



# Heterogeneous catalysis in pulsed-flow reactors with nanoporous gold hollow spheres



Giacomo Falcucci <sup>a,\*</sup>, Giorgio Amati <sup>b</sup>, Vesselin K. Krastev <sup>c</sup>, Andrea Montessori <sup>d</sup>, Grigoriy S. Yablonsky <sup>e</sup>, Sauro Succi <sup>f,g</sup>

<sup>a</sup> Dept. of Enterprise Engineering "Mario Lucertini", University of Rome "Tor Vergata", Via del Politecnico 1, 00133 Rome, Italy

<sup>b</sup> SCAI – SuperComputing Applications and Innovation Department, CINECA, Via dei Tizii, 6, 00185 Rome, Italy

<sup>c</sup> DEIM, University of Viterbo "Tuscia", Largo dell'Università, 01100 Viterbo, Italy

<sup>d</sup> Dept. of Engineering, University of Rome "Roma Tre", Via della Vasca Navale 79, 00143 Rome, Italy

<sup>e</sup> Dept. of Chemistry, Saint Louis University, Parks College, St. Louis, MO 63103, USA

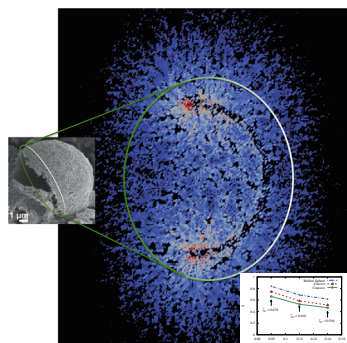
<sup>f</sup> Istituto per le Applicazioni del Calcolo, CNR, Via dei Taurini 19, 00185 Rome, Italy

<sup>g</sup> John A. Paulson School of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA

## HIGHLIGHTS

- A novel application of the Lattice Boltzmann Method to the study of pulsed reactive flows is proposed.
- LBM proves accurate and reliable in the transitional Knudsen flow regime, i.e.  $0.1 < Kn < 1$ .
- The reactivity is found to increase with the Knudsen number of the flow.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 25 August 2016

Received in revised form 8 March 2017

Accepted 14 March 2017

Available online 22 March 2017

### Keywords:

Pulsed Reactive Flow

Lattice Boltzmann

Nanoporous Gold Catalyst

TAP Experiments

## ABSTRACT

We present a novel application of the Lattice Boltzmann Method to the study of pulsed reactive flows in transitional Knudsen number regimes, namely  $0.1 < Kn < 1$ .

We characterize the conversion efficiency of catalytic particles for different geometries and configurations, including single catalytic particle and nanoporous gold (npAu) spheres, within pulsed-flow reactors.

For all the explored configurations, the reactivity is found to increase with the Knudsen number of the flow, consistently with previous theoretical models and in reasonable agreement with experimental results in the literature.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

A precise characterization of the catalytic activity of gas-solid reactions is one of the most topical problems of physical chemistry and chemical engineering. The most popular models for the steady-state kinetic characterisation of catalytic devices are the

\* Corresponding author.

E-mail address: [giacomo.falcucci@uniroma2.it](mailto:giacomo.falcucci@uniroma2.it) (G. Falcucci).

Continuously-Stirred Tank Reactor (CSTR) and the Plug-Flow-Reactor (PFR): the CSTR assumes a perfectly-mixed vessel, while the PFR assumes perfect radial mixing and absolutely no mixing in the axial dimension.

As to the non-steady-state kinetic characterization, popular pulse-response methods are Temporal Analysis of Products (TAP) methods (Shekhtman et al., 1999, 2003; Feres et al., 2009a; Marin and Yablonsky, 2011) and Unsteady-State Processes in Catalysis (USPC) (Suzuki et al., 2008). These models typical apply to high-vacuum,  $10^{-3} \div 10^{-4}$  torr conditions, characterized by substantial values of molecular mean free path as compared to the typical size of the device. The analytical characterization of the above domain is still an open issue, and consequently it is of interest to develop efficient numerical methods to investigate the non-high-vacuum regime. In this paper, we report the development of a mesoscale computational framework based on the Lattice Boltzmann Method (LBM), (Succi, 2004; Benzi et al., 1992), which may provide new computational insights into the aforementioned scenario.

