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Axial and transversal patterns during CO oxidation in fixed beds

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Abstract

This work analyses the possible axial- and transversal thermal spatio-temporal patterns that may emerge in a two-dimensional thin annular catalytic bed model using a detailed micro-kinetic model for CO oxidation. This work is motivated by experimental IR-imaging observations made with a cylindrical catalytic surface impregnated with Pd. Stationary, oscillating- and travelling axial-pulses are shown to emerge, in agreement with the experimentally observed axial patterns, and simulations, backed by linear analysis, show that transversal patterns may emerge as well. The implications for fixed-bed reactor modelling are discussed.

Keywords: Mathematical modelling; Nonlinear dynamics; Packed bed; Reaction engineering; Catalysis

1. Introduction

CO oxidation is the simplest catalytic reaction and it is of significant commercial importance as the main reaction occurring in the catalytic converter as well as in other processes. A century of research into this reaction revealed a plethora of unique phenomena that are of academic and of technological importance like optimal rate, bistability, oscillatory behaviour and pattern formation. Patterns due to the interaction of diffusion and nonlinear kinetics has been extensively investigated in chemical and catalytic systems for a variety of geometries like a wire, a ring, a disk and a rectangle (see review by Luss and Sheintuch, 2005). Patterns in fixed beds are different from those known to exist in reaction–diffusion systems due to convective effects. While such patterns have been analysed for one-dimensional (1-D) reactor models for simple thermo-kinetic models (Sheintuch and Nekhamkina, 1999), the actual underlying model typically requires a micro-kinetic model, coupled with heat and mass balances, and yields significantly different results, as we demonstrate below. The purpose of this work is to analyse the possible axial- and transversal-spatio-temporal patterns that emerge in a 2-D fixed bed model using a detailed micro-kinetic model.

This work is motivated by experimental observations of thermal spatio-temporal patterns during CO oxidation on a 20 mm diameter and 85 mm long cylindrical catalytic surface made of a glass fibre cloth (GFC), impregnated with Pd (Fig. 1 after Digilov et al., 2006). IR thermal images of the entire surface of the horizontally held catalytic tube were obtained with a specially designed aluminium mirror built in the reactor. With flow in the main axial direction and through the tube surface we observed a periodic motion of a pulse that is born downstream and propagates upstream. This behaviour was predicted with a model that incorporated a surface oscillator, a thermal balance assuming that the fluid–temperature is fixed, and a simplified mass balance for the limiting reactant (see below), while using previously determined kinetic and transport parameters. A similar model with a mixed gas phase balance was previously employed to account for the main features observed on the GFC disk (Nekhamkina et al., 2003; Digilov et al., 2004).

The surface oscillator employed a micro-kinetic model. The significance of this feature is that a simple bistable version of it, with fixed temperature and/or fluid concentration, can lead to stationary fronts on a wire and in a bed. That differs from the propagating temperature fronts that emerge on a catalytic wire or in a fixed bed, with generic first-order kinetics or a single-valued Langmuir–Hinshelwood rate-expression, which have been extensively studied. The incorporation of a micro-kinetic model does not allow to reduce the model to

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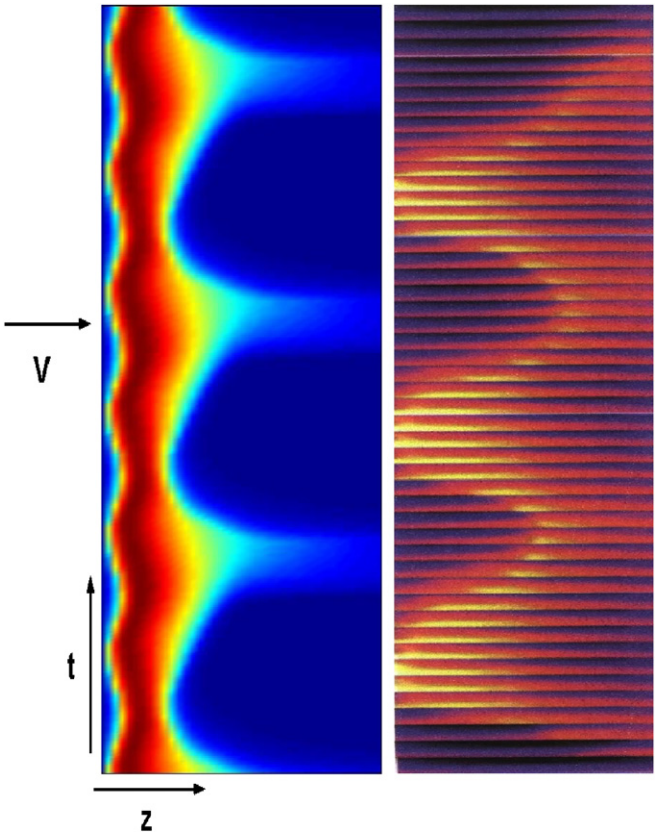

