Development of Methanol Synthesis Catalyst by Means of Materials Informatics

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Abstract: Hydrogenation of carbon dioxide to methanol is one of key technologies to achieve a low-carbon society. New type of catalyst is required for direct CO_2 hydrogenation catalyst to reduce energy consumption of the synthesis process. For finding new additives, the catalyst was designed by means of "materials informatics" to shorten the catalyst development period. The kinetics of the catalyst was essential information for scale-up simulation. Genetic algorithm approach was developed to determine rate equations, rate constants, and activation energies based on a limited number of experimental dataset.

Keywords: carbon dioxide hydrogenation, materials informatics, genetic algorithm.

1. Introduction

Methanol is an excellent fuel and a key intermediate for the matured petrochemical industry[1]. It is produced industrially from synthesis gas (mixtures of H_2, CO and CO_2) at elevated pressures (5∼10 MPa) and temperatures (200∼300°C) over Cu-Zn based catalyst[2,3]. Methanol synthesis through hydrogenation of captured CO_2 has also attracted continuous worldwide research interest because of its environmental impact to achieve low-carbon society. Extensive studies concerned with methanol synthesis from CO_2 has been carried out involving the development of efficient catalyst, the reaction mechanism, the optimization of the reaction conditions, the design of reaction process, and so on. Recently new type of indium-zirconium catalyst was reported, where direct hydrogenation of CO_2 to methanol is the main route[4]. In this study effective additives to the catalyst was searched by means of material informatics. The new methodology was also applied to determined the reaction kinetics for scale-up simulation.

2a. Experimental

Catalyst was prepared according to oxalic acid-ethanol method. In/Zr/X molar ratio was 5/9/1. The precursor was calcined at $950 \circ C$ to form mixed oxides. The high pressure reaction was conducted in a fixed bed flow type apparatus. The product was analyzed with gas chromatographs. Support vector machine(svm) was applied to make a catalyst model to predict the activity. "e1071" library of R was used to make the svm.[5] The principal components of physico-chemical properties such as atomic weight , melting point, ionic radius, thermal conductivity, and so on, of the elements were used as input to the svm.

2b. Theoretical

(1) CO hydrogenation, (2) CO_2 hydrogenation, and (3) reverse water-gas shift reactions were considered.[6,7] Equilibrium constants (K_1, K_2, K_3) were calculated *a priori.*

$$(1)\ r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right) \cdot P_{\mathrm{CO}}^{a} \cdot P_{\mathrm{H_2}} \cdot \left(1 - \frac{P_{\mathrm{CH_3OH}}}{K_1(1 + b \cdot P_{\mathrm{CO}})P_{\mathrm{H_2}}^2}\right) \cdot \left(\frac{1}{1 + c \cdot P_{\mathrm{H_2O}}}\right)$$

$$(2)\ r_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) \cdot P_{\mathrm{CO_2}}^{d} \cdot P_{\mathrm{H_2}}^{e} \cdot \left(1 - \frac{P_{\mathrm{CH_3OH}} P_{\mathrm{H_2O}}}{K_2 P_{\mathrm{CO_2}} P_{\mathrm{H_2}}^3}\right) \cdot \left(\frac{1}{1 + f \cdot P_{\mathrm{H_2O}}}\right)$$

$$(3)\ r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) \cdot \left(1 - \frac{P_{\mathrm{CO}} P_{\mathrm{H_2O}}}{K_3 P_{\mathrm{CO_2}} P_{\mathrm{H_2}}}\right) \cdot (1 + g \cdot P_{\mathrm{H_2O}})$$

These differential equations were solved using "deSolve" library of R[7] to determine CO_2 conversions, methanol yields, and CO yields. Then, "A" factors(A_1, A_2, A_3), activation energies(E_1, E_2, E_3) and constants $(a \sim g)$ were fitted to the experimental results. The optimization was conducted using genetic algorithm ("rgenoud" library of R[8]).

3. Results and discussion

In order to make svm model, effect of additives (Na, Mg, Fe, Zn, Pd, Pd, Cs, Pr, W) were investigated. According to the prediction of the initial svm, catalyst candidates were prepared and checked. The result was fed back to reform the svm. The repeated results are summarized in Fig.1. While Pd was included in the initial "training data", acceleration effect of Pt or Ni was discovered. It was confirmed that effective additive can be unveiled according to the svm modeling.

Home-made $Cu/Zn/Al_2O_3$ catalyst was used to confirm the validity of developed R code for catalyst kinetics. Symbols in Fig.2 illustrates the experimental result at 235 or 240°C, 2 MPa, $H_2/CO_3=1/3$. CO_2 conversion levels off because of the equilibrium limit. With this catalyst the contribution of reaction 2 was negligible and the identical parameters were successfully applied to the both results at 235 and 240°C. The activation energies of CO_2 hydrogenation and RWGS were 27 and 52 kJ/mol, respectively. Using a limited number of experimental results, parameters of the complicated kinetics were determined.

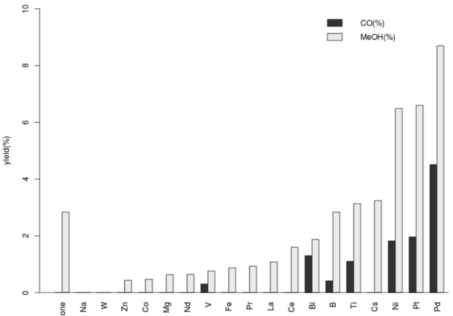

Figure 1. Effect of additives to In-Zr catalyst

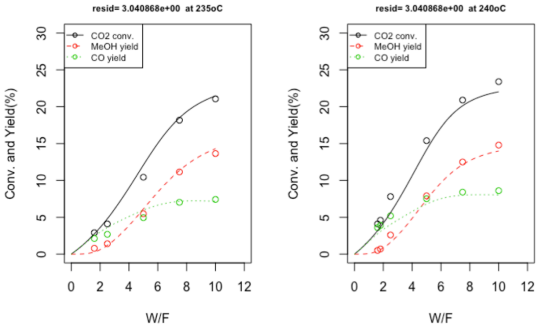

Figure 2. Kinetic simulation result.

4. Conclusions

Typical two methodologies of materials informatics such as support vector machine for data-mining, and genetic algorithm for optimization, were applied successfully to the catalyst development. These tools can assists the experimental chemists at their desk, and accelerate the research works.

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