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General expression for primary characterization of catalyst activity using TAP pulse response experiment

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Abstract

A general expression for primary catalyst characterization using TAP pulse response data has been obtained for porous and non-porous catalysts, and for one- and two-step irreversible catalytic reactions. Using this expression or the corresponding nomogram, the apparent kinetic parameter can be obtained. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Temporal analysis of product (TAP) Knudsen pulse response experiments are being increasingly used in a variety of laboratories to characterize non-porous and porous catalysts. A TAP experiment is performed by injecting a narrow gas pulse of "reactant molecules" into an evacuated microreactor containing a solid sample usually in particle form. The observed characteristic in a TAP experiment is the time-dependent gas flow $F(t)$ (mol/s or molec/s) that escapes from the exit of the microreactor.

The simplest TAP microreactor configuration is the one-zone reactor which is uniformly packed with particles, and uniformly heated over its entire length. An extensive theory for the one-zone reactor has been developed and discussed in detail [1,2]. In practice, it is difficult to obtain temperature uniformity at high temperatures in a one-zone reactor, and it is now more common to use a reactor configuration in which the catalyst zone is sandwiched between two inert zones. The main advantage of a "three-zone" reactor is that the catalyst zone can be easily maintained in an isothermal condition. Theoretical analysis of a three-zone model is difficult, however, and currently, curve-fitting is the method used to describe experimental data.

Recently, we described a new TAP reactor configuration called a "thin-zone" TAP reactor, and demonstrated its application to irreversible adsorption/reaction and reversible adsorption [3]. In a thin-zone reactor, concentration gradients across the catalyst bed can be neglected, and diffusion and chemical reaction can be separated.

The thin- and one-zone TAP reactors can be viewed as special (extreme) cases of a three-zone TAP reactor. In this note, we present a general theoretical relation for a three-zone reactor that also describes the one- and thin-zone reactors to characterize both non-porous and porous catalysts.

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Nomenclature

A_r	cross-sectional area of the reactor (cm^2)
C_g	gaseous concentration in the interparticle space (mol/cm^3)
C_p	gaseous concentration in the porous space (mol/cm^3)
$D_{g,cat}$ and $D_{g,in}$	effective Knudsen diffusivities of gas in the interparticle space in the catalyst and inert zones (cm^2/s), respectively
D_p	effective Knudsen diffusivity of gases in the porous space (cm^2/s)
$F(t)$	gas flow time dependency (mol/s) or (molec/s)
J	gaseous flow from interparticle space to the pores per unit of reactor volume (mol/cm^3 s)
k_{ads}	apparent first-step adsorption constant (1/s)
k_{app}	apparent kinetic parameter (1/s), (activity)
k_{des}	apparent first-step desorption constant (1/s)
k_{reac}	apparent second-step reaction constant (1/s)
L	length of the reactor (cm)
l_{cat} and l_3	lengths of the catalyst and third inert zones (cm), respectively
N	number of moles of gas in a single inlet pulse
t	time (s)
$\text{Term}_{\text{kin}}(C_g)$	first-order kinetic term (1/s) (see Table 1 for detail)
X	conversion
x	reactor axial coordinate (cm)

Greek symbols

α	reactor parameter related to the geometry and transport properties
ε	fractional voidage in the packed bed
θ	transformed surface concentration (mol/cm^3)
σ	surface area of pores on the catalyst surface per unit volume of catalyst (cm^{-1})
ψ	parameter related to interplay of diffusion and chemical reaction

2. Primary characterization of catalyst activity

Primary characterization of catalyst activity should satisfy the following experimental and theoretical requirements:

1. insignificant change of the chemical composition and structure of the catalyst during the experiment (this requirement is realized in a TAP "state defining" experiment [1]);
2. assumption of first-order reaction;
3. general analytical expression that relates catalyst activity and observed characteristics (e.g. conversion).

The primary characterization of catalyst activity can be considered as an important first step in a methodology we call interrogative kinetics [1]. The goal of this paper is to present a general expression that can be used for the primary characterization of catalytic activity using TAP data from any of the above mentioned reactors.

