Surface concentration distribution due to irreversible adsorption as governed by the effectiveness factor under TAP conditions

Phungphai Phanawadee[1,2*], Wisuthchai Boonwatcharapunsakun[1]

[1] Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand
[2] Center of Nanotechnology, Kasetsart University Research and Development Institute, Bangkok 10900, Thailand
* Corresponding author: Tel. 662-579-2083, Fax 662-561-4621, Email: fengphi@ku.ac.th

Introduction

The TAP (Temporal Analysis of Products) Knudsen pulse response technique (Gleaves et al., 1997) has been recognized as an important tool for heterogeneous catalytic reaction studies. The experiment involves injecting a small gas pulse of very short duration into an evacuated microreactor containing a packed bed of catalyst pellets. The gas molecules that leave the reactor are monitored by a mass spectrometer providing a time-dependent response curve whose intensity is proportional to the gas exit flow rate. The size and the shape of the response carry the information of the processes in the reactor. A number of TAP theoretical works have been reported and proved to be useful for design of the experiment as well as interpretation of TAP response data.

Recently, it has been reported that the analytical expression of the reactant gas conversion for first order irreversible adsorption/reaction in the TAP reactor packed with porous catalyst involves the effectiveness factor, η, like in steady-state conditions (Phanawadee et al., 2005). In steady-state conditions, the quantity η for the first order irreversible reaction is the ratio of the unvaried average gas concentration in the pellet to the gas concentration at the outermost of the pellet. In TAP conditions, the gas concentration changes with time. It was suggested that η in the conversion expression for TAP conditions is an average quantity of the whole pulse experiment. In addition, η was found to be a key factor for the non-uniform change of catalyst activity during a multi-pulse TAP experiment (Wongnuch et al., 2008).

The role of η in TAP transient experiment is of great interest. It is expected that detailed analysis of the surface concentration profile due to irreversible adsorption process would provide more information on the characteristics of TAP porous system. Detailed study should be performed starting with a single pulse experiment with fresh catalyst prior to a multi-pulse experiment. This paper focuses on the single pulse experiment. Unique characteristics related to η will be reported.

Calculation method

The mathematical model for spherical porous catalyst pellets packed in the TAP reactor follows that reported in Wongnuch et al. (2008). The processes including gas diffusion and irreversible adsorption in the reactor are described by mass balance equations in the inter- and intraparticle void regions and on the catalyst surface in the pellets. Initial and boundary conditions include zero gas and surface concentrations before pulsing, Dirac-delta-function inlet flow at the reactor entrance, and zero gas concentration at the reactor exit. The set of partial differential equations were transformed into Laplace domain. The solution of the occupied fractional surface coverage, θ, in Laplace domain was determined. The exact solution of θ at the end of the pulse experiment in time domain (θ at $t = \infty$ or θ_∞) was obtained by using the final value theorem. described by $\lim_{t\to\infty}\theta(t) = \lim_{s\to 0} s\theta(s)$.

Results

Fig. 1 shows the distribution of $\theta_\infty(\rho,\xi)$ for the case in which the reactor is uniformly packed with catalyst pellet when the gas conversion is 0.8, the effectiveness factor is 0.6, and the ratio of intraparticle to interparticle void volumes is 0.75; ρ is the dimensionless radial coordinate of the pellet and ξ is the dimensionless axial coordinate of the reactor. Line abcde shows the profile of θ_∞ at the outermost of the catalyst pellets (ρ=1) along the axial coordinate of the reactor. Lines af, bg, ch, and di shows the profiles of θ_∞ in the pellet placed at ξ = 0, 0.25, 0.50, and 0.75 respectively. At ξ=1, θ_∞=0 due to zero gas concentration at the reactor outlet.

