

# Independence of Active Substance Profiles From the Pulse Response Experimental Procedure

**Phungphai Phanawadee and Nattapong Pongboutr**

Center for Petroleum, Petrochemicals, and Advanced Materials, Dept. of Chemical Engineering, Faculty of Engineering, and Center for Advanced Studies in Nanotechnology and Its Applications in Chemical, Food and Agricultural Industries, Kasetsart University, 50 Ngamwongwan Road, Bangkok 10900, Thailand

**Gregory S. Yablonsky**

Parks College of Engineering, Aviation and Technology, Dept. of Chemistry, Saint Louis University, 3450 Lindell Blvd, St. Louis, MO 63103

**Denis Constaes**

Dept. of Mathematical Analysis, Ghent University, Galglaan 2, B-9000 Gent, Belgium

**Chukiat Jarungmanorom and Watcharin Soikham**

Center for Petroleum, Petrochemicals, and Advanced Materials, Dept. of Chemical Engineering, Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Road, Bangkok 10900, Thailand

**Jumras Limtrakul**

Dept. of Chemistry, Faculty of Sciences, and Center of Nanotechnology, Kasetsart University Research and Development Institute, Kasetsart University, 50 Ngamwongwan Road, Bangkok 10900, Thailand

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## Significance

The described computational experiment focuses on producing a controlled catalyst activity distribution. Using TAP technique, the activity profile on the solid catalytic material surface is created by adsorption of pulsed feed gas or the like process and is controlled by the total amount of pulsed gas following the coincidence property. The coincidence property is also applicable for other diffusion + irreversible adsorption processes like wet impregnation to prepare catalyst with nonuniform distribution of catalytic material. © 2013 American Institute of Chemical Engineers *AICHE J.*, 59: 3574–3577, 2013

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## Introduction

An analysis of the nonuniform distribution of substances within catalytic systems (catalyst bed and catalyst pellets) has been an important issue in catalysis research over the past decades. A number of studies have shown that catalysts with nonuniform intraparticle distribution of catalytic substances, including the distribution of active component, catalyst coverage, etc., improve on catalytic performance, such as the effectiveness factor, yield and

selectivity toward desired products in many processes.<sup>1,2</sup> It is undoubted that a nonuniform distribution of catalytic substances can give positive results in many cases. However, it is not simple to prepare the catalyst with a given distribution reproducibly for both scientific and commercial applications. The reproducibility of catalyst activity has been focused on in many articles and some preparation factors affecting the activity profile have been reported.<sup>3–7</sup> A challenge in this area is to develop a special experimental procedure provide precisely a controlled that can spatial distribution of the catalyst coverage. In our opinion, a strong basis for the development of this procedure is provided by the temporal analysis of products (TAP)-experiment, which is known in heterogeneous catalysis since 1988.<sup>8,9</sup>

Correspondence concerning this article should be addressed to P. Phanawadee at fengphi@ku.ac.th.

The TAP Knudsen pulse response experiment provides the possibility to monitor a gradual change in catalyst state or activity by the way the experiment is performed. The experiment involves injecting a gas pulse of very short duration into an evacuated microreactor containing a packed bed of catalyst pellets. Typically, the number of reactant gas molecules is small compared with the number of active sites of the catalyst, and, therefore, the catalyst does not change significantly within a single pulse. For a fixed catalytic system, the degree of change in catalyst activity depends on the pulsing procedure, which is characterized by the pulse intensity (the number of moles of inlet reactant gas in each pulse experiment) and the number of pulses.

