Journal of Catalysis 266 (2009) 391–392

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Letter to the Editor

Mass transport on composite catalytic surfaces

ARTICLE INFO

Article history:
Received 13 April 2009
Revised 3 July 2009
Accepted 12 June 2009
Available online 31 July 2009

Keywords:
Heterogeneous catalysis
Composite surfaces
Supported nanoparticles
Desorption
Diffusion
Reaction–diffusion equations
Detailed balance principle

ABSTRACT

Mattos and Aarao Reis [T.G. Mattos, F.D.A. Aarao Reis, J. Catal. 263 (2009) 67] have proposed a kinetic model of catalytic reaction including mass transport on a composite catalytic surface. We show that the boundary conditions for the reaction–diffusion equation they use contradict the prescription of the detailed balance principle for the relation between the rate constants for adsorbate diffusion jumps via the boundary and desorption from different areas, and, for certain parameters, the predictions of their model are qualitatively inconsistent. Quantitatively, their results are inconsistent in the situations where the role of the diffusion jumps from the catalytically active regions to the inactive regions is significant.

Kinetic models of heterogeneous catalytic reactions are often based on the assumption that a reaction occurs on an infinite homogeneous surface and there is no adsorbate mass transport (for instructive examples, see a good review by Stoltze [1]). In reality, such reactions usually occur on supported nanoparticles or composite surfaces, and the corresponding kinetics can sometimes be complicated by adsorbate transport between catalyst particles and a support [2] or between different regions of a composite surface [3]. To describe such situations, one can use reaction–diffusion equations or Monte Carlo simulations with appropriate boundary conditions [2,3]. Under steady-state conditions, for example, the reaction–diffusion equations should be integrated prescribing that the reactant diffusion fluxes along the surface on both sides of the boundary separating different regions are equal,

$$J = -D_L \frac{\partial \theta_L}{\partial x}\bigg|_l = -D_R \frac{\partial \theta_R}{\partial x}\bigg|_l, \tag{1}$$

where x is the coordinate perpendicular to the boundary located $x = l$, and θ_L, θ_R, D_L and D_R are the adsorbate coverages (at $x \to l$) and diffusion coefficients on the left- and right-hand side of the surface. This condition depending only on coverages and diffusion coefficients guarantees mass conservation on the boundary (the boundary should not be a sink or source for mass). Another boundary condition, specifying J, depends on the details of the potential energy for diffusion jumps via the boundary and can be expressed as

$$J = j_L(\theta_L, \theta_R) - j_R(\theta_L, \theta_R), \tag{2}$$

where j_L and j_R are the jump rates from the left-hand side to the right-hand side and back, respectively. If diffusion is rapid and each term on the right-hand side of condition (2) is larger compared to J, the situation near the boundary is close to local equilibrium, and condition (2) can be replaced by

$$\mu_L(\theta_L) = \mu_L(\theta_R), \tag{3}$$

where μ_L and μ_R are the adsorbate chemical potentials on the left- and right-hand side of the boundary.

One of the simplest models including the 1D mass transport on a composite catalytic surface has recently been proposed by Mattos and Aarao Reis (MAR) [4]. They treat an $A \to B$ reaction occurring via reversible A adsorption, conversion of adsorbed A to B, accompanied by instantaneous B desorption. The surface is considered to consist of a periodic array of catalytically active and inactive strips. The A jump rates via the boundary are represented as [see their Eqs. (11) and (15) and note that we use slightly different designations for coverages]

$$j_L = \frac{D}{a^2}\theta_L(1-\theta_R), \tag{4}$$

$$j_R = \frac{D}{a^2}\theta_R(1-\theta_L), \tag{5}$$

where D is the A diffusion coefficient, and a is the lattice spacing. θ_L and θ_R are calculated by MAR taking into account

0021-9517/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2009.06.015

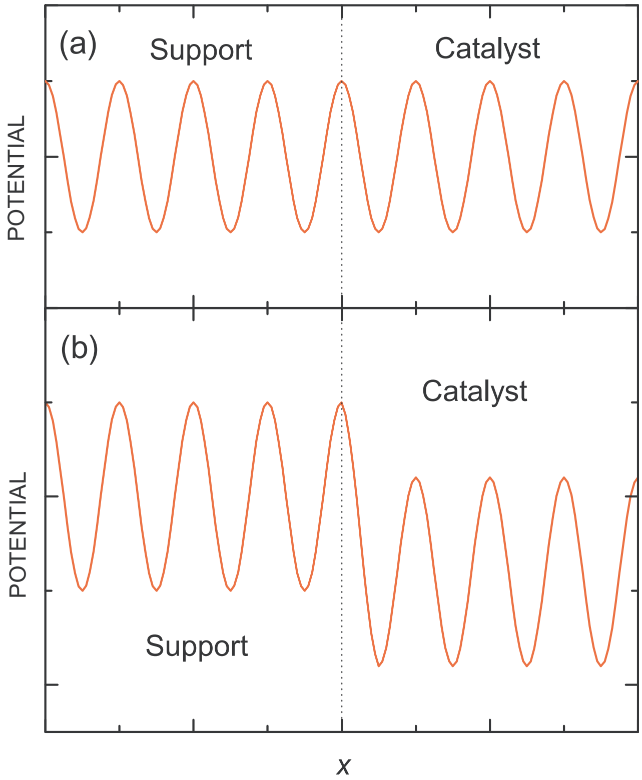

Fig. 1. Schematic potential energy for adsorbate diffusion along the surface.

the A balance on different regions. Condition (1) [or (3)] is not used.

