Heat dissipation in exothermic reactions on non-traditional supported catalysts

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Employing modern fabrication technologies, one can prepare catalysts consisting of nm metal crystallites deposited on μm oxide particles located on a planar oxide or metal support. We derive general equations for estimation of the time scales characterizing dissipation of heat released in exothermic reactions occurring on such catalysts. Using the results obtained, we show that in such systems overheating of oxide particles is usually negligible.

KEY WORDS: nanometer catalysts; μm supporting particles; exothermic reactions; local temperature; heat transfer

A major class of practical catalysts – so-called supported catalysts – consists of small metal particles deposited on the internal surface of a more or less inactive porous support [1]. In practice, such catalysts are shaped either as porous pellets (2–20 mm in diameter) or monoliths with many parallel channels, $\sim$1 mm in width and $\geqslant$100 mm long, with a porous "washcoat" on the channel walls [1,2]. The size of pores varies over a large range from 1–2 nm (micropores) to $\geqslant$50 nm (macropores). The size of the catalytically active metal particles, d, may vary over a wide range as well (typically $d \approx$ 1–20 nm). Reaction kinetics on such particles are often unique compared to those observed on single-crystal samples due to modification of the catalyst band structure (for the smallest particles) and also due to pure kinetic effects inherent for nm chemistry [3].

Experimental studies of the reaction kinetics in real porous catalysts are complicated because there is restricted access to nm metal particles for analysis. Recent surface-science based academic studies [3–6] addressing this and related problems are aimed at fabrication of non-traditional catalysts consisting of well controlled arrays of supported particles on planar surfaces and measurements and simulations of the corresponding reaction kinetics. For very small particles, the methods allowing fabrication of model catalysts are carefully controlled evaporation and annealing of condensed particles, or deposition of clusters by cluster beams [5,6]. For somewhat larger sizes, electron beam lithography can be employed (so far for particles $\geqslant$10 nm) to make nearly perfect arrays of supported particles [3,4]. These and other experimental preparation techniques have demonstrated that it is possible to prepare particle arrays of fairly uniform size and shape distributions, which can be varied systematically with respect to important control parameters. Such catalysts can be used in model studies (see, *e.g.*, [7–9]) and also in applications instead of or in combination with conventional catalysts. This motivates parallel simulations of the reaction kinetics on such particles. In this letter, we discuss heat dissipation in exothermic reactions on model supported particles and specifically address the question of local heating or so-called "hot spots".

In real catalytic systems, most reactions are exothermic, and the reactant conversion is then often accompanied by heating of the catalyst. In chemical engineering, this effect is usually analyzed by employing the mean-field (MF) mass- and heat-transfer equations with effective diffusion and heat-conductivity coefficients. The understanding of effects which can be described by using this approach (*e.g.*, of the macroscopic temperature profiles in the catalyst bed, which in turn affect the reaction kinetics and reactant concentration profiles) is now fairly complete. Some other practically important phenomena (*e.g.*, local overheating in a catalyst) require approaches beyond the MF approximation, however. Detailed treatments of such phenomena are still lacking. For non-traditional supported catalysts fabricated on a planar surface, application of the MF approximation is not straightforward, because such catalysts can hardly be replaced by an effective medium. For this reason, the heat transfer from catalyst particles to the planar support or gas phase needs to be analyzed explicitly. In this letter, we treat a generic case when a nm metal crystallite or a few nm metal crystallites are deposited on a spherical μm oxide particle which is located on a planar support (figure 1). The questions we are interested in are: *How long are the time scales characterizing different channels of heat dissipation in this case?* and *Can the temperature of a metal or oxide particle be much higher than that of the planar support?*

The response to one of the questions above has long since been given by Steinbrüchel and Schmidt [10]. They studied in detail heat transfer from a nm metal crystallite to the oxide support. Their analysis indicates that just after an elemen-

