



# Catalytic effectiveness of porous particles: A continuum analytic model including internal and external surfaces



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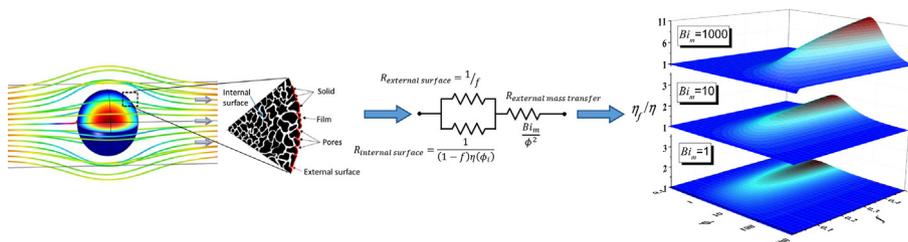
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## HIGHLIGHTS

- Pseudo-continuum analytic model explicitly including external and internal surfaces.
- Correct description of nonporous and highly porous limits.
- Influence of external surface on catalytic effectiveness derived and explained.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The well-known pseudo-continuum model of porous catalysts was based on the generally realized assumption that the external surface of the particle is negligible compared to the internal one. While valid for most industrial applications, this assumption may be inapplicable in some cases, especially for micro- to nano-catalytic particles and low internal surface cases. Herein, we developed a descriptive analytic model that explicitly accounts for both the internal and external surfaces. The model correctly describes the two limiting cases of non-porous and highly porous materials. Moreover, we show that by accounting for the external surface, the present model produces substantially different estimation of the catalytic effectiveness compared to that achieved with the traditional pseudo-continuum model.

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## 1. Introduction

The pioneering concept of catalytic activity on porous structures was independently published in the late 1930s by Thiele in the United States (Thiele, 1939), Damkohler in Germany (Damkohler, 1937), and Zeldovitch in Russia (Zeldovitch, 1939). They formulated a pseudo-continuum model of coupled mass transfer and reaction kinetics in a porous structure, and introduced the well-known effectiveness factor estimator for the porous catalyst. One of their important assumptions was the negligibility of the external surface. According to Thiele, “the greater part of the surface available for reaction is assumed to be on the walls of the pores in the catalyst. The actual external surface is assumed

to be negligible in comparison” (Thiele, 1939). Under this assumption, the reactions and heat production/consumption on the external surface of the porous particle are both ignored.

This assumption is valid for many applications. For example, a typical catalyst particle with a modest specific surface area of  $50 \text{ m}^2/\text{g}$  (Salmi et al., 2011), a diameter of 0.5 cm, and a weight of 0.1 g has an external to total surface area ratio as small as  $\approx 10^{-5}$ . A thin outer catalyst shell of  $\approx 10^{-5}$  cm in thickness would contain the same surface area as the external surface. This shell will emulate the external 2D surface in the pseudo-continuum volume model. Hence, this assumption is commonly realized and is taken for granted in most published research articles (Bischoff, 1965; Gottifredi and Gonzo, 2005; Kim and Lee, 2006) and textbooks (Davis and Davis, 2013; Froment et al., 2011; Levenspiel, 1999; Mann, 2009; Salmi et al., 2011).

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## Nomenclature

$a$	characteristic length, $V/S$ . $r_0/3$ for sphere [l]	$R_j$	reaction rate per unit catalyst volume [m/t l <sup>3</sup> ]
$C$	concentration [m/l <sup>3</sup> ]	$R'$	reaction rate per unit catalyst area [m/t l <sup>2</sup> ]
$C_b$	bulk fluid concentration [m/l <sup>3</sup> ]	$S$	geometric surface area [l <sup>2</sup> ]
$\bar{C}$	dimensionless concentration [Dimensionless]	$S_j$	active surface area per unit catalyst volume [l <sup>2</sup> /l <sup>3</sup> ]
$D$	effective diffusion coefficient [l <sup>2</sup> /t]	$V$	geometric volume [l <sup>3</sup> ]
$f$	fraction of the external active surface from the total surface area [Dimensionless]	$\phi$	Thiele modulus [Dimensionless]
$k$	first-order reaction rate constant [1/t]	$\phi_e$	external pellet's surface area Thiele modulus [Dimensionless]
$k'$	first-order reaction rate constant per pellet surface area [l/t]	$\phi_i$	internal pellet's surface area Thiele modulus [Dimensionless]
$k_g$	mass transfer coefficient [l/t]	$Bi_m$	biot number for mass transfer [Dimensionless]
$r$	radius [l]	$\eta_f$	effectiveness factor [Dimensionless]
$r_0$	particle radius [l]		$j = p, i, e$ subscripts pellet, internal, external
$\bar{r}$	dimensionless radius [Dimensionless]		

In some systems, however, the external area is not negligible as was pointed out by [Farcasiu and Degnan \(1988\)](#). Examples include silver-catalyzed partial oxidation of ethylene ([Varghese et al., 1978](#)), Zr<sub>2</sub>Fe non-evaporated hydrogen getter ([Cohen et al., 2016](#)), and materials with functionalized internal and external surfaces ([French et al., 2004](#)). Moreover, porous nano-sized particles have been made possible due to the advances in industrial catalyst synthesis ([Valtchev and Tosheva, 2013](#)). Their large surface-to-volume ratio means that the external surface is also expected to be important.