Our comments on the MAR model are as follows:

1. Expressions (4) and (5) imply that the potential energy for A diffusion on the catalytically active regions is the same as that on the inactive regions, as shown in Fig. 1a. In reality, the potentials are different as shown in Fig. 1b, and this difference should be taken into account in the expressions for j_L and j_R. In fact, describing adsorption and desorption, MAR implicitly assume that the potentials are different, because setting equal impingement rates (F) for different regions they consider that the desorption rate constants are different. In expressions (4) and (5), the corresponding difference is however lacking. For these reasons, the MAR reaction–diffusion equations are inconsistent. In particular, at least one of the expressions (4) and (5) is not applicable and should be modified. If, for example, we accept that the diffusion coefficients on both sides of the boundary are equal and there is no Ehrlich-Schwöbel barrier (this case is shown in Fig. 1b), the right-hand side of Eq. (5) should be multiplied by $\exp(-\Delta E/k_BT)$ where ΔE is the difference of the adsorption energies on the two areas.
2. Expressions (4) and (5) in combination with equal adsorption rate constants and unequal desorption rate constants, k_L and k_R, contradict the prescription of the detailed balance principle for the relation between these rate constants and the rate constants for diffusion jumps via the boundary, κ_L and κ_R, and predict the flux via the boundary even in the absence of reaction. For equal adsorption rate constants, this principle prescribes
$$\frac{\kappa_L}{\kappa_R} = \frac{k_L}{k_R}. \tag{6}$$
If the vibrational partition functions of adsorbed particles are equal in both areas, the ratio of the rate constants (6) should be equal to $\exp(\Delta E/k_BT)$. In general, relation (6) guarantees that at adsorption–desorption equilibrium there is no adsorbate flux along the surface. Otherwise, one could easily construct a perpetuum mobile at adsorption–desorption equilibrium or make various predictions which would be physically senseless at equilibrium and/or reactive conditions. One of such predictions by MAR is discussed below in item 3. Here, we may add that the prescriptions of the detailed balance principle for different rate constants hold provided that the adsorbed overlayer is at thermal equilibrium (note that thermal equilibrium does not necessarily imply chemical equilibrium or adsorption equilibrium) or, more specifically, provided that the distribution of vibrational energy of adsorbed particles is canonical. In heterogeneous catalytic reactions, this condition is usually fulfilled because as a rule the vibrational relaxation of adsorbed particles is fast on the time scale of reaction steps (see e.g. Sec. 5 in Ref. [5] or any other review of mechanisms of vibrational relaxation). If this is not the case, the vibrational relaxation should be treated explicitly, and expressions (4) and (5) are not applicable anyway.
3. For slow reaction [e.g., for $k_r/F = 0.1$ in the MAR Fig. 3a or $k_r/F = 0.5$ in Fig. 3b], the MAR model predicts that the reaction rate *decreases* with *increasing* D. In their model, this is related to high coverage of catalytically active regions and domination of A transport from these regions to the inactive regions. In reality, the reaction on the catalytically active regions reduces the A chemical potential there compared to that on the inactive regions, and accordingly the correct model should predict net A transport from the inactive regions to the active regions irrespective of the reaction rate. This transport should increase with increasing D, and the reaction rate should increase as well. Thus, for slow reaction, the MAR predictions are qualitatively inconsistent. Quantitatively, the MAR results are inconsistent in the situations where the role of the adsorbate diffusion jumps from the catalytically active regions to the inactive regions is significant.

References

[1] P. Stoltze, Prog. Surf. Sci. 65 (2000) 65.
[2] V.P. Zhdanov, B. Kasemo, Surf. Sci. Rep. 39 (2000) 25.
[3] V.P. Zhdanov, B. Kasemo, Phys. Rev. B 62 (2000) R4849.
[4] T.G. Mattos, F.D.A. Aarao Reis, J. Catal. 263 (2009) 67.
[5] Y. Matsumoto, K. Watanabe, Chem. Rev. 106 (2006) 4234.

Vladimir P. Zhdanov
Boreskov Institute of Catalysis,
Russian Academy of Sciences,
Novosibirsk 630090,
Russia
E-mail address: zhdanov@catalysis.ru