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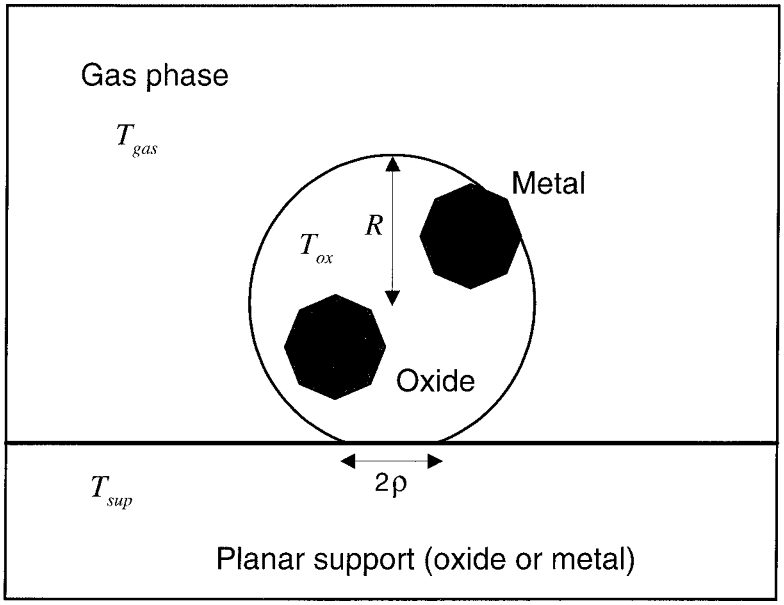

Figure 1. Structure of a model supported catalyst.

tary reaction event the increase of temperature of a crystallite may be considerable (up to several hundred K) due to the high reaction exothermicity and low heat capacity of nm particles. High excess temperature of a crystallite may however be maintained only during a very short period of time (about 10^{-11} s) characterizing heat dissipation to the support. For this reason, such overheating is in fact negligible in practical catalysis, because the time between reaction events on a nm crystallite is usually several orders of magnitude longer than the time required for energy dissipation. Taking into account these findings, we consider in our treatment that the heat transfer from metal particles to the oxide particle is instantaneous and focus our analysis on the heat transfer to the gas phase and to the planar support and on possible overheating of the oxide particle. (If this effect was appreciable, it might be important for interpretation of the reaction kinetics observed on non-traditional supported catalysts and also could be used in applications.)

In the system we are interested in (figure 1), there are several time scales including the average time between the reaction events, $\tau_{\rm rea}$, and the time scales characterizing temperature relaxation in the oxide particle, $\tau_{\rm ox}$, and heat transfer from the oxide particle to the gas phase, $\tau_{\rm gas}$, and to the planar support, $\tau_{\rm sup}$. In addition, there is a time scale, $\tau_{\rm int}$, related to the temperature relaxation in the small region near the interface between the oxide particle and planar support. The former two time scales are given by $\tau_{\rm rea} = 1/NW$ and $\tau_{\rm ox} = R^2/\kappa_{\rm ox}$, where N is the number of adsorption sites on the metal particle(s), W the turnover rate (*i.e.*, the rate per site, per second), R the radius of the oxide particle, and $\kappa_{\rm ox}$ the oxide heat diffusivity. In practically important situations, $\tau_{\rm rea}$, $\tau_{\rm ox}$ and $\tau_{\rm int}$ are short compared to $\tau_{\rm gas}$ and $\tau_{\rm sup}$. To calculate the latter two time scales, it is sufficient to describe the heat-transfer process for times longer than $\tau_{\rm rea}$, $\tau_{\rm ox}$ and $\tau_{\rm int}$. In practice, this means that we may consider that the temperature over the oxide particle is nearly constant and employ the steady-state approximation in order to describe heat fluxes from the oxide particle to the gas phase and planar support, $F_{\rm gas}$ and $F_{\rm sup}$.