LBM is a mesoscale technique based on a minimal (lattice) version of Boltzmann's kinetic equation, that has proven to be an efficient and reliable numerical tool for the investigation of a variety of complex flows across many scales of motion (Succi, 2004, 2002; Succi et al., 1991; Calí et al., 1992; Fyta et al., 2006; Bernaschi et al., 2010; Falcucci et al., 2007; Aidun and Clausen, 2010; Falcucci et al., 2013; Falcucci et al., 2011; Machado, 2012; Zarghami et al., 2014; Zhou et al., 2015; Montessori et al., 2015). In this work, we apply LB method to compute the reactivity of catalytic shells under single-pulse flow regimes. To the best of our knowledge, this is the first time that LB method is employed for pulsed, chemically-active flows, with a Knudsen number in the transitional slip-flow regime. The potential advantage of using LB rests with its computational efficiency versus numerical methods for rarefied gas dynamics, typically Direct Simulation Monte Carlo (Bird, 1994). The conversion efficiency predicted by our model is compared to the experimentally observed conversion rates for methanol oxidation over a nanoporous gold disk, using a quartz tube microreactor (Falcucci et al., 2016). We observe good agreement in terms of conversion efficiency and spatial distribution of reactant and product species, indicating that our LB model may offer a viable computational tool for design optimization of future nanoporous catalyst architectures.

## 2. Heterogeneous catalysis with LBM

In this paper, we employ a 2D multi-component Lattice Boltzmann with 9-speed lattice (i.e. D2Q9, (Qian et al., 1992)) and single-relaxation time collision operator, (Succi, 2004; Falcucci et al., 2016). One of the aims of this paper is precisely to assess how far one can go with the  $Kn$  number for reactive flows through complex porous geometries, without using higher-order methods, (Succi, 2002; Montessori et al., 2015). Indeed, even though higher-order methods are still much cheaper than Monte Carlo simulations, (Bird, 1994; Di Staso et al., 2016), they are nevertheless computationally more demanding and laborious than the D2Q9 scheme used in the present paper, especially in terms of implementing the boundary conditions.

The species are labeled according to an index  $\alpha$ : an inert Carrier (C) and two species, Reactant (R) and Product (P).

The fluid-dynamic evolution is governed by the following discretized Boltzmann kinetic equation,

$$f_i^\alpha(\mathbf{x} + \mathbf{c}_i, t + 1) - f_i^\alpha(\mathbf{x}, t) = \omega [f_i^{\text{eq},\alpha}(\mathbf{x}, t) - f_i^\alpha(\mathbf{x}, t)], \quad (1)$$

where  $f_i^\alpha(\mathbf{x}, t)$  is the probability density function of finding a particle of species  $\alpha$  at site  $\mathbf{x}$  at time  $t$ , moving along the  $i$ -th lattice direction

defined by the discrete speeds  $\mathbf{c}_i$ , with  $i = 0, \dots, b$ . The lattice time step  $\Delta t$  has been taken as the unit of time for simplicity. The left hand-side of Eq. (1) represents the free-streaming of molecules, whereas the right-hand side accounts for the collisional relaxation towards the local equilibrium  $f_i^\alpha(\mathbf{x}, t)$ , which is expressed as a low-Mach, second-order expansion of a local Maxwellian,

$$f_i^{\text{eq},\alpha}(\mathbf{x}, t) = w_i \rho^\alpha(\mathbf{x}, t) \left[ 1 + \frac{\mathbf{c}_i \cdot \mathbf{u}(\mathbf{x}, t)}{c_s^2} + \frac{(\mathbf{c}_i \cdot \mathbf{u}(\mathbf{x}, t))^2}{2 c_s^4} - \frac{|\mathbf{u}(\mathbf{x}, t)|^2}{2 c_s^2} \right]. \quad (2)$$

The relaxation to local equilibrium takes place on a time-scale  $\tau = 1/\omega$ , taken to be equal for all species.

