM.

```
library(e1071)
model3<-svm(response~., data=training, cost=10000, scale=F)
(rss<-sum((training$response-fitted(model3))^2))
plot(training$response, fitted(model3))
cbind(symbol, predict(model3, prediction))
```

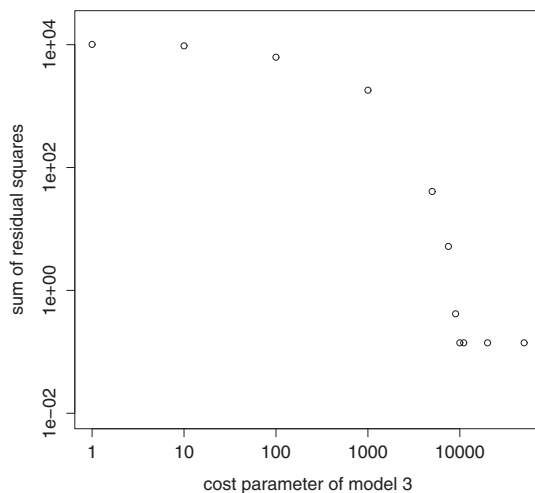


Fig. 3. Optimization of cost parameter of model 3.

3.5 Support vector regression (Model 4)

In model 4, gamma parameters of SVM (the kernel parameter of the RBFs) and cost parameter were optimized simultaneously using a grid search (Fan et al., 2005). *tune.svm()* function was used as below to decrease the sum of squared error between the experimental and the predicted STY other than Cu-Pr and Cu-Sc. The ranges of cost and gamma were gradually narrowed whereas the optimum parameters should not be located at the edge of the range. For example the range of cost parameter was changed from $10^4 \sim 10^{-4}$ to $10^{2.3} \sim 10^{2.4}$ with smaller steps. Predicted STY by the final model was plotted as shown in Fig. 2 and then the activities of Cu-Pr and Cu-Sc were predicted by the SVM.

```
library(e1071)
cost=10^c(seq(2.3,2.4,0.01))
gamma=10^c(seq(-0.3,-0.2,0.01))
model=tune.svm(response~., data=training, gamma=gamma, cost=cost, scale=F,
  tunecontrol=tune.control(sampling="fix"),
  validation.x=training[, -ncol(training)],
  validation.y=training[, ncol(training)])
model4=model$best.model
plot(training$response,fitted(model4))
cbind(symbol,predict(model4,prediction))
```

3.6 Support vector regression (Model 5)

In model 5, leave-one-out method (in this case, 14-fold cross validation) were used instead of the grid search to prevent the over-fitting problem. The ranges of cost and gamma were gradually narrowed as in model 4. Predicted STY by the final model was plotted as shown in Fig. 2 and then the activities of Cu-Pr and Cu-Sc were predicted by the SVM.

```
library(e1071)
cost=10^c(seq(3.85,3.95,0.01))
gamma=10^c(seq(-1.15,-1.05,0.01))
model=tune.svm(response~., data=training, gamma=gamma, cost=cost, scale=F,
  tunecontrol=tune.control(sampling="cross",cross=14))
model5=model$best.model
plot(training$response,fitted(model5))
cbind(symbol,predict(model5,prediction))
```

4. Result and discussion

The activity of Cu-Pr and Cu-Sc were predicted using model 1–5. As mentioned above, activity data of Cu-Sc(159 g-MeOH/kg-cat/h) and Cu-Pr(4.1 g-MeOH/kg-cat/h) were not included in the construction of model 1–5. In Fig. 4 the prediction errors are compared. The activity of Cu-Pr was predicted to be larger than the experimental result in the all model. The precision of the prediction was high as follows: model 5 > model 3 > model 4 > model 2 \approx model 1. Physicochemical properties such as $II(1st\ ionization\ energy)$ and $AW(atomic\ weight)$ of lanthanoid are plotted in Fig. 5. Based on the open circles (training data for the regression), activities corresponding to the closed circle (target data) should be predicted. It is understandable that prediction error of Cu-Pr is smaller than that of Cu-Sc because Sc is located far from the training elements. Among the model 1–5, only model 5 is equipped with a mechanism to avoid over-fitting. Using the unevenly distributed training data as shown in Fig. 5, leave-one-out (14-fold cross-validation) was proved to be effective for the

precise prediction. Thus, SVM will give the best regression if the parameters are optimized by leave-one-out method.