The balance equation for the oxide temperature is as follows:

$$(4\pi/3)R^3C_{\rm ox}\frac{{\rm d}T_{\rm ox}}{{\rm d}t} = NW\Delta H - F_{\rm gas} - F_{\rm sup}, \qquad (1)$$

where R is the radius of the oxide particle, $C_{\rm ox}$ the oxide heat capacity (per cm^3), and ΔH the reaction exothermicity (per one product molecule). In the steady-state approximation, the heat fluxes from the oxide particle can be represented as

$$F_{\rm gas} = A(T_{\rm ox} - T_{\rm gas}) \qquad (2)$$

and

$$F_{\rm sup} = B(T_{\rm ox} - T_{\rm sup}), \qquad (3)$$

where A and B are constants calculated below. Using expressions (2) and (3), we can rewrite equation (1) as

$$\frac{{\rm d}T_{\rm ox}}{{\rm d}t} = \frac{3NW\Delta H}{4\pi R^3C_{\rm ox}} + \frac{T_{\rm gas} - T_{\rm ox}}{\tau_{\rm gas}} + \frac{T_{\rm sup} - T_{\rm ox}}{\tau_{\rm sup}}, \qquad (4)$$

where

$$\tau_{\rm gas} = 4\pi R^3C_{\rm ox}/3A \qquad (5)$$

and

$$\tau_{\rm sup} = 4\pi R^3C_{\rm ox}/3B. \qquad (6)$$

To calculate $F_{\rm gas}$, we neglect the effect of the planar support on the temperature distribution in the gas phase. In this approximation, the conventional steady-state solution of the continuum heat-transfer equation for the gas phase is as follows:

$$T(r) = T_{\rm gas} + (T_{\rm ox} - T_{\rm gas})R/r, \tag{7}$$

where $r \geqslant R$ is the radial coordinate ($r = R$ corresponds to the interface between the gas phase and the oxide particle). Employing this distribution, one can easily find that $F_{\rm gas}$ is given by equation (2) with

$$A = 4\pi\lambda_{\rm gas}R, \tag{8}$$

where $\lambda_{\rm gas}$ is the gas-phase thermal conductivity. Substituting this expression into equation (5) yields

$$\tau_{\rm gas} = R^2 C_{\rm ox}/3\lambda_{\rm gas}. \tag{9}$$

The flux $F_{\rm sup}$ is defined by the temperature gradients in the small region where the oxide particle contacts the planar support. The effect of the gas phase on the temperature distribution is negligible in this case. Using this approximation, we can represent the steady-state solutions of the heat-transport equations for the oxide particle and planar support by analogy with equation (7), *i.e.*,

$$T(r) = T_{\rm ox} + (T_{\rm con} - T_{\rm ox})\rho/r \tag{10}$$

and

$$T(r) = T_{\rm sup} + (T_{\rm con} - T_{\rm sup})\rho/r, \tag{11}$$

where ρ is the radius of the contact area (we assume that $\rho \ll R$), $r \geqslant \rho$ is the radial coordinate defined so that $r = 0$ corresponds to the center of the contact area, and $T_{\rm con}$ is the temperature in the contact region. Equations (10) and (11) should be consistent. This means that these equations should give the same heat fluxes in the oxide particle and in the planar support. Employing this condition, we obtain

$$T_{\rm con} = \frac{\lambda_{\rm ox}T_{\rm ox} + \lambda_{\rm sup}T_{\rm sup}}{\lambda_{\rm ox} + \lambda_{\rm sup}}, \tag{12}$$

$$B = \frac{2\pi\rho\lambda_{\rm ox}\lambda_{\rm sup}}{\lambda_{\rm ox} + \lambda_{\rm sup}}, \tag{13}$$

where $\lambda_{\rm ox}$ and $\lambda_{\rm sup}$ are the oxide and support thermal conductivities. Substituting the latter expression into equation (6) results in

$$\tau_{\rm sup} = \frac{2R^3 C_{\rm ox}(\lambda_{\rm ox} + \lambda_{\rm sup})}{3\rho\lambda_{\rm ox}\lambda_{\rm sup}}. \tag{14}$$

In addition to the equations derived above, it is useful to notice that under steady-state reaction conditions with $T_{\rm gas} = T_{\rm sup}$ the excess temperature of the oxide particle is defined by equation (4) as

$$\Delta T = \frac{3NW\Delta H\tau_{\rm gas}\tau_{\rm sup}}{4\pi R^3 C_{\rm ox}(\tau_{\rm gas} + \tau_{\rm sup})}. \tag{15}$$

