Hyperbolic Heat Conduction in Catalytic Supported Crystallites

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Many investigators (*1-9*) have attempted to explain the sintering of catalysts which is frequently found during coke burn-off. It is known that this sintering is associated with the anomalous temperature rise which occurs during exothermic reactions (*1-3*). Cusumano and Low (*4*) have recently used an infrared radiometric method to show such high temperature rises during the sorption of O_2 on SiO_2-supported Ni.

The early work of Damkohler (*5*) determined the maximum steady state temperature rise of a bulk catalyst. Subsequent work by Prater (*6*) predicted a maximum temperature rise of only 2°C., while the study by Wei (*7*) predicted a possible rise of 34°C. for a 2 Å hot spot. Such small temperature rises do not appear to be comparable to the experimental observations (*4*). More recently, Luss and Amundson (*8*) employed a shell progressive model to predict a rise of 250°C. for a typical cracking catalyst. Luss (*9*) has recently proposed two simple analytical models which will give upper and lower bounds on the temperature rise. It appears that the predicted values of the temperature rise tend to be more realistic, but it also seems that they cannot successfully explain the catastrophic catalyst sintering which is occasionally encountered.

It is possible that all of these analytical studies may have a fundamental flaw in that they have been based on the conventional Fourier and Fick laws which result in the conventional heat conduction and mass diffusion equation of the parabolic type

$$\frac{\partial \theta}{\partial t} + \alpha \nabla^2 \theta = S$$

θ, α and S can be interpreted respectively as temperature, thermal diffusivity, and heat of reaction in the case of energy transport and as concentration, mass diffusivity, and rate of reaction in mass transport. The propagation velocities of heat and mass resulting from such a parabolic formulation are infinite, which is of course unrealistic. In fact, Morse and Feshbach (*10*) postulated that the governing equation must depend on the velocity of propagation C which should be finite. The correct differential equation for a transient conducting system is

$$\frac{\alpha}{C^2}\frac{\partial^2 \theta}{\partial t^2} + \frac{\partial \theta}{\partial t} + \alpha \nabla^2 \theta = S$$

which is a hyperbolic type of equation. The latter equation can also be derived (*11*) using a truncation of the more general Maxwell equation (*12*) for an ideal gas. The basic difference between the parabolic and hyperbolic equations is that the latter has an additional term which involves a finite propagation speed. Other differences between these two types of equation were recently demonstrated by Baumeister and Hamill (*13*).

The effect of the finite propagation speed may become important when the system is at very low temperature or when the time of interest is very short. In the present problem of exothermic catalytic reactions, the maximum temperature may occur in a very short time. For example, time periods as short as 10^{-13} sec. after reaction were considered by Luss (*9*). Under such circumstances the hyperbolic type equation may give significantly different results than the parabolic equation. It is the purpose of this paper to investigate the effect of finite speed of heat transfer on the temperature rise of catalytic supported crystallites.

ANALYSIS

The simple yet interesting physical model employed by Luss (*9*) is adopted here to demonstrate the effect of the finite speed of heat transfer. A crystal is assumed to have the shape of a disk of thickness L one face of which is attached to the carrier. The temperature of the support beneath the crystal is assumed to be always constant. Heat is assumed to be generated at the other face of the crystal at a uniform rate during the reaction period t_r, followed by a period $T - t_r$ during which no heat is being generated. The crystal disk is further simplified to be an infinite strip so that only one dimensional flow of heat in the direction normal to the support needs to be considered.

According to the hyperbolic heat conduction equation, the temperature differential between crystal and supported can be obtained from the equation

$$\frac{1}{C^2}\frac{\partial^2 \theta}{\partial t^2} + \frac{1}{\alpha}\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial x^2} \tag{1}$$

subject to the initial conditions

$$\theta = 0, \ \frac{\partial \theta}{\partial t} = 0 \ \text{at} \ t = 0 \quad 0 < x < L \tag{2}$$

and the boundary conditions

$$\theta = 0 \quad x = 0 \tag{3}$$

$$-k\frac{\partial \theta}{\partial x} = \phi + \frac{\alpha}{C^2}\frac{d\phi}{dt} \equiv -f(t), \ x = L \tag{4}$$

where

$$\phi(t) = \begin{cases} -q/t_r & rT < t < rT + t_r, \quad r = 0, 1, 2 \ldots \infty \\ 0 & rT + t_r \leq t \leq (r+1)T \end{cases} \tag{5}$$