3. Model

The general diffusion-reaction model for a TAP three-zone reactor can be represented as follows:

$$\varepsilon \frac{\partial C_g}{\partial t} = D_{g,cat}\frac{\partial^2 C_g}{\partial x^2} - \text{Term}_{\text{kin}}(C_g) \quad \text{(in the catalyst zone)} \qquad (1)$$

$$\varepsilon \frac{\partial C_g}{\partial t} = D_{g,in}\frac{\partial^2 C_g}{\partial x^2} \quad \text{(in the inert zones)} \qquad (2)$$

where t is the time (s), x the reactor axial coordinate (cm), C_g the gaseous concentration in the interparticle space (mol/cm^3), $D_{g,cat}$ and $D_{g,in}$ the effective Knudsen diffusivities of gas in the interparticle space in the catalyst and inert zones (cm^2/s), respectively, and ε the fractional voidage in the packed bed. $\text{Term}_{\text{kin}}(C_g)$

Table 1
Mechanisms, kinetic terms and apparent constants for different processes in a TAP experiment

Catalyst	Non-porous	Non-porous	Porous
Process	Irreversible adsorption or reaction, one-step	Irreversible reaction, two-step	Irreversible adsorption/reaction, one-step
Mechanism	$\mathrm{A}+\mathrm{Z}\overset{k_{\mathrm{app}}}{\rightarrow}\mathrm{AZ}$	$\mathrm{A}+\mathrm{Z}\ \underset{k_{\mathrm{des}}}{\overset{k_{\mathrm{ads}}}{}}\mathrm{AZ}$, $\mathrm{AZ}\overset{k_{\mathrm{reac}}}{\rightarrow}\mathrm{B}+\mathrm{Z}$	Diffusion into pores $\mathrm{A}+\mathrm{Z}\overset{k_{\mathrm{ads}}}{\rightarrow}\mathrm{AZ}$
Kinetic term, $\mathrm{Term}_{\mathrm{kin}}(C_{\mathrm{g}})$	$k_{\mathrm{app}}C_{\mathrm{g}}$	$k_{\mathrm{ads}}C_{\mathrm{g}}-k_{\mathrm{des}}\theta$, θ is given by $\frac{\partial\theta}{\partial t}=k_{\mathrm{ads}}C_{\mathrm{g}}-(k_{\mathrm{des}}+k_{\mathrm{reac}})\theta$, see Appendix A for details	$J\ (C_{\mathrm{g}})$, flow from interparticle space into the pores, see Appendix B for details
Apparent constant, k_{app}	k_{app}	$\frac{k_{\mathrm{ads}}k_{\mathrm{reac}}}{k_{\mathrm{reac}}+k_{\mathrm{des}}}$	$\frac{1-\varepsilon}{\varepsilon}\sigma\sqrt{k_{\mathrm{ads}}D_{\mathrm{p}}}\tanh\left(L_{\mathrm{p}}\sqrt{\frac{k_{\mathrm{ads}}}{D_{\mathrm{p}}}}\right)$

is the first-order kinetic term (1/s). The explicit form of this term for different cases is given in Table 1.

The TAP initial and boundary conditions are given by

$$\text{Initial condition}:\quad t=0\rightarrow C_{\mathrm{g}}=0 \tag{3}$$

$$\text{Boundary conditions}:\quad x=0\rightarrow\frac{\partial C_{\mathrm{g}}}{\partial x}=-2\frac{N}{D_{\mathrm{g,in}}A_{\mathrm{r}}}\delta(t),\quad x=L\rightarrow C_{\mathrm{g}}=0, \tag{4}$$

where N is the number of moles of gas in a single inlet pulse, L the length of the reactor (cm), and A_{r} the cross-sectional area of the reactor (cm^2). Standard conditions for insuring continuity of concentration and flow between the inert zones and the catalyst zone were applied.