Hence, the external surface clearly can and should be included in an effectiveness model for certain porous materials. In the words of Thiele, “it is obvious that there may be all degrees between smooth platinum or nickel and a very porous material” ([Thiele, 1939](#)). Such a model should remain valid for the two limiting cases of bulk and highly porous materials (with the external to total surface area ratio being one and zero, respectively), and intermediary cases. Nevertheless, only a few attempts have been made to formulate a descriptive analytic model that explicitly accounts for the external surface, and they have achieved only partial success. Catalysis on the external and internal surfaces were treated separately, and the results were then combined algebraically to obtain the composite expression for the effectiveness and yield ([Farcasiu and Degnan, 1988](#); [Goldstein and Carberry, 1973](#); [Kramer, 1966](#)). However, only a simultaneous account of reactions on both surfaces can reproduce the correct behavior and asymptotic limits.

[Varghese et al. \(1978\)](#) formulated an external-internal surface coupled model. Although the presented analytic solution limits to the case with negligible external surface, it does not satisfy the model boundary conditions. Moreover, the model itself doesn't limit to the case of negligible external surface since the external surface source-term in the boundary condition does not vanish for negligible external surface ([Varghese et al., 1978](#)). [Fraenkel \(1990\)](#) developed a different, simple kinetic model that explains isomer shape selectivity in zeolite catalysts. However, the model was based on simplifying the system using specific kinetic and asymptotic assumptions.

Most of the textbooks on reaction chemistry and chemical engineering bypass the subject of external surface when describing the effectiveness of porous materials, and take Thiele's assumption for granted ([Davis and Davis, 2013](#); [Froment et al., 2011](#); [Levenspiel, 1999](#); [Mann, 2009](#); [Salmi et al., 2011](#)). While discussing the overall effectiveness factor, Fogler starts with a detailed formulation for the external and internal surfaces but ends with the application of Thiele's assumption. Moreover, the total catalytic surface area is erroneously used when formulating the area of the internal surface ([Fogler, 2016](#)).

Additionally, the topic of non-uniform catalyst distribution has been studied extensively in the quest to optimize catalyst activity. Pellets with different material profiles and consisting of various solid species were examined. However, none of the suggested models explicitly account for the external surface ([Au et al., 1995](#); [Melchiori et al., 2015](#); [Morbidelli et al., 1982](#)).

In this study, we present a general, steady state, descriptive model for the reaction of  $A \rightarrow B$  in the case of a porous particle with internal and external mass transfer limitation, explicitly accounting for the external to total surface area ratio ([Fig. 1](#)). We then solve the model for an isothermal first-order reaction in a porous sphere, and compare the analytic results to the well-known effectiveness factor where external surface was neglected ([Thiele, 1939](#)).

Although the computational resources nowadays permit very detailed numerical modeling ([Andersen and Evje, 2016](#); [Pereira et al., 2014](#)), we believe that a simple analytic model, such as the one presented here, enables a better understanding of the role of external surface in porous materials that is relevant in some cases.

## 2. Theoretical method

### 2.1. Actual differences between external and internal surface areas

First, we define the concept of surface area and related terms. In the ideal theoretical case, the particle surface is perfectly smooth (no surface roughness), and the external surface area equals the geometric area. The ratio between the volume and the geometric external surface area is defined as the characteristic length,  $a$ . The geometric volume and surface can be calculated from the weight and density of the pellets ( $V = m_p/\rho_p$ ,  $S = f(V)$ ).

The *specific surface area* is the total (internal and external) physical area of the solid surface per unit mass of the material. The internal surface consists of the walls of the open pores excluding the external surface. The open pores refer to pores that are connected to the external surface. The external surface can be defined as the surface boundary that encloses the solid substance with the smallest possible area. In this boundary, we take into account all cavities that are wider than deep.

The specific surface area of the porous catalyst support, which can also be the catalyst itself, is commonly measured by physical gas adsorption experiments using the Brunauer–Emmett–Teller (BET) method ([Lowell et al., 2012](#)), since it allows assessment of a wide range of pore sizes. A combination of mercury porosimetry and gas adsorption techniques permits the pore size analysis over the range from 0.35 nm up to 400  $\mu\text{m}$  ([Lowell et al., 2012](#)). The ratio between the external adsorbing surface and the geometric surface areas may be taken as the roughness factor.

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