and q is the heat released to the unit surface in period T and the negative sign indicates heat is transferred in the negative x direction. Figure 1 shows the schematic diagram of $[-\phi(t)]$. It should be mentioned that in the conventional parabolic heat conduction equation, the heat flux ϕ, is given by

$$\phi = -k\frac{\partial \theta}{\partial x}$$

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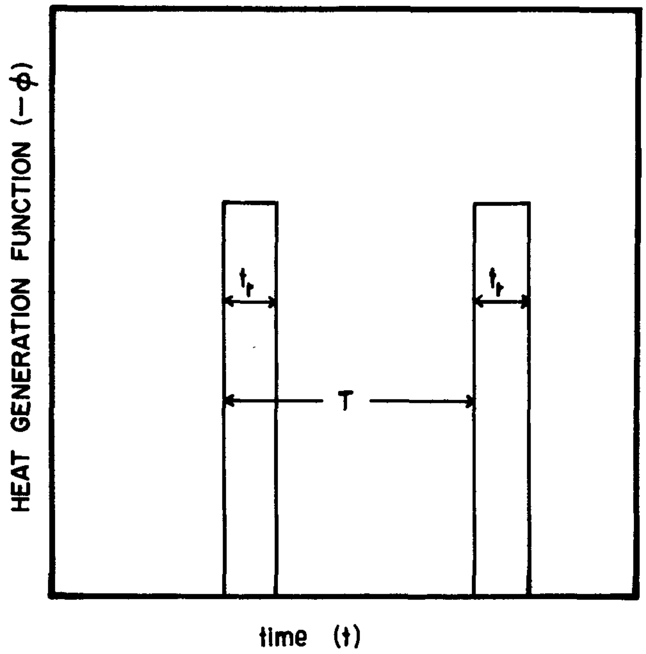

Fig. 1. Time dependent heat generation function.

while in the present hyperbolic heat conduction, the heat flux is given in Equation (4).

Various mathematical methods can be used to solve Equation (1) with its conditions Equations (2 to 5). For example, one may first assume f to be independent of time and then solve for the temperature θ by making use of the method of superposition and the technique of separation of variables. The resulting solution can be used to construct the actual solution where f is a function of time by the use of the Duhamel integral theorem. Alternatively, one may simply use the Laplace transform technique to solve for the real solution directly. In either method, the procedure is standard and straightforward. Therefore, we present only the final solution here

$$\theta = \sum_{n=0}^{\infty} \frac{2(-1)^n \alpha}{kLB_n} \sin\left(\frac{c\lambda_n}{2\alpha} x\right) \int_0^t f(t') \left[e^{-\mu_{n1}(t-t')} - e^{-\mu_{n2}(t-t')} \right] dt' \quad (6)$$

where

$$B_n = \sqrt{1-\lambda_n{}^2}, \quad \lambda_n = \frac{(2n+1)\pi\alpha}{CL}$$

$$\mu_{n1} = A(1-B_n), \; \mu_{n2} = A(1+B_n) \text{ and } A = C^2/2\alpha$$

Like Luss, we are interested in the steady periodic solution, that is, the solution when the surface temperature oscillations have been going on long enough so that the influence of initial temperature has disappeared. Our purpose is to compare the present solution with the existing parabolic solution obtained by Luss at time $t = t' = rT + t_r$ and $x = L$, because at such location and time the crystal reaches its maximum temperature according to the parabolic equation solution. Parallel to Luss, we set $t = rT + t_r$ and perform the integration shown in Equation (6). Then, taking the limit by allowing r to be very large and noting that in the present interest, $T >> t_r$, $A(1 - B_n)\ T >> 1$ and $A(1 + B_n)\ T >> 1$, we have the final solution

$$\theta(t, L) = \sum_{n=0}^{\infty} \frac{4q\alpha^2}{t_r kLC^2B_n} \left\{ \frac{1-e^{-\mu_{n1}t_r}}{1-B_n} - \frac{1-e^{-\mu_{n2}t_r}}{1+B_n} + 2\left(e^{-\mu_{n1}t_r} - e^{-\mu_{n2}t_r}\right) \right\} \quad (7)$$