Fig. 1. Typical 1-D oscillatory spatio-temporal patterns observed on a cylindrical surface: simulations (left, $P_{CO,in}=1000$ Pa; $T_g=493$ K) vs. experiments (right, $P_{CO,in}=1200$ Pa; $T_g=500$ K). Flow is from the left.

such a simple form. Thus, under strictly isothermal fixed fluid-composition conditions, in a 1-D system, we can produce infinitely many solutions in which the discontinuity in surface state occurs at a certain arbitrary spatial position. Obviously, introducing surface diffusion will destroy this infinitude of solutions. But since supported catalysts are organized as a set of (nm size) crystallites or (mm size) pellets, this inter-crystallite or inter-pellet communication is absent under isothermal fixed (gas) composition conditions. Thermal effects are always present at atmospheric-pressure oxidation, but their corresponding effect on temperature rise may be small; yet, even weak thermal effects become highly important for communication and in a recent study we showed that stationary fronts are generic for weak-thermal fronts coupled with a micro-kinetics model (Sheintuch and Nekhamkina, 2005).

Convection can produce propagating (creeping) fronts in an adiabatic fixed bed with simple kinetics or in an isothermal model with single-valued LH kinetics. The front moves then at a velocity that is determined by the kinetic and thermodynamic parameters and by the fluid velocity (u). Typically, stationary fronts are not generic and exist only as a boundary between ignition- and extinction-fronts. In fixed beds with micro-kinetic models fronts may emerge even with weak thermal effects. Again, due to the absence of inter-crystallite communication the fronts are likely to become stationary as we show below.

Our next step is to extend this understanding to fixed-bed behaviour in a system with oscillatory micro-kinetics models. The existence of stationary fronts will also alter the expected results in oscillatory models, which couple the model described above with a slow-changing variable. A condition for symmetry breaking and the emergence of transversal patterns was derived in a recent study (Nekhamkina and Sheintuch, 2005) of such kinetics on a ring or a catalytic slice. From linear analysis we derived the wavelength of the emerging pattern at the Hopf bifurcation point. Transversal patterns are likely to emerge when the reactor perimeter is larger than this wavelength. Transversal patterns may emerge in reaction-convection-diffusion (R-C-D) systems with oscillatory kinetics, in which the thermo-kinetics model is coupled with a slow non-diffusing inhibitor. Symmetry breaking in the azimuthal direction, of a cylindrically shaped thin catalytic reactor, was simulated when the perimeter is sufficiently large (Sheintuch and Nekhamkina, 2003) in realistic reactors models of high *Le*, ratio of solid- to fluid-phase heat capacities, and high *Pe*, ratio of convection to conduction numbers. Transversal patterns may also emerge in simple thermo-kinetic (i.e., non-oscillatory) model but apparently only with a sufficiently large reactant diffusivity ($Pe_C/Pe_T<1$) (Balakotaiah et al., 1999; Yakhnin and Menzinger, 2001) contrary to most observations. It has been recently proven, for systems described by macro-kinetics models, that all the patterns with realistic diffusivity values are unstable (Viswanathan et al., 2005).

2. Modeling

We briefly describe the model features and equations. The surface micro-kinetic model accounts for CO adsorption and desorption, for oxygen dissociative (and irreversible) adsorption and for reaction between the two surface species (Slinko and Jaeger, 1994)

$$\frac{dx}{dt}=k_1P_{CO}(1-x-y)-k_1x-k_3xy-[k_5xz], \tag{1a}$$

$$\frac{dy}{dt}=k_2P_{O_2}e^{-\alpha z}(1-x-y)^2-k_3xy-[k_4y(1-z)], \tag{1b}$$

$$\frac{dz}{dt}=k_4y(1-z)-k_5xz, \tag{1c}$$

where x and y are the concentration of adsorbed carbon monoxide and adsorbed oxygen, respectively; z is the concentration of oxygen in a subsurface layer.

We consider an annular cylindrical fixed bed or a cylindrical catalyst cloth within such a reactor, assuming the fluid temperature (T_g) is fixed. The heat and mass balances assume that the catalyst is thin, but its temperature (as well as x, y and z) is spatially distributed. The heat balance accounts for accumulation (ρ_sC_{ps} is the heat capacity), conduction (λ_s is the conductivity), reaction and heat transfer, subject to mixed boundary conditions at inlet and no-flux at outlet (2b):

$$\tau_T\frac{\partial T}{\partial t}-\frac{L_T^2}{L^2}\frac{d^2T}{d(s/L)^2}-\frac{L_T^2}{R^2}\frac{d^2T}{d\varphi^2}=(T_g-T)+aR_{CO}, \tag{2a}$$