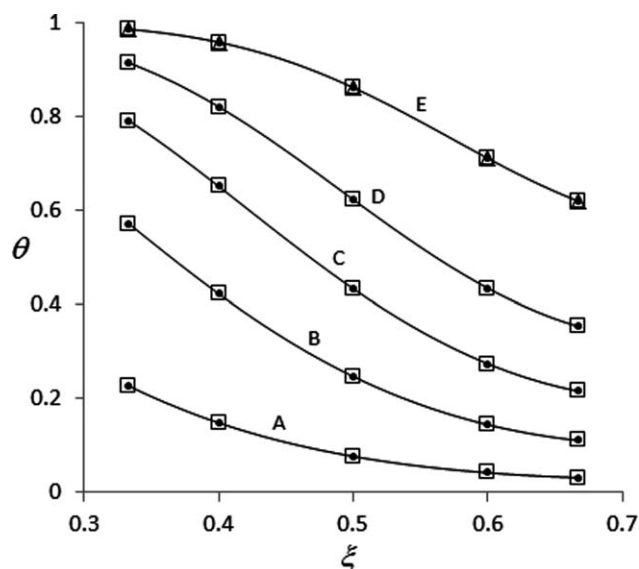
Although typical TAP experiments are performed in such a way that the catalyst changes gradually from pulse to pulse, considerably high-pulse intensity may be applied in order to alter the catalyst surface significantly in one pulse or a small number of pulses. Questions then arise: what are the characteristics of the catalytic substance distribution generated by high-pulse intensity? How does the distribution depend on the pulsing procedure? Answering these questions in this article, we will pay special attention to how the total number of molecules consumed by the catalyst affects its nonuniformity.

## Mathematical Models and Scope of Simulation

In TAP-experiments, two main cases can be distinguished: nonporous catalyst particles and porous particles, respectively. For the nonporous catalyst particle case, the spatial distribution of catalytic substance is established across the reactor. If the catalyst particle is porous, generally two types of distribution must be considered: the distribution across the reactor (the longitudinal nonuniformity), and the distribution within the catalyst particles (the intraparticle nonuniformity) as well. In this study, simulation was performed using the same mathematical models for the first-order irreversible adsorption process for nonporous catalyst pellets<sup>10</sup> and porous ones<sup>11,12</sup> as in our previous works and the activity distribution is represented by the distribution of the dimensionless concentration of surface species (the fractional surface coverage).

Numerical simulation results will be presented for nonporous and for porous catalyst pellets packed in a three-zone reactor in which the catalyst bed is sandwiched between two beds packed with nonporous inert particles. In calculations, the diffusion regime is considered the same, viz the well-defined Knudsen diffusion, in which the diffusion coefficient does not depend on the gas composition. We also consider that the temperature does not change during the experiments, so that the diffusivity and adsorption coefficients are constant and uniform.

To investigate the effect of the pulse intensity/pulsing procedure, in our numerical simulations, the distributions of surface species are calculated in such a way that the total number of pulsed molecules, i.e., the product of the number of pulses by the pulse intensity, remains the same. The pulse intensity is mathematically indicated by the catalyst number  $N_{\text{cat}}$ , which is the ratio of the number of catalyst active sites to the number of inlet reactant molecules in each pulse. In



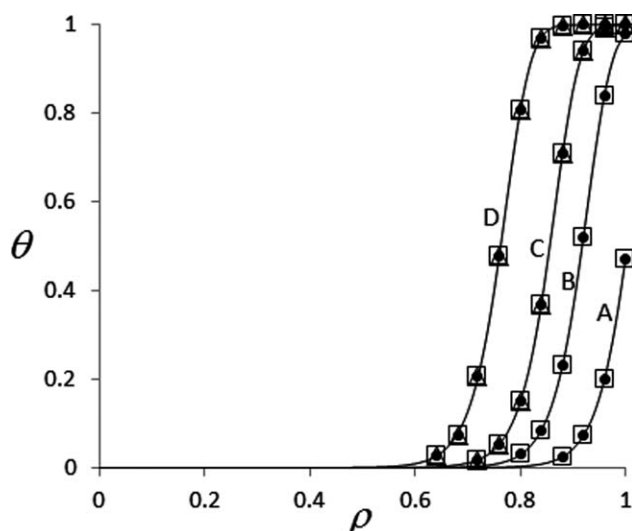
**Figure 1.** Distribution of occupied surface coverage ( $\theta$ ) along the axial coordinate of the catalyst bed packed with nonporous catalyst pellets for  $L_{\text{cat}}/L = 1/3$ , and different values of  $N_{\text{cat}}$  of 10,000 (solid circles), 10 (open squares), and 1 (open triangles).