It should be mentioned that in cases where $\lambda_n > 1$, it is more convenient to set $b_n = i\ B_n$ in Equation (6). Then the nth term in the summation in Equations (6) and (7) reduces to

$$\frac{4(-1)^n\alpha}{kLb_n} \sin\left(\frac{C\lambda_n}{2\alpha} x\right) \int_0^t f(t') e^{-A(t-t')} \sin b_n(t-t') dt' \quad (8)$$

and

$$\frac{8qL}{kt_r(2n+1)^2\pi} \left(1 - e^{-At_r} \frac{\sin(Ab_nt_r)}{b_n} + \cos(Ab_nt)\right) + \frac{4\alpha^2 q \sin(Ab_nt)}{kt_rC^2Lb_n} e^{-At_r} \quad (9)$$

respectively.

RESULTS AND DISCUSSIONS

Numerical computations were performed in order to determine the effect of the finite speed of heat transfer on the temperature rise of crystal. The typical values used in the computation were taken from Luss (9), that is, the properties of the crystal were taken as equal to those of platinum $\rho = 21.5$ g./cu. cm., $k = 0.175$ cal./(sec.) (cm.) C° and $\alpha = 0.254$ sq. cm./sec. For other values, $q = 5 \times$

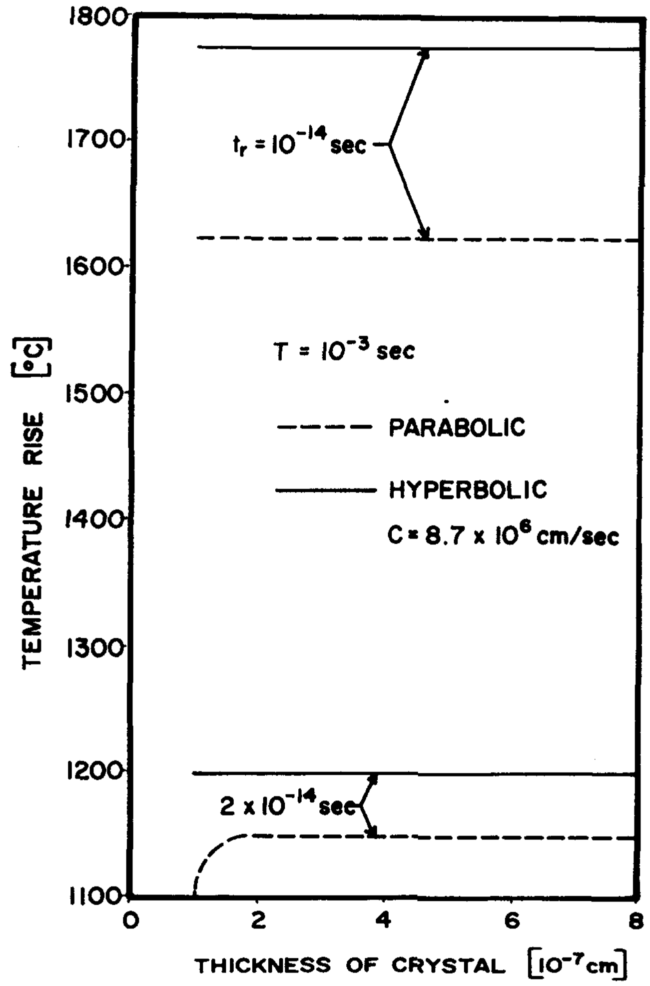

Fig. 2. Dependence of temperature rise on speed of heat transfer.

