Modeling of TAP experiments with COMSOL. Case of dry reforming of methane.

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ABSTRACT. Many important phenomena are governed by systems of differential equations, ordinary (ODE) or partial (PDE). Examples of such systems are TAP ("Transient Analysis of Products") reactors, or evacuated fixed-bed catalytic microreactors, operated in Knudsen regime, where narrow pulses of gases are introduced in a bed of solid catalyst, and the product gases are analyzed by mass spectrometry. The resulting outgoing flows are used to obtain information on the phenomena taking place in the reactor (diffusion, adsorption, chemical reactions) [1-3].

Comsol (ex-Femlab) is a software based on the Finite Elements method, created to deal with models of systems governed by PDE's; the user selects the domains of the physics which should be taken into account, builds the geometric model of the system, sets the values of the pertinent parameters for the subdomains of the model and for their boundaries [4]. Comsol provides a meshing routines, various solvers and rich graphic means for the posttreatment of the obtained results. Easier problems may be treated entirely using standard forms of differential equations corresponding to selected domains of physics, while more specialized tools can be applied to deal with less standard situations. Comsol models can be transformed to Matlab procedures to be used e.g. in conjunction with an optimization procedure to find the estimations of model parameters.

Comsol seems to be particularly adapted to analyze results obtained in TAP experiments [5]. While some cases can be dealt with using analytical solutions based on Laplace transformation, situations arise when the numerical methods must be used [6]. An example may be alternating pulse (AP), or pump-probe experiments, where pulses of two different gases separated by a variable time interval are used to study e.g. the time of life of an

adsorbed intermediate generated by the first pulse ("pump pulse") and reacting with the second ("probe pulse").

Comsol modeling will be applied to TAP experiments on dry methane reforming [7] on Ni/SiO_2 catalyst. Principal stoechiometric reaction is

$CH_4 + CO_2 = 2CO + 2H_2$

but at least three others must be taken into account:

$CO + H_2O = CO_2 + H_2$ ("Water-Gas Reaction")

$CH_4 = C + 2H_2$

$2CO = C + CO_2$ ("Boudouart reaction", CO disproportionation)

This is a very interesting catalytic reaction: two gases with strong greenhouse effect, CH_4 and CO_2 are reacted to give a valuable synthesis gas with low ratio H_2/CO, well adapted to the synthesis of oxygenates, and its high positive enthalpy, 247 kJ/mol, could be advantageous in energy storage and transport applications. However, this relatively low hydrogen fraction is responsible for the fast deactivation of the catalyst by coking. Thus, to make it industrially viable, both the catalyst and the kinetics of the reaction must be studied. In particular, TAP reactors have been already used to this purpose.

In this study, a 5% Ni/SiO_2 catalyst has been studied, using a TAP reactor of the Tokyo University. The one-zone catalyst bed had a diameter of 0.5 cm and length 1 cm. Pulses of CH_4+Ar (CH_4/Ar = 1) were used as pump pulses, and those of CO_2/Ar (CO_2/Ar = 1) as probe pulses. The time interval between pulses was varied between 0 and 5 s, and the reactor was maintained at 600°C. Analyses were carried on at m/e = 15 (CH_4) and 43.5 (maximum of the CO_2 response in the apparatus).

Modeling was performed using Comsol 3.4 with the Chemical Engineering Module, on a HP work station (3 GHz, 3 GO). The model was 1D, Diffusion, Transient.

The PDE representing TAP experiment in the simplest case,

$$\varepsilon_b \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} + R_i$$

with ε_b = bed porosity, D_i = effective (Knudsen) diffusion coefficient, R_i = source term (adsorption, reactions), can be compared with the standard Comsol equation for the case specified above:

$$\delta_{ts} \frac{\partial c}{\partial t} + \nabla(-D\nabla c) = R$$

As the forcing function representing methane pulse ("pump pulse"), following "Ansatz" has been chosen (flux, boundary condition at the entrance of the reactor) :

$$F = F^\circ \, t/\tau^2 \exp(-t/\tau)$$

For CO_2, a gaussian-type expression was used :

$$F = F^\circ (1/\sigma\sqrt{\pi}) \exp(-(t-\Delta t)^2/\sigma^2)$$

where Δt = time interval between pulses.

The other boundary condition for the exit of the reactor was taken as Concentration, c = 0 for all species, as usual in TAP studies. The mass-spectrometric analysis results were considered as proportional to the fluxes of corresponding species at the exit of the reactor. The results will be presented.

In conclusion, Comsol makes it easy to model such TAP experiments, or to apply non-standard models of TAP experiments. Such studies have been often undertaken in the past, with considerable efforts of analysis and computation. The approach outlined here seems much easier and inviting, even to novices in the field.

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