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Letter to the Editor

Response to the letter "Mass transport on composite catalytic surfaces by V. Zhdanov"

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ABSTRACT

In the model studied in [T.G. Mattos, F.D.A. Aarão Reis, J. Catal. 263 (2009) 67], the constant external reactant flux drives the system far from equilibrium, thus detailed balance conditions are expected to fail and chemical potentials are not useful to determine equilibrium conditions. This is similar to other far from equilibrium models, some of them also applied to catalysis. There is a nonzero net flux of reactants across the catalyst–support interface, but mass conservation is satisfied there, although the original solution of the model was based on a global mass conservation. Thus, the claim that the results of [T.G. Mattos, F.D.A. Aarão Reis, J. Catal. 263 (2009) 67] are wrong is unjustified, and the far from equilibrium conditions may be observed experimentally.

1. Introduction

In a recent paper [1], we presented a model of catalyzed reactions on a line with active (catalyst particles) and inactive (support) regions. It includes a constant external flux of reactants, their diffusion and desorption. The turnover frequency (TOF) was analytically calculated, but most qualitative conclusions were justified by scaling concepts, which can be extended to more complex models and experiments. Different relations among the rates of the main processes (which may depend on activation energies) lead to a net reactant flux from the catalyst to the support or vice-versa, which affects the TOF. These possible relations and the effects of catalyst particle size were subsequently explored.

Our model is a far from equilibrium statistical model closely related to those presented in Refs. [2–4] and subsequent works by the same authors. It also shares some features with other reaction-diffusion models [5], particularly those accounting for heterogeneity of the catalytic materials [6], with submonolayer deposition models [7], and with models of reactions with absorbing transitions [8].

Zhdanov's letter criticizes the assumptions and methods of solution of our model, and states that we obtained wrong results. This gives us an opportunity to discuss important features of far from equilibrium statistical models and of our methods. In summary, we will show that our model was correctly solved in Ref. [1] and that the failure of some thermodynamic equilibrium conditions is expected, while the applicability to real systems will depend on the experimental conditions matching our far from equilibrium assumptions.

First, violation of detailed balance is usual in nonequilibrium statistical mechanics. Indeed, satisfying detailed balance seems to be an exception in this field. With a focus on catalysis, it is useful to recall the absorbing transitions of the Ziff–Gulari–Barshad (ZGB) model for catalytic oxidation of carbon monoxide [9]. In the original ZGB model, there is an external flux of CO and O_2 toward a catalytic surface, with fixed fractions of each species in the incident gas, and there is no desorption nor diffusion. An absorbing state, where the surface is poisoned by CO, can be attained from any other state after a finite time in a finite system. However, the opposite does not occur: once in the absorbing state, always there. This is one of the simplest illustrations of violation of detailed balance. It is certainly an approximation, since at long times desorption will play a role. However, in the time scale where the model is applicable, there is no chemical equilibrium between the gas above the surface and the adsorbed gas. Instead, the fixed external fluxes are responsible for driving the adsorbed gas far from thermodynamic equilibrium. Other examples of absorbing transitions and extensions of the ZGB model can be found in Ref. [10].

Our simple model for catalyzed reactions contains the main ingredient for detailed balance violation: the fixed external flux of reactants (rate *F*), which stick to the surface with probability one if the target site is empty, independently of the desorption rate. This is possible if some external source is controlling the gas flux toward the surface. The analysis of the experimental conditions and comparison with the experimental results will determine if these assumptions are valid or not. The shorter the experimental time scale, the farther from equilibrium a system is expected to be.

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For the above-mentioned reasons, our results are not the consequence of equal chemical potentials of the gas and the adsorbate, i.e. there is no chemical equilibrium. Instead, adsorption is driven by the fixed external flux and depends on the available surface area, while desorption occurs with a fixed rate. The latter may depend on temperature if thermal contact with the neighboring substrate is assumed, as done in Section 4.2 of Ref. [1].

