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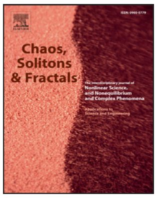

Thiele modulus having regard to the anomalous diffusion in a catalyst pellet

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ABSTRACT

In the present paper, Thiele modulus (TM) for a catalytic reaction with the anomalous diffusion of a reagent in a catalyst pellet is introduced. Different cases of the TM are considered related to the anomalous diffusion process governed by a diffusion equation with the space-fractional, time-fractional, and space-time fractional derivatives. In addition, each fractional derivative is used according to the Caputo and the Riemann–Liouville definitions. Closed-form expressions of the TM for each definition of the fractional derivative are provided. For the time-fractional derivative, the TM is obtained under the assumption of the reaction dynamics nonlinearity. We demonstrate and critically discuss the applicability of the TM obtained for the reaction-diffusion equation with non-integer order derivatives to the evaluation of the parameters of the heterogeneous catalytic process.

1. Introduction

Thiele modulus provides a relationship between a heterogeneous catalytic reaction rate and a size of a catalyst pellet [1]. An overall process rate is defined by a reagent diffusion rate in the pores of a catalyst pellet to a catalyst surface and a chemical reaction rate on a surface of a catalyst. Therefore, depending on the size of a catalytic pellet the process rate is different because for larger catalyst pellet the longer distance is traveled by a reagent in a catalyst pores. Thiele modulus provides a ratio between the reaction rate and the diffusion rate in a catalyst pellet. Based on the value of the Thiele modulus it may be concluded on the catalyst surface utilization during a catalytic reaction, particularly, the lower is the value of the Thiele modulus the higher is the degree of a catalyst utilization and vice versa [2].

The concept of the Thiele modulus is widely used in R&D and its application may not be limited only to the heterogeneous catalytic systems. It may be also used in electrochemical reactions on the electrodes [3]. In recent years, a number of Thiele moduli approaches having regard to different catalyst characteristics and catalytic reaction kinetics have been developed. For instance, the Thiele moduli accounting for the fractal structure of the catalyst pores [4], catalyst pellet shape [5], catalyst pore size distribution [6], a transition between the orders of the reaction kinetics [7] have been employed. It is worth noting that in engineering systems, the effectiveness factor is often used except the Thiele modulus [8]. However, the Thiele modulus is a ground for evaluating the effectiveness factor. The effectiveness factor is connected to the Thiele modulus by a simple relation, which may be approximated as follows [9]: $\frac{\tanh(TM)}{TM}$. The Thiele modulus, as well as the effectiveness factor, allow one to evaluate the main technical parameters of the heterogeneous catalytic reactor, e.g. reactor length, catalyst mass, reactor productivity [10].

For the derivation of the Thiele modulus, the diffusion of reagents in a catalyst pellet is usually considered as standard Fickian [11]. However, the anomalous diffusion in various systems including solid porous media has been identified recently [12–16]. The anomalous diffusion has been observed in spatial [17], temporal [18], and spatiotemporal domains [19]. Moreover, one certain physical reason for the anomalous diffusion appearance does not exist [20]. Therefore, the anomalous diffusion behavior may be potentially discovered in any system including the reagent transport in pelletized catalysts. Contrary to the standard diffusion, the anomalous diffusion is typically described by the equation that contains the fractional-order derivatives. Application of the fractional derivatives originates different mass transfer kinetics comparing to the standard diffusion and, as a result, different relation between a reaction rate and mass transfer rate in a catalyst pellet.

Recently, several attempts to investigate the heterogeneous reaction systems with regard to the anomalous diffusion has been made both, theoretically and experimentally [21–23]. In addition, the reaction-diffusion system with the fractional derivatives in a porous media has been theoretically revisited [24]. In the present paper, we develop the Thiele modulus for a reaction-diffusion system with a fractional derivative used under different definitions.

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Here, we consider the time-fractional and the space-fractional as well as a more general space-time fractional case of the anomalous reaction diffusion. For the purpose of the present paper, the time-fractional derivative in the fractional reaction-diffusion equation is used under the assumption that the chemical reaction kinetics is also time-fractional and the reagent concentration evolves in time according to the non-exponential law.

2. Preliminaries

A chemical reaction accompanied by a mass transfer process in the pores of a catalyst is usually described by a reaction-diffusion equation:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - k \cdot C \tag{1}$$

where C is concentration, mole/cm^3; t is time, sec; D is a diffusion coefficient, cm^2/sec; x is a space coordinate, cm; k is a first-order reaction constant, sec^{-1}. In the present paper, for the sake of simplicity, we use a chemical reaction of the first order. Evidently, using the chemical reaction of different order leads to the same results for the TM corrected by the reaction order.