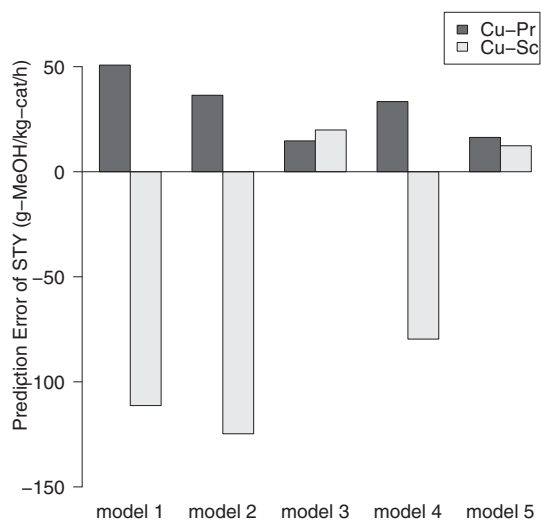


Fig. 4. Comparison of the Prediction Error by Various Regression Method.

In order to find the correlation between the physicochemical properties and the activity of Cu-lanthanoid for methanol synthesis, the best regression model was constructed using the all data in Table 1.

The model 6 was constructed using the SVM of which parameters were optimized by leave-one-out method as same as model 5.

In the model 6, correlation between the physicochemical properties and the activity of methanol synthesis should be unveiled.

The STY of Cu-Sc catalyst is plotted in Fig. 6 as a function of some physicochemical property. Even when the property change is imaginary, the STY change can be predicted by the regression model 6 if one properties is changed. As shown in the figure, effect of TC on the activity of Cu-Sc should be small: even if TC can be changed, the activity of the resulting catalyst is almost same. On the contrary, BP should be influential on the activity. The difference of the maximum and the minimum of such imaginary activity of Cu-Sc was predicted as shown in Fig. 7 for each physicochemical property. In this figure is shown that the five properties are remarkably influential. They can be categorized in two groups:

group 1:EN, II

group 2:BP, HV, CR

In methanol synthesis active site of Cu catalyst is not clear yet. However, in Cu/ZnO-based ternary catalysts for methanol synthesis from CO₂ and H₂, Cu⁰/Cu⁺ ratio influences the activity (Saito et al., 1996). According the results it is natural that the ligand effect of the lanthanoid is influential.

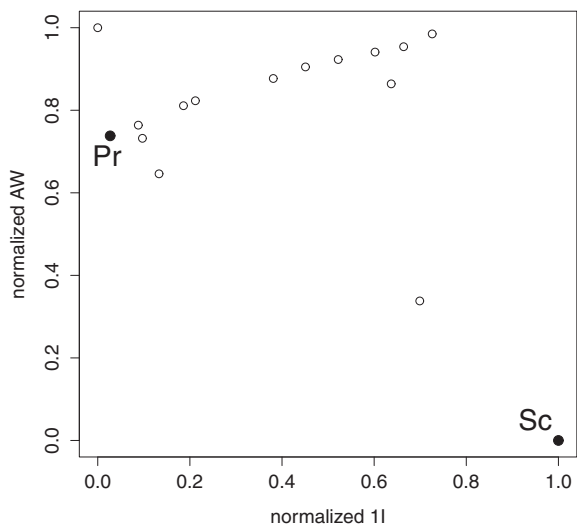


Fig. 5. Distribution of some training data. Open circle = training data.