Using equations (9), (14) and (15), it is of interest to estimate $\tau_{\rm gas}$, $\tau_{\rm sup}$ and ΔT for typical oxides employed in heterogeneous catalysis. For example, let us consider the case when the oxide particle and planar support are fabricated of Al_2O_3 and the gas phase is air (table 1). For heat transfer to the gas phase, we have in this case

$$\tau_{\rm gas}\ ({\rm s}) = 2.6 \times 10^{-5} R^2\ (\mu{\rm m}). \tag{16}$$

Heat transfer to the planar support depends on the ratio R/ρ. For $R/\rho = 10$, we obtain

$$\tau_{\rm sup}\ ({\rm s}) = 1.0 \times 10^{-6} R^2\ (\mu{\rm m}). \tag{17}$$

Comparing equations (16) and (17) indicates that in this case the heat transfer from the oxide particle occurs primarily to the planar support, because $\tau_{\rm sup} \ll \tau_{\rm gas}$.

To calculate ΔT, we need the number of adsorption sites. This number can be estimated as $N \approx 4\pi R^2 \alpha N_0$, where $4\pi R^2$ is the surface area of the oxide particle, α is the fraction of the area covered by metal and N_0 is the number of adsorption sites per unit area. (For half-spherical metal particles, the number of sites is about two times larger, but such details do not change our conclusions.) With this estimate (for $\alpha = 0.1$) and $\tau_{\rm gas}$ and $\tau_{\rm sup}$ given by equations (16) and (17), equation (15) yields

$$\Delta T\ ({\rm K}) = 6.8 \times 10^{-7} WR\ (\mu{\rm m}). \tag{18}$$

The turnover rates of catalytic reactions are usually much lower than 10^7. For this reason, we can conclude from equation (18) that in the case under consideration the overheating of μm-sized oxide particles is negligible. Although with decreasing ρ, the conditions for overheating will be slightly more favourable, but for reasonable reaction rates the effect can, nevertheless, hardly be appreciable.

Finally, we should note that expressions (9) and (14) for $\tau_{\rm gas}$ and $\tau_{\rm sup}$ have been derived by using the continuum heat-transfer equations. This approach holds provided that the mean free path of heat carriers is shorter than the system size. In particular, equation (9) is applicable if the mean free path of the gas molecules is shorter than the size of the oxide particle. Equation (14) can be employed when the phonon mean free path is shorter than the size of the contact area between the oxide particle and planar support. For μm-sized oxide particles, these conditions usually hold. For smaller particles, equations (9) and (14) may need modifications, but our conclusion that overheating is negligible will still be correct because the excess temperature decreases with decreasing particle size. To prevent confusion, we should also articulate that our conclusion concerning the excess temperature has been obtained for a single oxide particle located on a planar support. Our analysis has however some implications for 3D arrays of contacting oxide particles as well, because in the latter case equation (14) will characterize the heat transfer between nearest-neighbour oxide particles. Thus, using our results, we conclude that the temperature difference be-

Table 1
Parameters used in calculations. In general, $C_{\rm ox}$, $\lambda_{\rm ox}$ and $\lambda_{\rm gas}$ depend slightly on temperature. The values presented correspond to $T \approx 500$ K.

Al_2O_3	$C_{\rm ox} = 3.1 \times 10^6\ {\rm J\,m^{-3}\,K^{-1}}$
Al_2O_3	$\lambda_{\rm ox} = 40\ {\rm W\,m^{-1}\,K^{-1}}$
Air (1 atm)	$\lambda_{\rm gas} = 0.04\ {\rm W\,m^{-1}\,K^{-1}}$
CO oxidation	$\Delta H = 4.67 \times 10^{-19}$ J
Number of sites	$N_0 = 1.5 \times 10^{19}\ {\rm m^{-2}}$

tween such particles is not appreciable. This of course does not exclude considerable local overheating of a large number of oxide particles (this effect was mentioned in the beginning of our letter). If overheating is desirable (in order, *e.g.*, to optimize the reaction performance), one can attempt to design 3D ensembles of such particles.

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