Another consequence of the external sources of reactants is the net flux across the catalyst-support interface, even in the absence of reactions. The perpetuum mobile to which Zhdanov's letter refers (comment 2) does not occur under adsorption–desorption equilibrium conditions; instead, it is a consequence of the external driving force. Due to this source, the net transport across the boundary cannot be predicted by comparison of chemical potentials, in contrast to comment 3 of Zhdanov's letter. However, a net flux across the boundary does not mean that there are sources or sinks of reactants at that boundary. The net flux immediately at the left of the boundary is certainly equal to the net flux immediately at the right of the boundary, as will be discussed below.

At this point, it is also interesting to note that our final solution (Eqs. (7)–(10), (16) and (17)) gives the expected results in the absence of reactions. In this case, $\alpha_c = \alpha_s = 0$, thus the coverages are position independent, and we obtain $\theta_c = r_c$ and $\theta_s = r_s$. The dependence of TOF/F on k_r for $D = 0$ can be observed in Fig. 3 of Ref. [1]. Unfortunately, there was an error in the values of the rates shown in the legend of the original paper, but the correct values are shown in an errata.

Concerning mass conservation, we agree with Zhdanov's proposal that the diffusion currents at the left and right sides of the boundary are equal, as shown in Eqs. (1) and (2) of his letter. It is obvious that our final results do lead to the same diffusion current at each side of the boundary (although jump rates are different and lead to a net mass flux across the boundary). The calculation is very simple: from Eqs. (7)–(10), (15) and (16) of Ref. [1], we obtain

$$\frac{d\theta_c}{dx}\left(x = \frac{la}{2}\right) = \frac{d\theta_s}{dx}\left(x = -\frac{da}{2}\right) = \frac{r_s - r_c}{\lambda_c/\tanh\left(\frac{la}{2\lambda_c}\right) + \lambda_s/\tanh\left(\frac{da}{2\lambda_s}\right) + a} \tag{1}$$

(note that the same value of D was assumed for both regions). This means that there is no sink or source of mass in the boundary, in contrast to Zhdanov's statement. The difference from our original solution is that mass conservation was not imposed at the boundary. Instead, it was done by matching the total gain and the total loss at the catalyst and support regions. Moreover, the jump rates across the boundary cannot be calculated from chemical potentials because the system is driven far from equilibrium by the external reactant flux. Thus, Eq. (3) of Zhdanov's letter cannot be used.

Other points of Zhdanov's letter also deserve comments.

First, we assumed equal diffusion coefficients in the catalyst and in the support, but we agree that they are different from a real-supported catalyst. Inside each region, the diffusion coefficient also depends on the local surface shape – for instance, adsorbate diffusion in surface kinks and planar regions is different. For this reason, even Fig. 1b of Zhdanov's letter is a drastic approximation of a real system. Anyway, his proposal can certainly be incorporated in our model by using four different diffusion coefficients: one for the catalyst, one for the support and one for each direction across the boundary. The quantitative results will certainly be different, but not the qualitative trends if they are interpreted via diffusion lengths (Eqs. (19) and (20) of Ref. [1]). For this reason, we believe that the assumption of the same D everywhere is a useful approximation to investigate several possible scenarios, as done in Ref. [1]. It is also useful to provide analytical results in a simple form, easier for direct interpretation.

Eqs. (11) and (15) of Ref. [1] (Eqs. (4) and (5) of Zhdanov's letter) are certainly correct, which is confirmed by the absolutely reliable final results. Eq. (11) of Ref. [1] simply states that the jump of a reactant from the catalyst edge to the support edge is possible only if there is a reactant at that catalyst site and if that support site is empty – Eq. (15) refers to the opposite jump. Energy barriers for these jumps could be incorporated in the model, possibly with a small reduction of the back-spillover current. However, big changes in that current are not expected because the system dynamics is dominated by the diffusion in the middle of the catalytic and the support regions, where the number of reactants is much larger than that in the boundaries.

Finally, as stated in comment 2 of Zhdanov's letter, vibrational relaxation of adsorbed particles is extremely fast on the time scale of reaction steps. That relaxation is also fast on the time scale of desorption and diffusion. For these reasons, in Section 4.2 of Ref. [1] we assumed that those processes take place in thermal contact with a neighboring substrate at temperature T, and used the Boltzmann factors in Eqs. (21)–(23). However, in the time scale of many diffusion, reaction and desorption steps, the far from equilibrium conditions (driven by the external flux) may prevail.

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