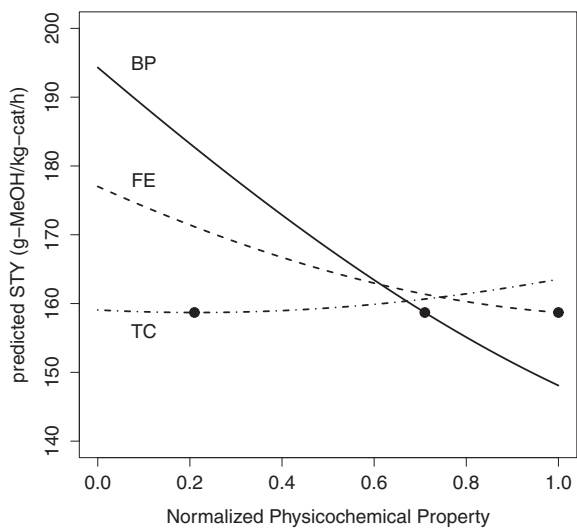


Fig. 6. Predicted Effect of Physicochemical Properties on STY of Cu-Sc Catalyst. Closed circles: experimental result of Cu-Sc.

On the other hand, in the case of metal alloy, metals with higher HV tend to be dominant on the surface. Thus, BP and HV in group 2 probably are the indexes of surface mobility. With Cu-Yb catalyst for hydrogenation, the catalyst morphology is influenced by the pretreatment temperature. Cluster-like ytterbium oxide homogeneously dispersed in copper metal when it is activated at the optimum temperature, and the morphology strongly affects the catalytic performance (Sakata et al., 1999). Because CR is one of the most principal character of the bimetallic catalyst (Cu-lanthanoid), CR can influence the morphology along with the HV or BP, on the surface Cu metal and can influence hydrogenation activity.

Generally, sintering of Cu metal is a serious problem for the stability of Cu catalyst. When highly dispersed and active Cu/Zn/Al catalyst was prepared by ethanol-oxalate method, the cautious start-up was necessary for the appearance of high activity because methanol synthesis is highly exothermic reaction and the facile start-up causes the heat-up and sintering of the catalyst. Thus, thermal-effect-related properties such as TC and HC are potentially the important factor for Cu catalyst. As shown in Fig. 7, however, the effect of TC and HC are negligible on Cu-Sc catalyst. The result brings some insights into the active site of the catalyst.

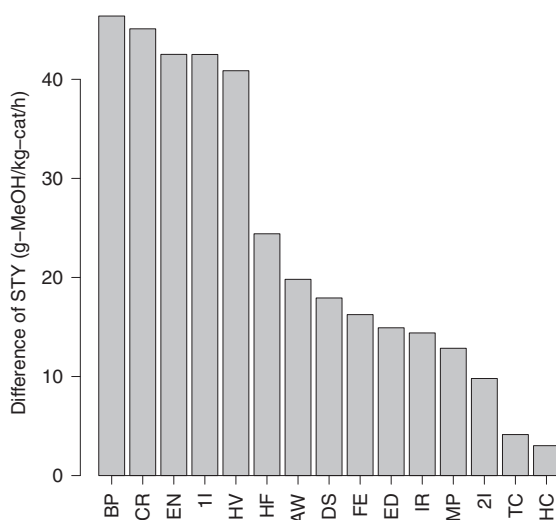


Fig. 7. Effect of Physicochemical Properties on STY Change of Cu-Sc Catalyst.

Thus the influential properties for Cu-lanthanoid catalyst were those for ligand effect (by EN and 1I) and geometric effect (by BP, HV, and CR). Thermal effect (TC and HC) plays a small role in this case.

5. Conclusion

Catalytic activities for methanol synthesis from syngas at 1 MPa and 498 K of Cu-Pr and Cu-Sc were precisely predicted. The activity of Cu-Sc was predicted to be much higher than those of the previous Cu-lanthanoid catalyst and the prediction was confirmed experimentally. For the prediction only the physicochemical properties of lanthanoid elements and the catalytic

activity of Cu-lanthanoid other than Cu-Pr and Cu-Sc were necessary. The best regression model was obtained by support vector regression when the parameters of the model was optimized by leave-one-out method. Such optimization method is important to prevent the over-fitting problem. The influential physicochemical properties were those for geometric effect and ligand effect for Cu catalyst, whereas thermal effect plays a small role. Support vector machine can be a robust tool for rapid catalyst development.

6. References

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