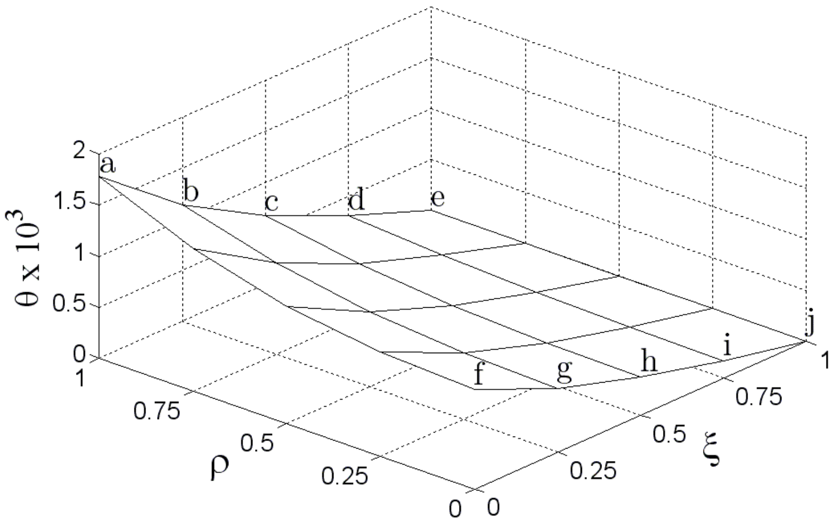

Fig. 1. Distribution of θ_∞ for the case in which the gas conversion is 0.8, the effectiveness factor is 0.6, and the ratio of intraparticle to interparticle void volumes is 0.75.

Although intraparticle profiles of θ_∞ are larger at the positions closer to the reactor inlet, all those profiles (except at ξ=1) have the same shape, i.e., the analytical expression of $\theta_\infty(\rho)/\theta_{\infty,\rho=1}$ at each axial coordinate is identical. In addition, the expression of $\theta_\infty(\rho)/\theta_{\infty,\rho=1}$ is the same as the expression of the gas concentration divided by the gas concentration at the pellet outermost, $C(\rho)/C_{\rho=1}$, for the irreversible reaction case in steady-state conditions. The expression is described by

$$\left.\frac{\theta_\infty(\rho)}{\theta_{\infty,\rho=1}}\right|_{\text{TAP}} = \left.\frac{C(\rho)}{C_{\rho=1}}\right|_{\text{Steady}} = \frac{\sinh(3M_T\rho)}{(\rho)\sinh(3M_T)} \qquad (1)$$

The quantity M_T is the typical Thiele modulus whose definition is related to the ratio of the adsorption/reaction rate parameter to the gas transport parameter. The profile of $\theta_\infty(\rho)/\theta_{\infty,\rho=1}$ is shown to be governed only by the Thiele modulus or the effectiveness factor. It is noted that Eq.(1) is also good for the case in which the catalyst bed is sandwiched between two beds of inert particles. As a result of Eq. (1), we can write

$$\left.\frac{\theta_{\infty,avg}}{\theta_{\infty,\rho=1}}\right|_{\text{TAP}} = \left.\frac{C_{avg}}{C_{\rho=1}}\right|_{\text{Steady}} = \eta = \frac{3}{3M_T}\left(\frac{1}{\tanh 3M_T} - \frac{1}{3M_T}\right) \qquad (2)$$

Since the amount of occupied active sites balances with the amount of gas conversion, Eq. (2) suggests the appearance of η in the gas conversion expression in TAP conditions like in steady-state conditions. In addition, it was found that the shape of the interparticle profile $\theta_{\infty,\rho=1}(\xi)$ (line abcde in Fig. 1) is governed by the gas conversion.

Conclusions

The correlation between the effectiveness factor and the occupied fractional surface coverage developed in an irreversible adsorption process in TAP conditions is the same as the correlation between the effectiveness factor and the gas concentration for irreversible reaction in steady-state conditions.

Acknowledgements

The financial support provided by the National Nanotechnology Center under the National Science and Technology Development Agency, the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, the Faculty of Engineering, and the Kasetsart University Research and Development Institute is gratefully acknowledged.

References

Gleaves, J.T., Yablonsky, G.S., Phanawadee, P., Schuurman, Y. (1997). A TAP-2: interrogative kinetice approach. *Appl. Catal. A: Gen.*160, 55-88.

Phanawadee, P., Phongaksorn, M., Chaimongkol, N., Jaree, A., Limtrakul, J. (2005). Mathematical analysis of TAP models for porous catalysts. *J. Chem. Eng.*, 11, 551-62.

Wongnuch, Y, Phanawadee, P., Hongsri,K., and Limtrakul, J.(2008) Uniformity of change in porous catalyst activity during a multi-pulse TAP experiment, Chemical Engineering Communications, 195:11, 1305-1314