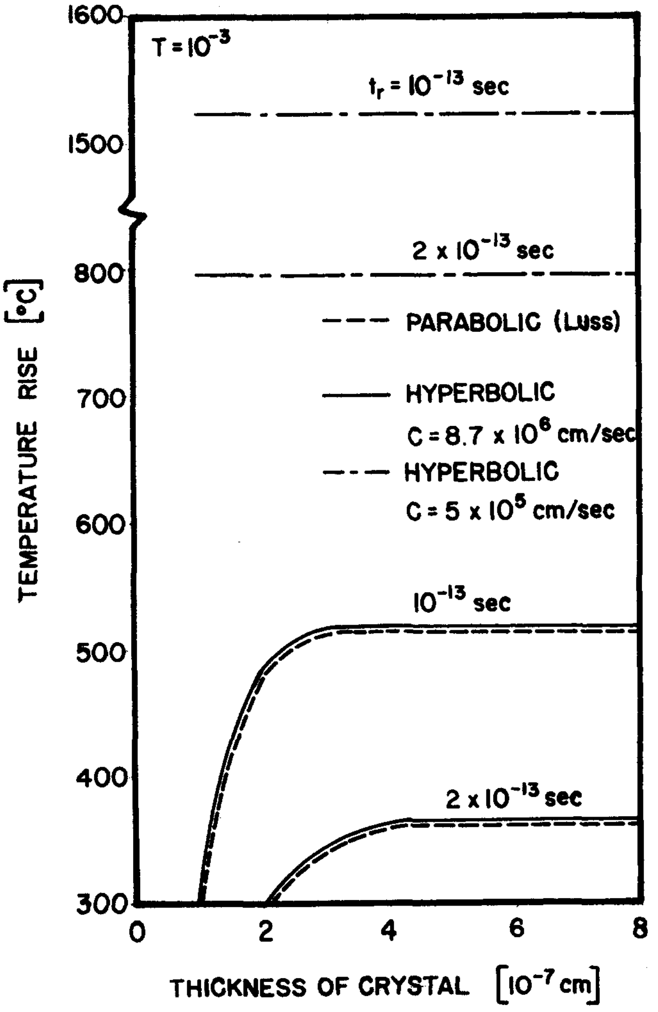

Fig. 3. Dependence of temperature rise on time t_r.

10^{-5} cal./sq. cm., $T = 10^{-3}$ sec., and t_r is taken to be of the order of 10^{-13} or 10^{-14} sec.

Figure 2 compares two sets of temperature rises based on two different solutions, namely, the conventional parabolic solution obtained by Luss and the present hyperbolic solutions. Two typical speeds were chosen because the values of heat propagation speed are not available. The one with $C = 5 \times 10^5$ cm./sec. implies that the heat propagation speed is approximated by the speed of sound in crystals, while the other with $C = 8.7 \times 10^6$ cm./sec. implies the speed is approximated by the velocity of a free electron gas at moderate temperature. It is expected that the actual heat propagation speed would fall within these limits. It is seen from Figure 2 that the difference between these two sets of temperature rises is negligibly small for $C = 8.7 \times 10^6$ cm./sec. but is very significant for the other value of C. In other words, the hyperbolic solution tends to approach the parabolic solution in the limit when the heat propagation speed is very large. That can be seen, for example, by taking C to be very large in Equation (6). Then Equation (6) reduces to

$$\theta = -\sum_{n=0}^{\infty} \frac{2\alpha(-1)^n}{kL} \sin\left[\frac{(2n+1)\pi}{2L} x\right] \int_0^t \phi(t') e^{-\frac{\alpha(2n+1)^2\pi^2}{4L^2}(t-t')} dt'$$

which is precisely the parabolic solution obtained by Luss (*9*). This is consistent with the conclusion of Baumeister and Hamill (*13*). However, when t_r, the time during which the heat of reaction is being released, is shorter by an order of magnitude, the difference between two sets of solutions becomes important even in the case when $C = 8.7 \times 10^6$ cm./sec. This is shown in Figure 3.

The temperature rises shown by the plots of Figure 3 ranging from 1100° to 1780°C., seem rather high. However, anomalously high surface heating rates have been reported, the experiments of Harrington (*14*) and of Kushida (*15*) leading to observed surface transients of 2000° to 3000°K. The results of Figure 3 thus do not seem to be unrealistic.

It should also be noted that for nonmetallic crystals, such as crystal of dielectric materials, the speed of heat propagation should be much less than the speed of the free electron gas and, consequently, the differences between two sets of solutions will be even more significant.

In both figures, the hyperbolic solutions always yield higher temperature rises. This is physically justifiable since the speed of heat transfer is finite in the hyperbolic case in contrast to the infinite speed in the parabolic case.

In conclusion, we have demonstrated that the finite propagation speed of heat transfer may have significant effects in determining the temperature rise of crystals caused by exothermic reactions. The effect is particularly significant when the speed in low or when the time of interest after heat of reaction is released is short.

NOTATION

C = speed of heat propagation
k = thermal conductivity
L = thickness of catalytic crystal
q = heat released to the surface per surface area
r = integer
T = time between consecutive reactions on same site
t_r = time during which heat of reaction is being released
x = coordinate
α = thermal diffusivity
θ = temperature difference between crystal and support
ρ = density of crystal
t = time

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