For  $N_{\text{cat}} = 10,000$ , curves A to E represent the distribution after the pulse numbers of 1,000, 3,000, 5,000, 7,000 and 10,000, respectively; for  $N_{\text{cat}} = 10$ , the corresponding pulse numbers are 1, 3, 5, 7, and 10; for  $N_{\text{cat}} = 1$ , curve E corresponds to the pulse number of 1; this is the case in which the first-pulse gas conversion is equal to 0.94 for  $N_{\text{cat}} = 10,000$ .

each multipulse experiment, the same  $N_{\text{cat}}$  is used for every pulse throughout the experiment. For a fixed number of active sites, the same total amount of inlet reactant gas is obtained for the same ratio of pulse number ( $n$ ) to  $N_{\text{cat}}$ .

## Simulation Results and Discussion

Figure 1 shows the surface coverage along the axial coordinate of the catalyst bed packed with nonporous catalyst when the ratio of catalyst zone length to the reactor length is  $1/3$ , and the system parameters are chosen providing a gas conversion in the first pulse experiment of 0.94 for the large  $N_{\text{cat}}$  (very small pulse intensity) of 10,000. The solid lines marked with solid circles represent the distribution after the pulse with numbers of 1,000 (curve A), 3,000 (B), 5,000 (C), 7,000 (D), and 10,000 (E) for  $N_{\text{cat}} = 10,000$ . Based on the same total amount of inlet reactant gas, when  $N_{\text{cat}} = 10$ , the profiles of  $\theta$  were calculated after pulse numbers of 1, 3, 5, 7, 10 corresponding, respectively to the pulse numbers of 1,000, 3,000, 5,000, 7,000, and 10,000 in the previous case with  $N_{\text{cat}} = 10,000$ . The calculation results show that the corresponding profiles are identically the same as appeared in Figure 1 as illustrated by the open squares on each line. The calculated values of  $\theta$  at each axial coordinate of the corresponding profiles differ from each other by the order of  $10^{-4}\%$ . These dependencies are identical to the point of being visually indistinguishable, their difference being only



**Figure 2.** Distribution of intraparticle occupied surface coverage ( $\theta$ ) in the catalyst pellet placed in the middle of the reactor for  $L_{\text{cat}}/L = 1/30$ , and  $N_{\text{cat}} = 10,000$  (solid circles), 10 (open squares), and 1 (open triangles).

For  $N_{\text{cat}} = 10,000$  curves A to D represent the distribution after the pulse numbers of 1,000, 5,000, 10,000, and 20,000, respectively; for  $N_{\text{cat}} = 10$ , the corresponding pulse numbers are 1, 5, 10, and 20; for  $N_{\text{cat}} = 1$ , curves C and D correspond to the pulse numbers of 1 and 2, respectively; the fresh-catalyst Thiele modulus is 9.6 in this case.

due to tolerances in the numerical integrator and roundoff errors.

For  $N_{\text{cat}} = 1$ , we calculated the profile at  $n = 1$  corresponding to the profile at  $n = 10,000$  in the first case. The calculation results are marked by the open triangles on curve E in Figure 1 showing that the two corresponding profiles are identical as well. This fact suggests that when in the course of the irreversible adsorption process the same total amount of gas is introduced into the reactor, the total amount of gas uptake is the same, and the longitudinal surface coverage distribution is the same. Obviously, the total gas conversion must then be the same due to the mass balance.

For the porous case, the distribution, including inter- and intraparticle, was found to be identical as well. For illustration, we will show the simulation results for the case in which  $L_{\text{cat}}/L$  is equal to  $1/30$ , and the system parameters are chosen to give the Thiele modulus calculated for fresh catalyst of 9.6. The same definition of the Thiele modulus typically used in steady-state conditions<sup>13</sup> is applied as in our previous work.<sup>12</sup> The distribution of  $\theta$  for the pellet placed in the middle of the reactor is shown in Figure 2. The solid lines marked with solid circles in Figure 2 shows the intraparticle surface coverage distribution for  $N_{\text{cat}} = 10,000$ , when  $n = 1,000$  (curve A) and 5,000 (B), 10,000 (C), and 20,000 (D). When  $N_{\text{cat}} = 10$ , the distributions at corresponding pulse numbers of 1, 5, 10, and 20 are the same as marked with open squares on each line in Figure 2. When  $N_{\text{cat}} = 1$ , the distributions at corresponding pulse numbers of 1 and 2 are illustrated by open triangles on the same curves C and D, respectively. It is noted that the interparticle  $\theta$  pro-

file (not shown) is completely determined by distribution of  $\theta$  at the pellet outermost along the axial coordinates.