The first two moments of the distribution functions provide the macroscopic gas densities,  $\rho^\alpha(\mathbf{x}, t)$ , and velocities,  $\mathbf{u}^\alpha(\mathbf{x}, t)$ , respectively:

$$\rho^\alpha(\mathbf{x}, t) = \sum_{i=0}^b f_i^\alpha(\mathbf{x}, t), \quad (3)$$

$$\rho^\alpha(\mathbf{x}, t) \mathbf{u}^\alpha(\mathbf{x}, t) = \sum_{i=0}^b \mathbf{c}_i f_i^\alpha(\mathbf{x}, t). \quad (4)$$

At local equilibrium all species move with the common barycentric velocity:

$$\mathbf{u}(\mathbf{x}, t) = \sum_{\alpha} \rho^\alpha(\mathbf{x}, t) \mathbf{u}^\alpha(\mathbf{x}, t) / \sum_{\alpha} \rho^\alpha(\mathbf{x}, t). \quad (5)$$

The weights  $w_i$  in the equilibrium distribution satisfy the following isotropy constraints:

$$\sum_{i=0}^b w_i = 1, \quad \sum_{i=0}^b w_i \mathbf{c}_i = 0, \quad \sum_{i=0}^b w_i \mathbf{c}_i \mathbf{c}_i = c_s^2 \mathbf{1}, \quad (6)$$

where  $\mathbf{1}$  denotes the identity matrix and  $b$  runs on the 9 directions within the lattice. The speeds are  $\mathbf{c}_i = (0; 0)$ , corresponding to a weight  $w_i = 4/9$ ,  $\mathbf{c}_i = (\pm 1; 0)$  and  $\mathbf{c}_i = (0; \pm 1)$ , with  $w_i = 1/9$ , and  $\mathbf{c}_i = (\pm 1; \pm 1)$ , with  $w_i = 1/36$ . Finally,  $c_s$  is the lattice sound speed equal to  $1/\sqrt{3}$ .

In the limit of small Knudsen number (defined as the ratio of mean free path to macroscopic length scale), Eq. (1) reproduces the Navier-Stokes equation for a carrier fluid of viscosity  $\nu = c_s^2(\tau - 1/2)$  in lattice units. In the hydrodynamic regime, typically  $\tau - 1/2 \ll 1$ . In the present application, which deals with gas flows characterized by Knudsen numbers  $Kn \sim 1$ , we work in the regime  $\tau - 1/2 \sim 1$ . The remaining two LB equations reproduce the dynamics of the reactants and products as advected by the carrier and diffuse across it.

Species inter-conversion due to catalytic reactions at the pore surface is accounted for by considering a local exchange of populations, as they meet and react on the solid walls of the pore. In the case of heterogeneous catalysis, such operation takes places when gas populations hit the surface of the porous catalyst. Here we consider a first order chemical reaction of the generic form  $R \rightarrow P$ , whereby  $R$  is converted into  $P$  upon contact with the porous catalytic walls (no reaction takes place in the gas region) on a time scale faster than the characteristic time of the molecular collisions in the bulk, (Falcucci et al., 2016; Montessori et al., 2016).

We have implemented a ‘‘sputtering’’ boundary condition (Falcucci et al., 2016; Krastev et al., 2016): specifically, the populations of reactants and products that enter or exit (superscripts ‘‘in’’ and ‘‘out’’) a node obey the following equations:

Download English Version:

<https://daneshyari.com/en/article/6467638>

Download Persian Version:

<https://daneshyari.com/article/6467638>

[Daneshyari.com](https://daneshyari.com)