4. Results

Eqs. (1) and (2) were solved using the Laplace transformation method, and a general analytical expression for an irreversible catalytic processes on non-porous and porous materials for a three-zone TAP reactor was obtained. The expression is given by

$$1-X=\frac{1}{\cosh(\Psi)+\alpha\Psi\sinh(\Psi)},\quad \Psi=\sqrt{\varepsilon\frac{l_{\mathrm{cat}}^2}{D_{\mathrm{g,cat}}}k_{\mathrm{app}}},\ \alpha=\frac{D_{\mathrm{g,cat}}l_3}{D_{\mathrm{g,in}}l_{\mathrm{cat}}} \tag{5}$$

where X is the conversion, l_{cat} and l_3 the lengths of the catalyst and third inert zones (cm), respectively, α the reactor parameter related to the geometry and transport properties (in a typical case, $\alpha=1$), and k_{app} the apparent kinetic parameter (1/s) (activity).[2]

The details of the models and apparent parameters for all three cases are given in Table 1. An analysis of more complicated pseudo-linear mechanisms that involve a sequence of irreversible steps indicates that the same relationship as (5) can be obtained. Details will be published in the future.

5. Extreme cases

Using Eq. (5), two extreme cases can be described as below

Case I: TAP "one-zone" reactor. In this case, there are no inert zones and the length of the whole reactor is equal to the length of catalyst zone. The parameter $\alpha=0$, and general equation (5) can be simplified as

$$1-X=\frac{1}{\cosh(\Psi)} \tag{6}$$

For irreversible adsorption/reaction, this is a well-known result [1].

Case II: TAP "thin-zone" reactor. In this case, the length of the catalyst zone is much smaller than the lengths of the inert zones and the length of the reactor.

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[2] In the irreversible adsorption case, for a three-zone TAP reactor with non-porous particles, Eq. (5) was previously published in Phanawadee's thesis [4] and, independently, by Dewaele and Froment [5] in dimensional form.

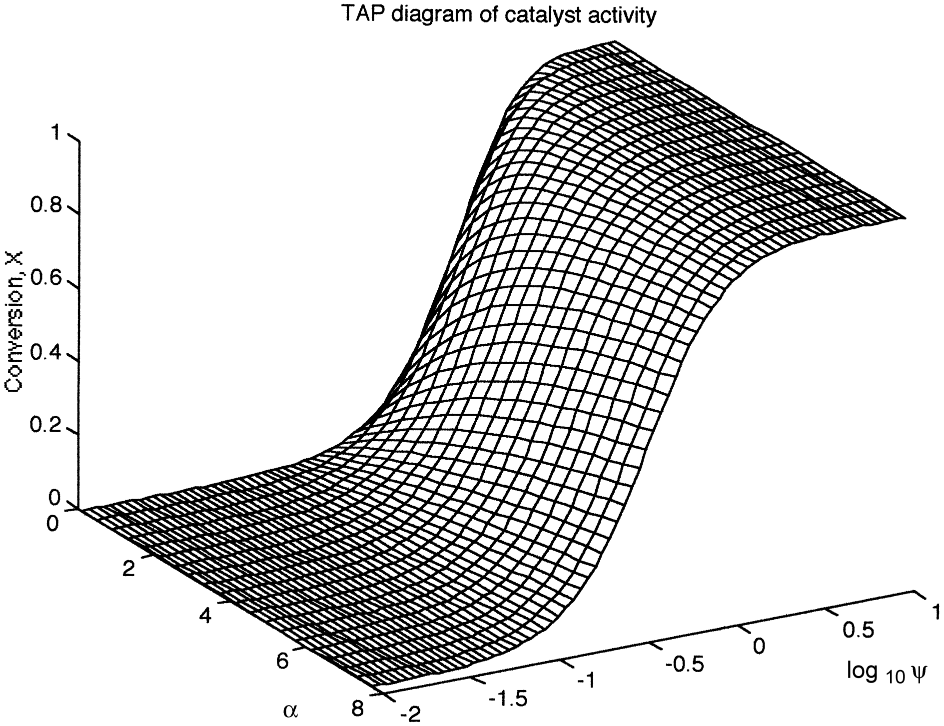

Fig. 1. TAP diagram of catalyst activity.

