



Reaction on a solid surface supplied by an anomalous mass transfer source



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HIGHLIGHTS

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- Anomalous mass transfer.
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- Fractional diffusion equation.

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ABSTRACT

The reaction process occurring on a solid surface where active sites are present is investigated. The phenomenon is described by a linear kinetic equation capable of accounting for memory effects in the adsorption–desorption and a first order reaction process. In order to broaden the formulation of the problem, the surface is in contact with a system defined in a half space where the dynamics is governed by a fractional diffusion equation, meaning, in principle, that the approach can be applied to complex systems such as biological fluids. Our results prove that the anomalous behavior has great importance on the reaction and, consequently, on the densities rates of particles at the surface and on the distribution of particles in the bulk. The results are particularly relevant for heterogeneous catalysis.

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1. Introduction

The limiting surfaces in a sample give rise to distinct chemical reactivity from the bulk. Particles from the bulk may be adsorbed to the surface by either two mechanisms, physisorption, where the particles are attracted to the surfaces through van der Waals forces, or chemisorption, where covalent bonds at active sites adsorb them. Frequently, more than one chemical species are present in the system and chemical reactions on solid substrates may occur, being subject of studies for

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over a century [1]. In fact, this phenomena is intimately related to several technologies such as for catalysts for producing fuel [2], in biochemical sensors [3], electro-optical [4] and solar energy devices [5] and so on. With catalysts support, there are some kinds of surface reactions mechanisms [6]: the Langmuir–Hinshelwood, where two different molecules, A and B , are adsorbed, bond together and then the combination $A - B$ is desorbed; the Rideal–Eley mechanism, where A , for example, is adsorbed by the surface. Then, B encounters A , react, and $A - B$ later is desorbed. The Precursor method assumes that one molecule is adsorbed (A). The second molecule latter collides with the surface and forms a precursor, which latter collides with A , react, forming $A - B$ and desorbs [6]. Another mechanism is the so-called Mars–van Krevelen, which is also very important and widely used in heterogeneously catalyzed oxidation reactions [7–13]. In the Mars–van Krevelen mechanism, the surface itself is a very important part of the reaction. One of the reactants forms a chemical bond with the surface. This catalytic surface layer then reacts with the other reactant from the gas phase and then desorbs. It was proposed as a first order process with respect to the reactant A and the fraction of sites covered by oxygen. In this oxidation reaction, only certain lattice ions O (oxygen) at the surface are involved. In addition, the rate of surface reoxidation, i.e., O_2 adsorption, is proportional to $P_{O_2}^n$ (pressure) and to the concentration of active sites not covered by oxygen. More details about this mechanism can be found in Ref. [7].

In the above mentioned reactions, the reacting species are in different phases, which is the case of heterogeneous catalysis [14]. Different from the homogeneous catalysis, the heterogeneous case has the reacting species embedded in the solid surface while the reactant is, for example, dissolved in a liquid. Therefore, the reaction rate depends crucially on the diffusion of the species involved [15]. Diffusion can be found in several situations such as drug dissolution [16] or delivery [17], transport in biological films [18], cytoplasmic crowding in living cells [19], irregular catalyst structures on diffusion and reaction, diffusion of proteins in sheared lipid membranes [20]. The diffusion can be usual, i.e., characterized by Markovian processes, or anomalous where non-Markovian processes govern the system. In this context, an important point is to understand the mechanisms behind these phenomena and how the presence of memory effects [21,22], long-range interactions [23] and the characteristics of the media (e.g., fractal structure [24–26]) may contribute to the presence of a usual or anomalous diffusion. The surface [27], i.e., the region where the boundary conditions are defined, also plays an important role in diffusion and in others processes such as adsorption and/or desorption [28,29] and catalysis [30,31].

In this article, our goal is to investigate a system with bulk anomalous diffusion in contact with a surface where adsorption–desorption and chemical reactions happen. We consider that the dynamics of particles in the bulk is governed by a fractional diffusion equation, which has been successfully applied in several physical situations [32,33]. We further consider that the processes occurring on the surface are described by linear kinetic equations. These kinetic equations are coupled in order to cover reversible reaction processes. This analysis is performed in Section 2 and in Section 3 the discussions and conclusions are presented. The analysis carried out here may be relevant for several systems of interest (such as heterogeneous catalysis) where surface reaction occur when the substrate is in contact with a media supplying mass to these reactions by means of an anomalous mechanism.

2. Mathematical model and discussions

Let us start our analysis by considering that the particle dynamics in the bulk is governed by the following fractional diffusion equation

$$\frac{\partial}{\partial t} \rho(x, t) = \mathcal{K} \mathcal{D}_t^{1-\alpha} \left[\frac{\partial^2}{\partial x^2} \rho(x, t) \right] \quad (1)$$

where $\rho(x, t)$ is the density of particles, \mathcal{K} is the diffusion coefficient, and the fractional time derivative is the Riemann–Liouville one, defined as [34],

$${}_0 \mathcal{D}_t^{\bar{\alpha}} [\rho(x, t)] = \frac{1}{\Gamma(n - \bar{\alpha})} \frac{d^n}{dt^n} \int_0^t dt' \frac{\rho(x, t')}{(t - t')^{\bar{\alpha}-n+1}} \quad (2)$$

with $n - 1 < \bar{\alpha} < n$, where $\bar{\alpha}$ is a real number and n integer. For the processes which may occur on the surface such as adsorption, desorption, and chemical reactions, we assume that they satisfy the following kinetic equations

$$\tau \frac{d}{dt} \Gamma_a(t) = \kappa \tau \rho(0, t) - \int_0^t dt' k_a(t - t') \Gamma_a(t') + \int_0^t dt' k_{b \rightarrow a}(t - t') \Gamma_b(t'), \quad (3)$$

$$\tau \frac{d}{dt} \Gamma_b(t) = \int_0^t dt' k_{a \rightarrow b}(t - t') \Gamma_a(t') - \int_0^t dt' k_b(t - t') \Gamma_b(t'). \quad (4)$$

In Eqs. (3) and (4), $\Gamma_{a(b)}(t)$ is the surface density, κ , $k_{a(b)}(t)$, and $k_{a \rightarrow b(b \rightarrow a)}(t)$ are the parameters connected to the processes on the surface. In particular, we can write a characteristic time $\tau_\kappa = (\mathcal{K}/\kappa^2)^{2/(2-\alpha)}$ which governs the diffusion and adsorption near the surface. Eq. (3) relates the rate of adsorption of species a with the amount in the bulk, minus the amount of a desorbed plus whatever quantity is reversibly reacted from b to a . Eq. (4) relates the rate of adsorption of species b with the

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