In our computer experiments, this *coincidence property* was found to be true for all other sets of system parameters, including the transport and kinetic parameters, the catalyst bed length and position, and catalyst number for both nonporous and porous cases. Summing up these results with the previous ones,<sup>10–12</sup> the general statement can be formulated as follows: the coincidence property is valid for both experiments of small pulse-intensities and high pulse intensities, as long as they remain within the domain of validity of Knudsen diffusion.

Hence, in all cases presented, the spatial distribution of catalytic species depends only on the total amount of reactant gas introduced into the reactor. This property is remarkable and somewhat counterintuitive, especially because the mathematical model of the reaction-transport process is *nonlinear even in the first-order adsorption case*. Nevertheless, despite the nonlinearity of the adsorption, a rigorous mathematical proof of this phenomenon has been found, based on these mathematical models. It will be given in a separate article.

The described computational experiment can be considered as a controlled modification of the catalyst via the pulse treatment of the solid material composition by some active component, say oxygen. Such modification can be used in processes of partial oxidation of hydrocarbons to achieve the desired profile of the catalyst oxidation degree. From the formal point of view, this process is identical to the irreversible adsorption process. The performance of catalyst with the prepared non-uniform profiles can be investigated using the TAP technique.

In this article, the coincidence property has been drawn from investigation of TAP pulse experiments. Since applying different pulse intensity is equivalent to using different feed flow rates of the reactant, the validity of the coincidence property is independent of the input gas flow rate. Our mathematical analysis (not shown here) suggested that this property, always assuming a constant diffusion coefficient even does not depend on the input flow pattern, i.e., the input flow pattern can be a nonpulse one, and it is only the total amount of input reactant gas that is crucial. This mathematical result leads to expansion of the application of the coincidence property to other diffusion + irreversible adsorption systems including catalyst preparation by wet impregnation. In the wet impregnation process, the transport of the precursor inside the pores is usually described by the Fick's law of diffusion for simplicity. When the precursor-surface interaction is strong enough, the adsorption can be assumed to be irreversible.<sup>1,14–16</sup> Assuming constant diffusivity, the distribution of precursor on the support's surface is controlled by the total amount of the precursor diffusing into the pellet and does not depend separately on other factors affecting the total amount, e.g., impregnation time and initial concentration of the precursor solution. If the Thiele modulus is equal to 9.6, the pattern of the fractional surface coverage of the precursor also follows Figure 2. In this case, the symbols for the pulse numbers appeared in Figure 2 are not relevant. Details will be discussed in a separate article.

## Conclusions

Using the model of temporal analysis of products (TAP) – pulse experiments in the first-order irreversible adsorption

case, it was shown that a catalytic bed of nonporous pellets and porous catalytic pellet are characterized by a nonuniform longitudinal profile and radial profile of catalytic active component, respectively. At a given number of pulsed molecules, these profiles are identical. This coincidence property can be applied to nonpulse input systems such as wet impregnation to prepare catalyst. The rigorous mathematical theory of this property will be presented in a separate article.

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## Notation

- $L$  = length of the reactor, m  
 $L_{cat}$  = length of the catalyst zone, m  
 $n$  = pulse number  
 $N_{cat}$  = catalyst number, the ratio of the number of active sites to the number of gas molecules in the inlet pulse  
 $r$  = radial coordinate of the pellet, m  
 $R_p$  = radius of the catalyst pellet, m  
 $z$  = axial coordinate of the reactor, m

## Greek letters

- $\theta$  = fractional occupied surface coverage  
 $\xi$  = dimensionless axial coordinate, defined by  $\xi = \frac{z}{L}$   
 $\rho$  = dimensionless radial coordinate, defined by  $\rho = \frac{r}{R_p}$

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