The hyperbolic function in general equation (5) can be simplified using the assumption that l_{cat} is very small as

$$1 - X = \frac{1}{1 + \varepsilon (l_3 l_{\mathrm{cat}} / D_{\mathrm{g,in}}) k_{\mathrm{app}}} \tag{7}$$

The TAP thin-zone reactor has been described elsewhere in detail [3]. Eq. (7) was analyzed and compared with the well-known equation for a CSTR.

6. TAP diagram of catalyst activity

Fig. 1 presents a graphical representation of general equation (5) to illustrate how it can be used to describe different TAP data. Using this diagram, the value of the parameter ψ can be obtained for a given reactor parameter, α, and an experimentally measured conversion. The apparent kinetic parameter, k_{app}, can be calculated using corresponding expressions for both porous and non-porous pellets.

7. Conclusions

A three-zone TAP reactor has been analyzed, and a general expression for primary catalyst characterization using TAP response data has been obtained. In this expression the zeroth moment/conversion is a function of only two effective parameters (reaction-diffusion parameter, ψ, and geometry-diffusion parameter, α) of reactor–catalyst system. This general expression was shown to be applicable to characterization of three different catalyst systems, i.e. porous and non-porous catalysts, and one- and two-step catalytic mechanisms. For these cases, expressions for effective parameters, particularly for apparent constant as a function of different model parameters, were presented.

Using the general expression or corresponding nomogram, the apparent kinetic parameter and corresponding model parameters can be obtained.

The expressions for TAP one- and thin-zone reactors have been shown to be particular cases of the general expression.

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Appendix A

The TAP model for an irreversible two-step reaction is given by the following equations:

$$\varepsilon\frac{\partial C_g}{\partial t} = D_{g,cat}\frac{\partial^2 C_g}{\partial x^2} - k_{ads}C_g + k_{des}\theta,$$
$$\frac{\partial \theta}{\partial t} = k_{ads}C_g - (k_{des} + k_{reac})\theta \quad \text{(in the catalyst zone)} \qquad \text{(A.1)}$$

$$\varepsilon\frac{\partial C_g}{\partial t} = D_{g,in}\frac{\partial^2 C_g}{\partial x^2} \quad \text{(in the inert zones)}, \qquad \text{(A.2)}$$

where θ is the transformed surface concentration (mol/cm^3), k_{ads} the apparent first-step adsorption constant (1/s), k_{des} the apparent first-step desorption constant (1/s) and k_{reac} the apparent second-step reaction constant (1/s).

Initial condition for surface concentration

$$t = 0 \rightarrow \theta = 0 \qquad \text{(A.3)}$$

Appendix B

The TAP model for the analysis of a catalytic process in porous particles takes into account the following two kinds of diffusion:

1. interparticle (Knudsen diffusion in the interparticle space);
2. intraparticle (diffusion in the particle pores).

The model for irreversible adsorption or reaction is given by the following equations:

$$\varepsilon\frac{\partial C_g}{\partial t} = D_{g,in}\frac{\partial^2 C_g}{\partial x^2} \quad \text{(in inert zones)} \qquad \text{(B.1)}$$

$$\varepsilon\frac{\partial C_g}{\partial t} = D_{g,cat}\frac{\partial^2 C_g}{\partial x^2} - J,$$
$$\frac{\partial C_p}{\partial t} = D_p\nabla^2 C_p - k_{ads}C_p \quad \text{(in catalyst zone)} \qquad \text{(B.2)}$$

$$J = \sigma(1-\varepsilon)D_p\nabla C_p|_{\text{at the particle surface}} \qquad \text{(B.3)}$$

where C_p is the gaseous concentration in the porous space (mol/cm^3), J the gaseous flow from interparticle space to the pores per unit of reactor volume (mol/cm^3 s), D_p the effective Knudsen diffusivity of gases in the porous space (cm^2/s), k_{ads} the rate constant of the first step and σ the surface area of pores on the catalyst surface per unit volume of catalyst (cm^{-1}).

$$\text{Initial condition:} \quad t = 0 \rightarrow C_p = 0 \qquad \text{(B.4)}$$

Boundary conditions:

$$C_p|_{\text{at the particle surface}} = C_g,$$
$$\nabla C_p|_{\text{at the end of the pore}} = 0. \qquad \text{(B.5)}$$

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