In the case, if the derivatives in Eq. (1) are replaced by the fractional derivatives, a space-time fractional reaction-diffusion equation may be obtained:

$$\frac{\partial^\alpha C}{\partial t^\alpha} = K \cdot \frac{\partial^\beta C}{\partial x^\beta} - k_\alpha \cdot C \tag{2}$$

where α and β are the fractional order of the temporal and spatial derivatives respectively ($\alpha \wedge \beta \in (0,\ 2)$), K is a fractional diffusion coefficient, cm$^\beta$/sec$^\alpha$; k is a fractional first-order reaction rate constant, sec$^{-\alpha}$. Evidently, for $\alpha = 1$ and $\beta = 2$, Eq. (2) reduces to Eq. (1). Fractional reaction rate in Eq. (2) arises due to the following considerations. It should be noted that a simple replacement of the temporal derivative in Eq. (1) by the time-fractional derivative is impossible because such fractional reaction-diffusion equation lacks physical meaning. The composition of the fractional (diffusion) and non-fractional (reaction) process rates contradicts the mass conservation principle. For the time-fractional diffusion, the fractional reaction kinetics should be introduced, which for the first-order chemical reaction may be described by the following expression [25]:

$$\frac{d^\alpha C}{dt^\alpha} = -k_\alpha \cdot C \tag{3}$$

In the present paper, we consider the fractional derivatives in Eq. (2) according to the Caputo notation [26]:

$$\frac{\partial^\alpha C}{\partial t^\alpha} = \frac{1}{\Gamma(m-\alpha)} \cdot \int_0^t (t-\tau)^{m-\alpha-1} \cdot \frac{\partial^m C}{\partial \tau^m} d\tau \tag{4}$$

and according to the Riemann–Liouville (RL) notation [27]:

$$\frac{\partial^\alpha C}{\partial t^\alpha} = \frac{1}{\Gamma(m-\alpha)} \cdot \frac{\partial^m C}{\partial \tau^m} \cdot \int_0^t (t-\tau)^{m-\alpha-1} d\tau \tag{5}$$

where m is a constant that satisfies the condition $m = 1 \Leftrightarrow \alpha \in (0,1) \vee \beta \in (0,1) \wedge m = 2 \Leftrightarrow \alpha \in (1,2) \vee \beta \in (1,2)$, τ is the shift, and Γ is the Euler gamma function. Caputo and RL fractional derivatives have different properties and, thus, the TM obtained under different notations of fractional derivatives is also different.

3. Thiele modulus derivation

In a steady state ($\frac{\partial C}{\partial t} = 0$) Eq. (1) reduces to the following relation:

$$D \cdot \frac{\partial^2 C}{\partial x^2} - k \cdot C = 0 \tag{6}$$

For the boundary conditions given by Thiele [1], the solution of Eq. (6) may be expressed as a Thiele modulus Φ [28]:

$$\Phi = L \cdot \sqrt{\frac{k \cdot C_S}{D}} \tag{7}$$

where L is a diffusion length, cm; C_S is a surface concentration, mole cm^3. Alternatively, the Thiele modulus sometimes is expressed irrespectively to the surface concentration [29]:

$$\Phi = \sqrt{\frac{k \cdot L}{D}} \tag{7a}$$

3.1. Thiele modulus for the time-fractional diffusion equation

For $\beta = 2$, Eq. (2) corresponds to the time-fractional diffusion equation:

$$\frac{\partial^\alpha C}{\partial t^\alpha} = K \cdot \frac{\partial^2 C}{\partial x^2} - k_\alpha \cdot C \tag{8}$$

If the fractional derivative in Eq. (8) is used in the Caputo sense, in a stationary case Eq. (8) simplifies as follows:

$$K \cdot \frac{\partial^2 C}{\partial x^2} - k_\alpha \cdot C = 0 \tag{9}$$

Similarly to the standard TM, the TM for the time-fractional diffusion (Φ_γ) based on Eq. (9) may be obtained:

$$\Phi_\gamma = L \cdot \sqrt{\frac{k_\alpha \cdot C_S}{K}} \tag{10}$$

Eq. (10) is quite similar to the results presented in Ref [22]. The dimension of the TM in Eq. (10) corresponds to the dimension of the standard Thiele modulus due to the reduction of the fractional dimensions of the k_α and K constants. It is also worth noting that the scaling relations between the fractional-order and usual integer-order diffusion coefficient and the reaction rate constant may be obtained. The corresponding scaling for the fractional reaction rate constant is given by:

$$k_\alpha = k \cdot t_1^{\alpha-1} \cdot \Gamma(2-\alpha) \tag{11}$$

where t_1 is a time value identical to 1 s. The physical sense of Eq. (11) reflects the degree of the deviation of the anomalous kinetic from the usual one. Eq. (11) is obtained by expressing the ratio between the fractional reaction kinetic equation (Eq. (3)) and the usual reaction kinetic equation (Eq. (3) with $\alpha = 1$) with respect to the unit time value equal to 1 s:

$$\frac{dC}{dt} \bigg/ \frac{d^\alpha C}{dt^\alpha} = \frac{k \cdot C}{k_\alpha \cdot C} = \frac{t^{\alpha-1} \cdot \Gamma(2-\alpha) \cdot k}{k_\alpha} \tag{11a}$$

Assuming the equality of $\frac{dC}{dt} / \frac{d^\alpha C}{dt^\alpha}$ and substituting $t = t_1$ the fractional reaction rate constant is expressed by Eq. (11). For the fractional diffusion coefficient, the similar relation may be obtained:

$$K = D \cdot t_1^{1-\alpha} \cdot \Gamma(1+\alpha) \tag{12}$$

However, while the physical sense of the relation between the fractional and the usual diffusion coefficient is clear enough, the situation may be not as simple as for the reaction rate constant. Scaling provided by Eq. (12) is based on the assumption of the mean square displacement equality for the standard and fractional diffusion process. However, for different physical models of the anomalous diffusion, which result in the fractional diffusion equation, the expression of the mean square displacement is also different [30]. Here, we use the expression for the mean square displacement derived for the continuous time random walk model of