New approach of TAP data analysis

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Introduction

The catalytic conversion of the model biogas, $CH_4 : CO_2$=1.5:1, was studied using an unique transient technique, the Temporal Analysis of Products (TAP) Reactor. Our main goal was to obtain detailed information on the mechanism of the reaction over a new prepared Ni/mesoporous SiO_2 catalyst, which proved to have high activity and selectivity. Qualitative and quantitative analysis of data was carried out. As a novelty, the quantitative kinetic data analysis was performed using the CFD software on one hand, and on another hand, a newly-developed optimisation technique. Results obtained through TAP measurements and data analysis allowed us to fill the gap within the structure/activity relationship for the series of Ni/mesoporous SiO_2 prepared catalysts. The final outcome was the proposal of the optimum formulation of the catalyst for a certain conversion and selectivity of the dry reforming of methane reaction with carbon dioxide.

Experimental

Catalyst preparation. A modified sol-gel method was used to prepare a series of Ni-Mesoporous Silica catalysts, with increasing Ni loadings, from 1 wt% to 30 wt%.
TAP experiments. Single-pulse, alternative pulse and multi-pulse experiments were performed over the 5 wt% Ni catalyst, at the following temperatures: RT, 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, and 600ºC respectively. Alternative pulse experiments or pump-probe experiments were performed at the following time intervals between the pump and probe molecules: 0, 50, 100, 500, 1000, 2000, and 5000 ms, respectively. All TAP experiments were performed using the TAP reactor available at The University of Tokyo.

Results

Single-pulse TAP experiments. The use of Ar as an internal standard allowed us to subtract information on the mechanism of the reaction from the experimental data. The statistical analysis of the experimental responses provided information on the activity and selectivity of the catalyst. Moreover, the regression of experimental data allowed the determination of the diffusion coefficients and adsorption/desorption/reaction rate constants.
Then the single-pulse responses, experimental and theoretical ones were compared with those obtained using commercial CFD (Computational Fluid Dynamics) software, Fluent (ANSYS, Inc.). We conducted unsteady simulations using the same diffusivities obtained from TAP data analysis. The number of mesh elements was 2000, and the time step was 0.0001 s. In the simulations, the tracer species was supplied for the first 0.001 s, and the flow rate was fixed at 10^{-10} m/s, which means that the effect of convection is negligible.

The results for Ar are shown in Figure 1.

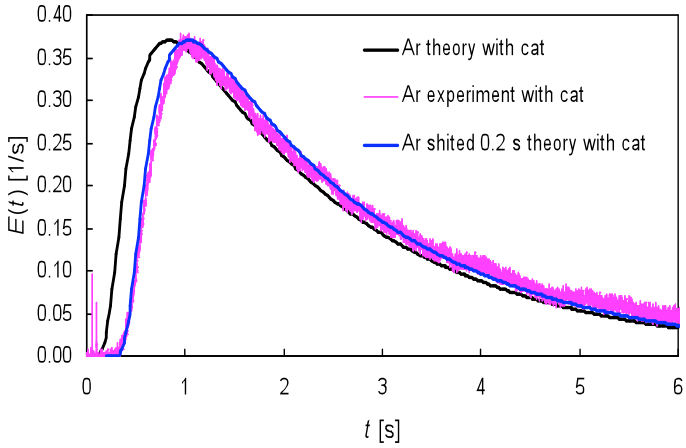

Fig. 1. Comparison of residence time distribution of Ar in a catalyst bed obtained through CFD calculations and TAP experiment (diffusivity $D = 4.0 \times 10^{-7}$ m^2/s, porosity $\varepsilon_b = 0.5$, room temperature).

Furthermore, this study provides details of several techniques and approaches that have been found to be of value in processing and analysing data from this type of experimental research. In particular data filtering and smoothing algorithms have been evaluated in order to remove experimental noise whilst retaining critical patterns within the data. Outlier removal algorithms have been applied to improve accuracy of results in data analysis stages. Steady state detection algorithms have been used to determine baseline readings for species flow rates. And finally, optimisation techniques have been utilised to investigate the accuracy of fit of the experimental data with the theoretical models of the processes under consideration.
The results generated are compared with those found using more traditional methods of data analysis and the findings (in terms of the benefits achieved in result accuracy) are discussed.
Alternating pulse experiments provided valuable information on the reaction mechanism and intermediates.
Multi-pulse experiments were performed to check the reversibility of the reduction/oxidation cycle over the studied catalyst.

Conclusions

The analysis of data from TAP reactors can provide much useful information regarding the key performance indicators of a catalyst together with improved understanding of the diffusion and adsorption mechanisms taking place. However the data is often difficult to interpret accurately because of the many unavoidable imperfections in experimental technique, measurement accuracy and equipment design.
Development of appropriate software tools can go so way towards reducing the impact of such problems on the results of the experimental analysis.

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